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Synthesis of poly(arylene phosphine oxide) by nickel-catalysed coupling polymerization

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An amorphous high molecular weight poly(arylene phosphine oxide) (PAPO) was synthesized from bis(4-chlorophenyl)phenylphosphine oxide by the nickel-catalysed carbon–carbon coupling reaction. The physical and thermal properties of PAPO were investigated. The material exhibited a glass transition temperature around 365°C and 5% weight loss around 550°C in nitrogen and air. Upon heating up to 750°C in air PAPO lost only 65% of its weight leaving significant amount of char behind which is due to the presence of phosphorous in the polymer. The polymer developed an intense red colour once the phosphine oxide groups in the polymer were reduced to phosphine. © 1997 Elsevier Science Ltd.

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Introduction

High performance aromatic polymers have been prepared by several methods. However, the majority of these methods involve the formation of carbon–heteroatom bonds. For example, the polycondensation or step polymerization of bisphenoxide anions with aromatic dihalides generates a carbon–oxygen bond. Commercially available poly(arylene ether sulfone)s, and poly(arylene ether ketone)s, are two examples of engineering thermoplastics which are made by nucleophilic substitution reactions[1]. The oxidative polymerization of substituted phenols to poly(phenylene oxide)s is another example where a polymeric chain is formed by carbon–heteroatom coupling[2].

Polymerization involving the formation of aromatic carbon–carbon bonds are of high interest due to the expectation that such polymerizations may allow for the preparation of a variety of unique structures. Several approaches to produce carbon–carbon bonds have been investigated[3]. The electrophilic Friedel–Crafts preparation of poly(arylene ether ketone)s and poly(arylene ether sulfone)s, e.g. using diacidhalides or disulfonylhalides, respectively, and aromatic hydrocarbons affords high molecular weight, somewhat branched materials[4]. The scope of this approach is limited to compounds capable of undergoing quantitative Friedel–Crafts acylation or sulfonylation such as biphenyl or diphenyl ether. Furthermore, this reaction requires a very large amount of Lewis acid and solvent.

The palladium-mediated coupling of aromatic bromides with aromatic boronic acids (Suzuki coupling) has been reported as a successful method to make substituted poly(phenylene)s[5–7]. Nickel coupling of aryl chlorides has been also utilized to make high molecular weight rigid-rod polymers[3,8–12]. The results, described by several research groups show that using the nickel coupling approach, a variety of polymers can be prepared by properly choosing the starting materials.

Herein we describe a nickel-catalysed polymerization which employs the coupling of bis(4-chlorophenyl)phenylphosphine oxide as a polymer-forming reaction to synthesize poly(4,4′-diphenylphenylphosphine oxide) (PAPO), **1**. The reaction utilized has general applicability to the synthesis of new processable engineering resins of superior thermal stability. Phosphorous-containing polymers have been widely studied in our laboratory for fire resistance and several other features[13–18].

It was anticipated that the non coplanar phenyl group would produce an amorphous morphology which result in an organic soluble, but still rather rigid chain.

Experimental

Materials. Bis(4-chlorophenyl)phenylphosphine oxide (DCPPO) (Akzo Chemical Co.) was dried under vacuum at room temperature over night. *N,N*-Dimethylacetamide (DMAc, Fisher Scientific) and chlorobenzene (Aldrich) were dried over calcium hydride for 24 h with constant stirring, followed by vacuum distillation and storage over 4-Å molecular sieves under dry nitrogen. Triphenylphosphine (Aldrich) was recrystallized from hexane. Zn powder (Aldrich) was washed with dilute hydrochloric acid, filtered, washed with dry diethylether, and dried under high vacuum at 150°C. Nickel(II) chloride (Aldrich) was dried under vacuum at 220°C. 2,2′-Bipyridine (bpy) and phenylsilane (Aldrich) were used as received.

Preparation of PAPO by polymerization of DCPPO. $NiCl_2$ (0.016 g, 0.125 mmol), bpy (0.02 g, 0.125 mmol), Zn powder (0.51 g, 7.75 mmol) and $(Ph)_3P$ (0.66 g, 0.25 mmol) were added inside a dry N_2 atmosphere drybag into a 50-ml flask equipped with a side tubing adapter capped by a rubber septum. After removal from the drybag, the flask was connected to a vacuum line through the side tubing for 24 h, during which the flask was purged with N_2 several times. Then, it was placed in an oil

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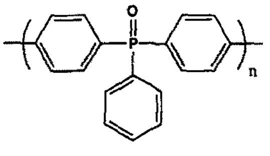
bath and kept under N_2. While heating the oil bath, 3 ml of DMAc was added by syringe through the septum. The solution was stirred magnetically and when the temperature reached 40°C a dark yellow colour formed, which slowly became dark brownish red as the temperature approached 70°C. At this point a solution of DCPPO (0.868 g, 2.5 mmol) in 2 ml DMAc was added to the catalyst mixture via a syringe, through the septum. After 2 h a viscous solution formed which was isolated by addition into a mixture of methanol and hydrochloric acid. The resulting white fibrous material was filtered and dried to give 0.6 g (92% yield) of the product.

