Soluble phosphine oxide containing aromatic polyamides

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Several novel soluble phosphine oxide containing aromatic polyamides (*3–6*) have been synthesized by phosphorylation reactions of aromatic diacids with diamines. The presence of phosphine oxide linkages in the backbone gives these polymers superior properties, namely thermooxidative stability, high char yield and solubility in aprotic polar solvents.

(Keywords: phosphine oxide containing polyaramides; solubility; thermal stability; thermogravimetry; char yield)

Introduction

Aromatic polyamides have found wide commercial acceptance due to their unique property combinations. They can be formed into strong abrasion-resistant fibres and films with very high modulus, good thermal stability and high solvent resistance. However, most of the aromatic polyamides are insoluble in organic solvents; they are only soluble in concentrated mineral acids. The insolubility and also high transition temperatures make these systems difficult to process. Therefore, much effort has been spent on synthesizing processible, tractable polyamides without compromising desired properties. To accomplish this goal, the incorporation of flexible bridging units into the rigid polyamide backbone has been widely used. On the other hand polymers containing phosphorus as an integral part of the backbone are known to be thermally stable and flame retardant. In particular, fire resistance is of prime importance for high performance applications of many polymers[1].

The polyaramides can be produced via interfacial or solution polycondensations of diacid chlorides with diamines. The phosphorylation reaction reported by Yamazaki and coworkers[2,3] has been found to be very useful for the synthesis of aromatic as well as aliphatic polyamides[4] via the polycondensation of diacids with diamines. According to these authors, this procedure produces high yields of high molecular weight polymers, and furthermore makes the preparation of the unstable diacid chlorides unnecessary.

$$\mathrm{Ar(COOH)_2 + Ar'(NH_2)_2} \xrightarrow[\mathrm{NMP/pyridine}]{\mathrm{(C_6H_5O)_3P,LiCl}} \mathrm{\left(COArCO{-}NHAr'NH \right)_{\mathit{n}}}$$

This paper describes a successful application of this reaction to the synthesis of soluble aromatic polyamides based on reaction of (i) bis[4-(*m*-aminophenoxy)phenyl]-phenylphosphine oxide (*1*, *m*-BAPPO) with aromatic diacids such as terephthalic acid (TA) or isophthalic acid (IPA) and (ii) bis[4-(*m*-carboxyphenoxy)phenyl]-phenylphosphine oxide (*2*, *m*-BCPPO) with 4,4′-oxydianiline (4,4′-ODA) or *m*-BAPPO (*1*) (*Scheme 1*).

Experimental

Materials. Unless specified otherwise, reagent grade reactants and solvents were used as received from chemical suppliers. Lithium chloride and calcium chloride were dried at 180°C in a vacuum oven for 48 h. Pyridine was distilled over calcium hydride. Triphenyl phosphite was freshly distilled prior to use. Syntheses of *m*-BAPPO[5] and *m*-BCPPO[6] have been published elsewhere.

Measurements. ^{1}H n.m.r. spectra were obtained at ambient temperature on a Varian Unity 400 MHz spectrometer using deuterated dimethylsulphoxide (DMSO) solutions with tetramethylsilane (TMS) ($\delta = 0$ ppm) as internal standard. I.r. spectra (KBr pellets) were recorded on a Nicolet MX-1 *FT*i.r. spectrometer. Intrinsic viscosity measurements were performed in 1-methyl-2-pyrrolidinone (NMP) at 25°C using a Canon-Ubbelohde viscometer. Molecular weights and molecular weight distributions were analysed by using a Waters 150-C17 gel permeation chromatograph equipped with an r.i. detector and Ultrastyragel column set (100, 500, 10^3, and 10^4 Å) in NMP/LiBr (5%) at 60°C; molecular weight calculations were based on polystyrene standards. The weight average molecular weight was determined using a Chromatix KMX-6 low angle laser light scattering (LALLS) in NMP. The glass transition temperatures (T_g) were obtained by d.s.c. on a DuPont DSC 912; scans were run at 10°C min^{-1} and the reported values were obtained from second heatings after quick cooling. Thermogravimetric analyses were performed on a DuPont 951 TGA at a scan rate of 10°C min^{-1} in air or N_2 atmosphere.

