Wilkinson's Salt: A Flame Retardant for Poly(methyl Methacrylate)

SUNIL J. SIRDESAI and CHARLES A. WILKIE, *Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233*

Synopsis

Poly(methyl methacrylate) reacts with $RhCl(PPh_3)_3$ at 260°C in a sealed tube to produce a material which is insoluble in common solvents. The infrared spectrum and CP/MAS ^{13}C-NMR spectrum indicate the presence of anhydrides. Differential scanning calorimetry shows that the transition temperature has increased by 15°C. Thermogravimetric analysis indicates that 25% of the material is not volatilized at 600°C. The oxygen index of the mixture of the rhodium compound with PMMA increases from 14 to 20 (bottom ignition).

INTRODUCTION

The current consensus is that poly(methyl methacrylate) (PMMA) invariably breaks down at elevated temperatures to give large amounts of monomer.[1-7] PMMA produced by a free-radical mechanism begins to decompose at the double bonds at the chain ends at 270°C. Polymer produced by anionic polymerization, since it lacks the terminal double bonds, does not decompose appreciably until its temperature is raised to 350°C.[8,9] The identities of the pyrolysis products are considered to be little affected by further increasing the temperature above these respective limits.[10,11] These pyrolysis products are the principal sources of fuel and smoke. The production of these pyrolytic products can be inhibited by using a flame retardant that will initiate crosslinking, thereby leading to the formation of nonvolatile, noncombustible char.

Earlier studies from this laboratory[12,13] have demonstrated that red phosphorus reacts with PMMA to produce anhydrides. This anhydride linkage is a second bond along the polymer chain that must be broken to liberate polymer. Since the locus of reaction with red phosphorus is the carbonyl group of the polymer, a reagent is required that will react at this site. Since Wilkinson's salt, $RhCl(PPh_3)_3$, is well known to react with carbonyls,[14,15] this compound was chosen for investigation. This paper reports on the reaction of this compound with PMMA.

EXPERIMENTAL

A tube with a volume of about 80 cm^3 was thoroughly evacuated on the high vacuum line for about 12 h. A 1.0 g sample of PMMA (Aldrich) and 0.5 g of Wilkinson's salt (Aldrich) were then placed in the vessel, and it was once again evacuated for 12 h before sealing it off from the line. The vessel was heated in a muffle furnace at 260°C for 2 h. After the vessel had cooled to room temperature, the vessel was removed from the oven. It was frozen in liquid nitrogen and opened and the product removed. (Vessels have been known to explode from gas pressure. Caution must be used in these manipula-

tions.) Approximately 60% of the sample was insoluble in solvents such as chloroform, tetrahydrofuran, acetone, hexane, etc. This material is black in color and quite fragile; it is referred to as char throughout this manuscript.

Some experiments were performed in a vessel equipped with a break-seal. This allows analysis of the volatiles that are produced in the reaction. The reaction of 1.0 g of PMMA and 0.5 g of $ClRh(PPh_3)_3$ produces only one volatile product. This product was 1.1 mmol of benzene and it was identified by infrared spectroscopy.

NMR spectroscopy was performed on a General Electric spectrometer. Infrared spectra were obtained with a Analect FX-6200 FT-IR spectrometer. Differential scanning calorimetry (DSC) experiments on the char were performed with a Perkin-Elmer instrument under a nitrogen atmosphere. The rate of heating was 20°C/min. Thermogravimetric analysis (TGA) of the char was performed on a DuPont 1090 instrument under a nitrogen atmosphere. The rate of heating was 20°C/min. Oxygen index (OI) measurements were carried out on a home-built apparatus. Thin films of PMMA and PMMA + Wilkinson's Salt, at concentrations of 10, 20, and 30%, were prepared and the flammability was tested by bottom ignition.[16]

RESULTS

The infrared (IR) spectra of starting material, i.e., PMMA, and that of the insoluble product differ only in the carbonyl region. The char shows absorbtion at 1805, 1760, and 1730 cm^{-1} in the carbonyl region. The spectrum of PMMA exhibits only an ester carbonyl vibration at 1730 cm^{-1}. The vibrations at 1805 and 1760 cm^{-1} may be attributed to anhydrides.[17] The characteristic C—O—C frequency is observed at 1016 cm^{-1}.

Anhydrides in the NMR appear in the range of 150–175 ppm.[18] The CP/MAS ^{13}C-NMR spectrum of the char shows, in addition to the resonances of PMMA,[19] peaks in this range.

Thermal studies on PMMA and char were performed by DSC and TGA. DSC measurements on the starting material, PMMA, show an endothermic transition (glass transition) at a temperature of 113°C, while the char exhibited this transition at 128°C, 15°C higher than that shown by PMMA.

Figure 1 shows the thermogravimetric curves obtained for the PMMA and the char. It can be observed that PMMA decomposes in a single stage, decomposition begins around 320°C. The char decomposes in three stages, decomposition begins around 125°C, subsequent steps begin near 220°C and around 350°C. No residue was obtained in the case of PMMA, as expected.[1-7] In the case of the char approximately 25% of the material was nonvolatile at 600°C.