Reduction of PAPO with phenylsilane. To a 50-ml flask was added 0.28 g of PAPO, 10 ml of PhCl and 0.4 ml of phenylsilane. The mixture was heated to 110°C under N_2 and stirred for 10 days. The reaction mixture was heterogeneous through the course of reaction. While heating, the colour of polymer changed from white to yellow and finally brownish red. Based on ^{31}P nuclear magnetic resonance (n.m.r.), 34% of the phosphine oxide groups were reduced to phosphine.

Characterization. ^1H and ^{31}P n.m.r. spectra were measured using a Varian Unity 400 spectrometer. ^1H n.m.r. chemical shifts are reported relative to the solvent (dimethylsulfoxide-d_6, DMSO, at 2.49 ppm) and ^{31}P n.m.r. chemical shifts are reported relative to 85% H_3PO_4 (external, 0.0 ppm). Intrinsic viscosity measurements of the polyimides were conducted in NMP (N-methyl pyrdlidone) at 25°C using a Cannon–Ubbelohde viscometer. The average molecular weights for the polymers were determined using a gel permeation chromatogram (g.p.c.) in LiBr modified NMP at 60°C, using concentration and viscometric dual detectors, with a universal calibration curve based on narrow polystyrene standards utilizing techniques as reported earlier[19].



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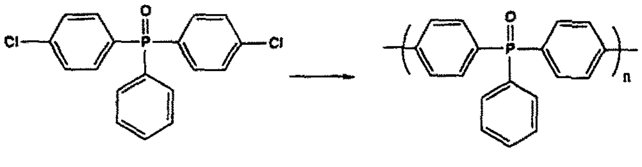


Scheme 1 Nickel-catalysed coupling polymerization of bis(4-chlorophenyl)phosphine oxide

Glass transition temperatures T_gs were determined by differential scanning calorimetry (d.s.c.) using a Perkin-Elmer DSC 7. Scans were run at a heating rate of 20°C min^{-1} and reported values were obtained from a second heat after quick cooling. Thermogravimetric analyses (t.g.a.s) were performed on a Perkin-Elmer TGA 7 thermogravimetric analyser at 10°C min^{-1} in air or nitrogen.

Results and discussion

Colon and Kwiatkowski have reported a detailed general procedure for the carbon-carbon polymerization