Polymerization. General procedure. Polymers were synthesized according to literature procedures[2]. A mixture of diacid (5 mmol), diamine (5 mmol), lithium

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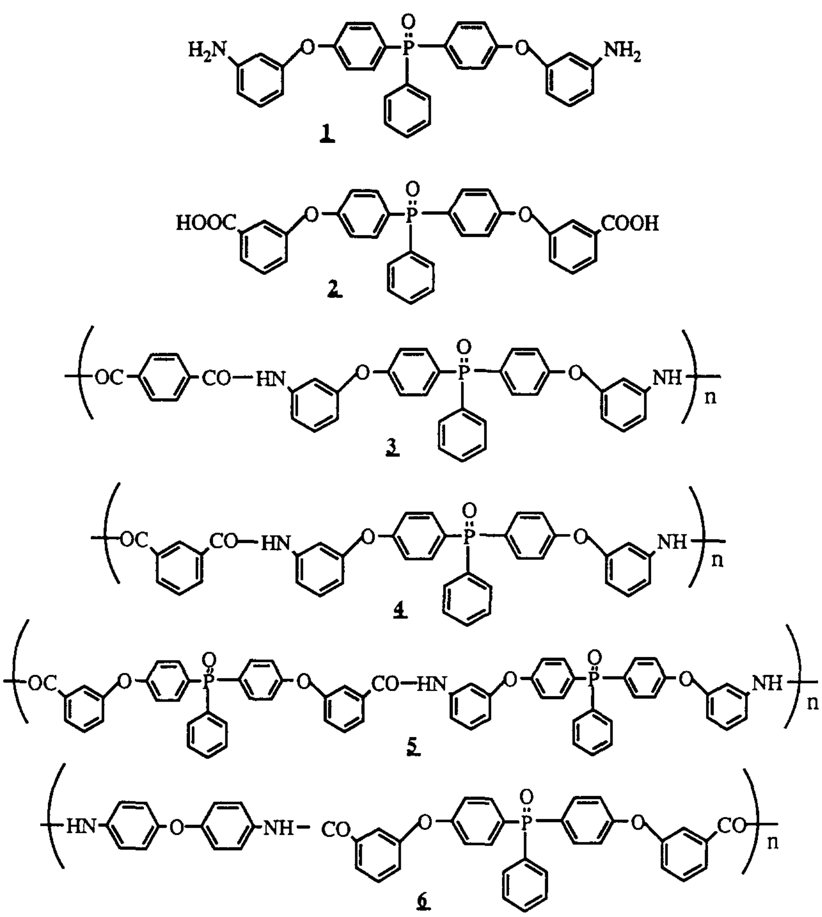

Scheme 1 Phosphine oxide containing polyaramides

chloride (0.5 g, 11.8 mmol), triphenyl phosphite (10 mmol), pyridine (2.5 ml, 31 mmol) and NMP (20 ml) was heated at 100°C for 3 h under nitrogen. When cooled, the reaction mixture was poured into methanol and the precipitated polymer was filtered. The polymers were dissolved in *N*,*N*-dimethylformamide (DMF) and precipitated into methanol, filtered, washed with hot methanol and dried *in vacuo* at 100°C for 48 h.

Polyamide *3*. From TA (0.83 g, 5 mmol) and *m*-BAPPO (*1*, 2.46 g, 5 mmol), a white fibrous polymer was obtained, 3.1 g (100%). I.r. ν: 3300 (N-H), 1669 (C=O), 1607, 1587 and 1539 (C=C), 1436 (Ar-P), 1260 (Ar-O-Ar) and 1170 (P=O) cm^{-1}; ^1H n.m.r. δ: 10.48 (2H, s, NH), 8.0–6.8 (25H, m, $H_{arom.}$).

