Thermal studies on poly(4,4'-isopropylidenediphenylene-phosphorochloridate)

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With 4 figures and 2 tables

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Introduction

By condensation of phenols with phosphorus oxychloride, good and resistant plastic materials have been obtained (1). These organophosphorous resinous materials have not been studied well. Thermal degradation and mechanism of degradation of cross-linked poly-aryl-ortho-phosphates have been studied (2), because organo-phosphorous esters find their use as additive in gasoline and plastic materials, as well as plasticizers and fire retardant. In these polymeric materials all the three chlorine atoms of phosphorous oxychloride have been replaced.

In the present communication we report the synthesis of phosphorochloridate polymer by condensation of phosphorous oxychloride with bisphenol A (4,4'-isopropylidene-diphenol), its thermal degradation and effect on the degradation of polystyrene.

Experimental

Materials: Bisphenol A (4,4'-isopropylidenediphenol) was obtained from Piramal Chemicals, Bombay (India) and was purified by crystallisation in toluene (M.P. 152 °C) phosphorous oxychloride used was Riedel quality. Pyridine was BDH quality and used as such during condensation.

Preparation of the polymer: A resinous material was prepared by polycondensation of an equimolar mixture of bisphenol A and phosphorous oxychloride in pyridine medium. Phosphorous oxychloride was used in slight excess to avoid its loss due to evaporation. The mixture was initially cooked at 95 °C for four hours. The reaction proceeded with the evolution of hydrochloric acid gas. There after the temperature was raised to 240–50 °C for six hours. A hard brittle solid of brown colouration was obtained. The unreacted pyridine and pyridine hydrochloride formed were removed by washing with acidified water and finally with water unreacted phosphorous oxychloride and bisphenol A were removed by washing it with ether.

TG and DTA of the polymer: - Dynamic TG and DTA were recorded by a stanton thermobalance at BARC, Bombay, using a sintered alumina crucible in flowing dry air atmosphere. The heating rate was maintained at 8 °C/min. DTA range was 50 mV.

Isothermal TG: - A 50 mg sample of polystyrene and polystyrene mixed with poly(4,4'-isopropylidenediphosphorochloridate) were used in isothermal TG studies. The samples were heated in constant temperature furnace at various temperatures in a platinum crucible. The mass loss were recorded as a function of time.

Dynamic TG of PS and PS mixed with the prepared polymer (I) were recorded from a TG apparatus supplied by P & D, Division, Sindri (India).

IR-spectra: - IR-spectra of the polymer was recorded using Perkin-Elmer IR-spectrophotometer, at Delhi University, Delhi (India).

Results and discussion

IR-studies: - Characteristic peaks in the IR-spectra of poly(4,4'-isopropylidenediphenyl-
ene phosphorochloridate) are assigned as given in table 1.

Table 1. Assignment of characteristic frequencies in IR-spectra

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Wave number Cm⁻¹</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500</td>
<td>Broad and strong</td>
<td>P - Cl (3)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>835</td>
<td>Sharp and medium</td>
<td>- C -(CH₃)₂</td>
<td>medium</td>
</tr>
<tr>
<td>3</td>
<td>950</td>
<td>Broad and medium</td>
<td>- P=O (4)</td>
<td>medium O</td>
</tr>
<tr>
<td>4</td>
<td>1245</td>
<td>Sharp and strong</td>
<td>- O - P - O - O</td>
<td>strong</td>
</tr>
</tbody>
</table>

Thus the table 1 shows that the desired polymer has been prepared.

TG and DTA of poly(4,4'-isopropylidenediphenylenephosphorochloridate).

Figure 1 shows the TG and DTA curves separately obtained for the polymer (I), heated in dry air. From TG it can be seen that there are three distinct stages in the degradation process. Thus the first stage ends at T₁, second at T₂ and so on. The values of T₁, T₂ and T₃ are 320 °C, 450 °C and 800 °C, respectively. In the first stage upto 320 °C there is about 20% weight loss and during second stage there is further weight loss. Ultimately the polymer decomposes at 800 °C leaving behind a residue which corresponds to the formation of P₂O₅ in air.

The DTA curve of the polymer shows that the polymer (I) does not melt at all, but there are two exothermic peaks at 300 °C and 380 °C and ultimately decomposes at 800 °C. These two transitions occur in the region of T₁ and T₂ recorded by TG and may be due to the decomposition of the polymer.

Effect of the polymer (I) on the decomposition of polystyrene

Isothermal weight loss were carried out on polystyrene without and with the polymer; at various temperatures. The results of various experiments are shown in figs. 2 (a) and 2 (b), as weight percent loss versus time of heating in air. The figures show that there is an initial period of rapid weight loss in presence of polymer (I), followed by an approach to constant weight values.

In order to establish values for the rate constant of the decomposition of polystyrene without and with the polymer (I), various kinetic expressions were tested. The data when fitted to \( \ln[-\ln(1-\alpha)] \) vs. Int, gave straightline with an average slope of \( \sim 0.8 \) for values of \( \alpha = 0.15 \) to 0.90. Hence the decomposition should be described by Avrami-Erofeev (5, 6), equation for nucleation and growth, namely,

\[
[- \ln (1 - \alpha)]^{1/n} = kt.
\]

Where \( \alpha \) is the degree of decomposition and \( n \) is a positive number, \( k \) is the rate constant. Values of \( k \) obtained from the intercept of the linear plot \( \ln[-\ln(1-\alpha)] \) vs. Int, this allowed the

![Fig. 1. TG and DTA curves for poly(4,4'-isopropylidenediphenylenephosphorochloridate)](image-url)