The oxygen index (OI) results are shown in Table I.

DISCUSSION

The combined use of IR and CP/MAS ^{13}C-NMR spectra provide firm evidence for the formation of anhydride linkages in the char. DSC measurements indicate a higher endothermic transition for the char, due to increased resistance to segmental motion for the char as compared with that of starting PMMA. The results of Maurer indicate that an increase in the anhydride content of the polymer causes a concomitant increase in the glass transition temperature.[20]
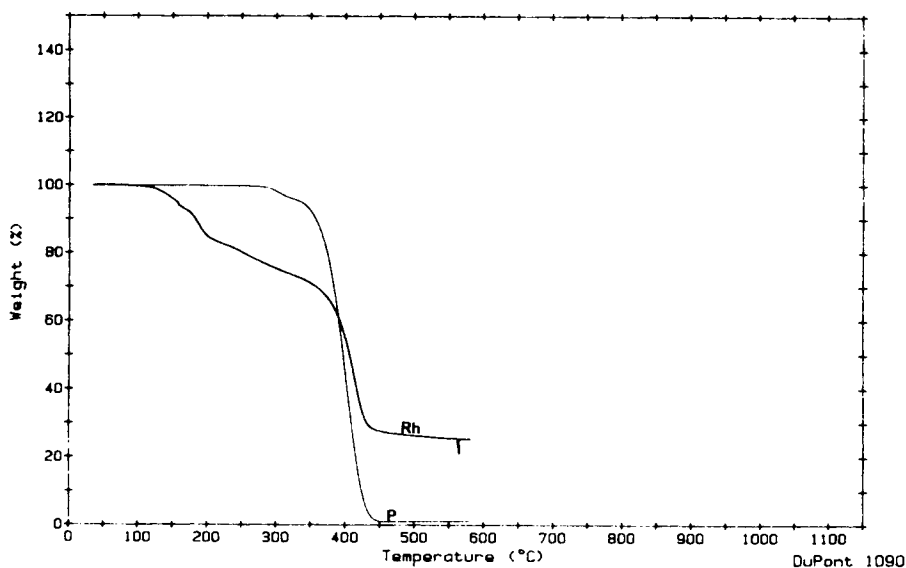
Fig. 1.   Thermogravimetric analysis for PMMA (P) and PMMA combined with $RhCl(PPh_3)_3$ (Rh). The rate of heating is 20°C/min.

TABLE I

Oxygen Index as a Function of $RhCl(PPh_3)_3$ Concentration[a]

O_2 (%)	Wilkinson's salt in PMMA (%)			
	0	10	20	30
12.9	B	No B	No B	No B
14.7	B	No B	No B	No B
19.1	B	I, D	I, D	I, NO D, EQ
21.0	B	B	B	B

[a] B = burns, I = ignites, EQ = extinguishes quickly, D = dripping.

The thermogravimetric curve for the char in Figure 1 shows three stages of decomposition. Heating a sample of char to the temperature of the lower transition, 150°C, causes the loss of chloroform, identified by infrared spectroscopy.[17] Chloroform is the solvent that was used for separation of the soluble and insoluble reaction products. Clearly, $CHCl_3$ is incorporated into the crosslinked polymer structure. Back analysis of the TGA data leads to 34% gelation, i.e., about 30% crosslinking has occurred. This agrees with the TGA result of 25% nonvolatile at 600°C. To the best of our knowledge, no prior claims have been made for crosslinking of PMMA under such mild conditions.

Removal of the chloroform and the subsequent acquisition of the TGA data yields a curve in which the latter two decomposition steps, at 220 and 350°C, are unchanged. Since the mass of starting material is now lower the amount of nonvolatile material is now about 32%.

The claim that Wilkinson's salt provides a degree of flame retardance can be confirmed by the oxygen index measurement. The oxygen index has increased from 14 to 20 in the presence of Wilkinson's salt. One may safely

conclude from these results that $RhCl(PPh_3)_3$ provides a degree of flame retardance.

Previous work by Camino et al.[21] has shown that ammonium polyphosphate causes the production of cyclic anhydrides upon reaction with PMMA. The carbonyl vibrations observed in that study, 1805 and 1770 cm^{-1}, may be compared to those, 1805 and 1783 cm^{-1}, in this work. The reaction with the polyphosphate produces several volatile products, methanol, carbon monoxide, dimethyl ether, carbon dioxide, and hydrocarbons. It is clear that the mechanisms of the two reactions are quite different, the only volatile that is produced with the rhodium compound is benzene. Further work is required to elucidate the pathway of the reaction between PMMA and Wilkinson's salt.

It is highly unlikely that Wilkinson's salt will ever be used as flame retardant due to its toxicity and cost. This study was undertaken to understand the mechanism of degradation, which is being vigorously pursued in this laboratory, rather than establish this material as a flame retardant. This understanding of mechanism will presumably lead to the designing of better flame retardants.

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