Polyamide *4*. This polymer was synthesized according to the method described by Krigbaum *et al.*[7]. A mixture of IPA (0.83 g, 5 mmol), *m*-BAPPO (*1*, 2.46 g, 5 mmol), lithium chloride (1.0 g), calcium chloride (3.0 g), triphenyl phosphite (2.6 ml), pyridine (10 ml) and NMP (50 ml) was heated at 115°C for 3 h under nitrogen. The work-up was the same as for the general procedure; 2.8 g (90%) of white powdery polymer was obtained. I.r. ν: 3300 (N-H), 1669 (C=O), 1607, 1587 and 1539 (C=C), 1436 (Ar-P), 1238 (Ar-O-Ar) and 1170 (P=O) cm^{-1}; ^1H n.m.r. δ: 10.6 (2H, s, NH), 8.5–6.8 (25H, m, $H_{arom.}$).

Polyamide *5*. From *m*-BAPPO (*1*, 2.46 g, 5 mmol) and *m*-BCPPO (*2*, 2.75 g, 5 mmol), a white fibrous polymer was obtained, 5.0 g (100%). I.r. ν: 3300 (N-H), 1670 (C=O), 1587, 1539 (C=C), 1436 (Ar-P) and 1170 (P=O) cm^{-1}; ^1H n.m.r. δ: 10.4 (2H, s, NH) and 7.9–6.8 (42H, m, $H_{arom.}$).

Polyamide *6*. From *m*-BAPPO (*1*, 2.77 g, 5 mmol) and 4,4′-ODA (1.01 g, 5 mmol), 3.7 g (100%) of polymer was obtained. I.r. ν: 3300 (N-H), 1659 (C=O), 1596, 1576, 1536 (C=C), 1436 (Ar-P), 1257 (Ar-O-Ar) and 1171 (P=O) cm^{-1}; ^1H n.m.r. δ: 10.3 (2H, s, NH) and 7.9–6.9 (29H, m, H_{arom}).

Results and discussion

Synthesis. Polymers *3*, *5* and *6* were synthesized according to phosphorylation reaction reported by Yamazaki *et al.*[2]. The presence of the phosphine oxide linkage does not interfere with phosphorylation reaction. During the synthesis of polyaramide *3* the clear and viscous solution turned to a solid gel after 45 min at 100°C; the other polymers stayed homogeneous (no gel formation) during the polymerization reaction. Polymer *4* was synthesized by the phosphorylation reaction reported by Krigbaum *et al.*[7] which is a modification of Yamazaki's method[2]. This method was more dilute ($0.08\,mol\,l^{-1}$) and was carried out in the presence of LiCl and $CaCl_2$. The polymerization yields were quantitative for *3*, *5* and *6* but only 90% for *4*.

Molecular weights. The results of molecular weight characterization of polymers are summarized in *Table 1*. The molecular weights of these polymers were reasonably high as inferred from intrinsic viscosities and g.p.c. based on polystyrene standards. An absolute $\bar{M}_w$ determined by LALLS for *3* was about one half the g.p.c. value in polystyrene equivalents, but still high, 191×10^3. Polymer *4*, which was synthesized somewhat differently, gave

Table 1 Summary of characterization of polymers

Polymer	Yield (%)	$[\eta]$ (dl g^{-1})	$\bar{M}_n$[a]	$\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$[a]	T_g (°C)	T.g.a. (°C), 5% loss Air	T.g.a. (°C), 5% loss N_2	Char yield at 750°C (wt%)
3[b]	100	0.74	154×10^3	441×10^3	2.86	258	464	512	20
4	90	0.63	34×10^3	59×10^3	1.73	254	428	452	20
5	100	0.35	10×10^3	30×10^3	2.92	207	464	464	40
6	100	0.38	16.3×10^3	25.8×10^3	1.58	240	455	466	35

[a] By g.p.c.

[b] Weight average molecular weight of this polymer based on LALLS in NMP was 191×10^3

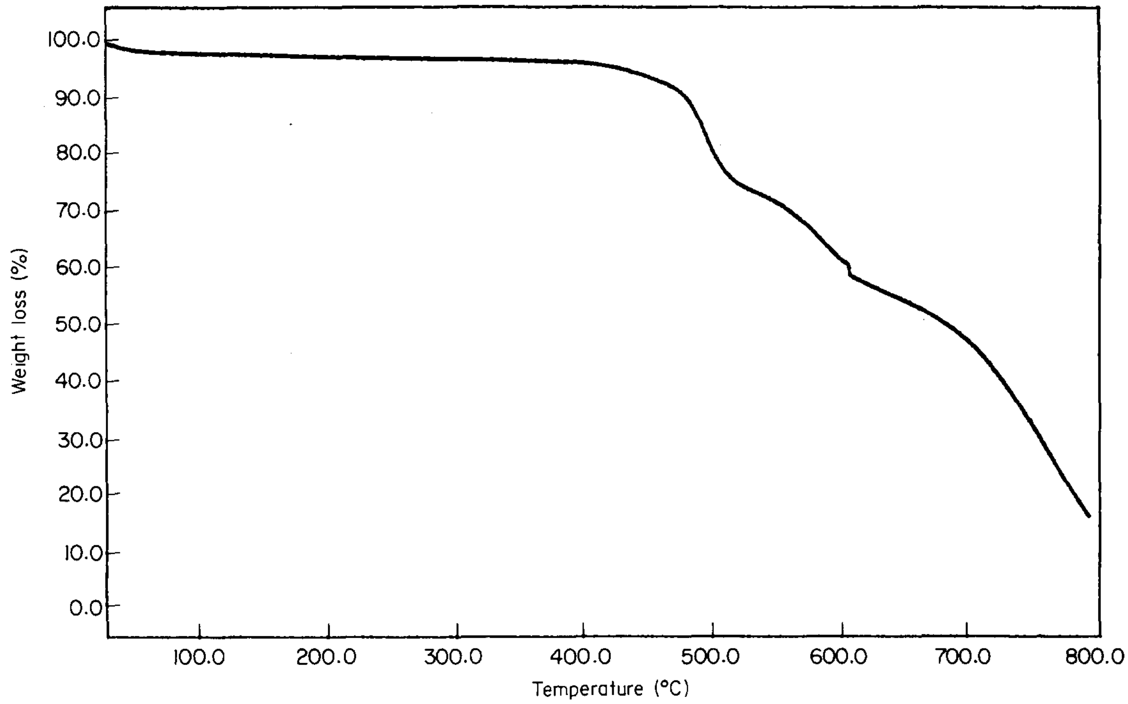

Figure 1 Thermogravimetric trace of polymer *6* in air flow

lower yield and lower molecular weight but lower polydispersity in comparison to *3* (*Table 1*). The molecular weights of *5* and *6* are also low relative to *3*. This is probably because of the presence of an impurity in *m*-BCPPO *2* monomer.

Solubility. The polymers were soluble in aprotic polar solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAC), DMSO and NMP, but insoluble in common organic solvents like tetrahydrofuran, chloroform or acetone. Use of *meta* linkages in the case of *4* did not extend the solubility of the polymer relative to *3*. Polymer *5*, which contains two flexible phosphine oxide linkages in the backbone per repeating unit, showed similar solubility behaviour. These polymers form transparent, flexible and tough films from solution.

Thermal properties. Phosphine oxide containing polyaramides *3*, *4* and *6* are amorphous by nature and show glass transition temperatures around 250°C (*Table 1*). Polymer *5*, which contains two flexible phosphine oxide linkages per repeating unit, is also amorphous, but shows much lower T_g, around 207°C. The presence of the unique phosphine oxide moiety in the backbone resulted in excellent thermooxidative stability. The thermogravimetric analyses of 5% weight loss in air and nitrogen atmospheres are summarized in *Table 1*. These results show that the polymers are stable up to 450°C and start degrading thereafter. Polymer *4* exhibits a lower thermal stability than the others probably due to the presence of *meta* linkages.

All of the phosphine oxide based polyaramides yielded substantial amounts of char. The char yields at 750°C under air flow are shown in *Table 1*. As an example, the thermogravimetric trace of polymer *6* in air is shown in *Figure 1*.

Conclusions

Soluble phosphine oxide containing polyaramides have been synthesized through the phosphorylation reaction approach. The presence of flexible phosphine oxide linkages provides solubility in aprotic polar solvents like DMF, DMSO, NMP and so on. The thermal data indicate that this class of polymers can be used in heat resistant and fire retardant applications.

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