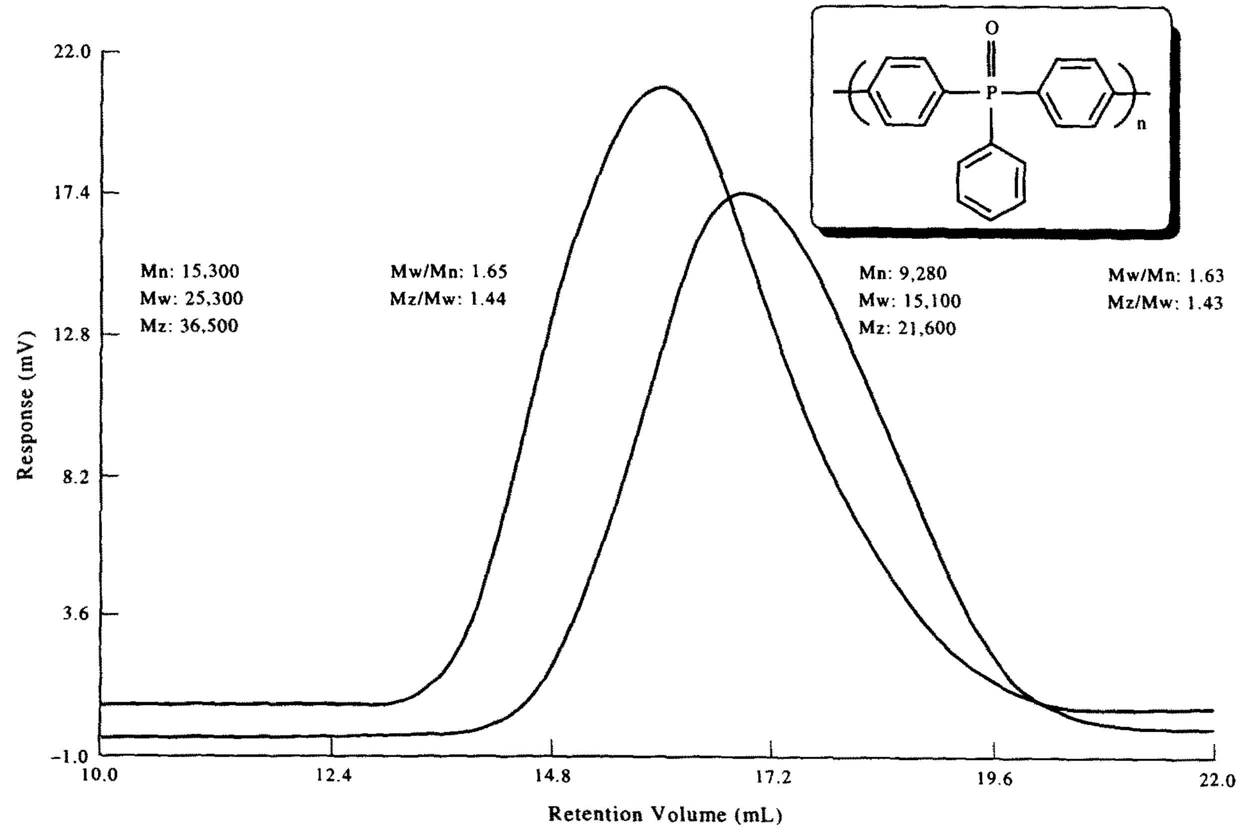


Figure 1 Size exclusion chromatogram of PAPO

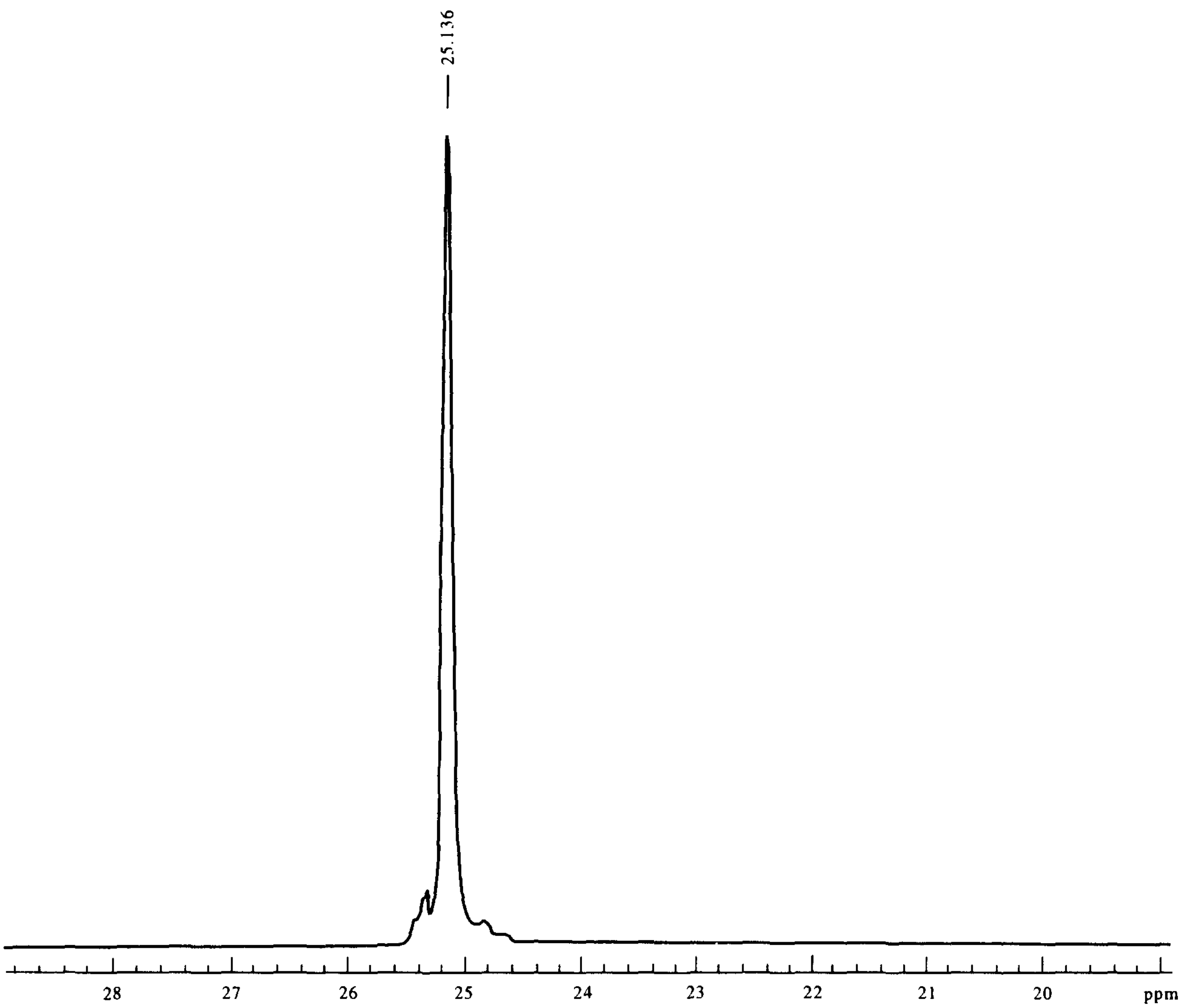
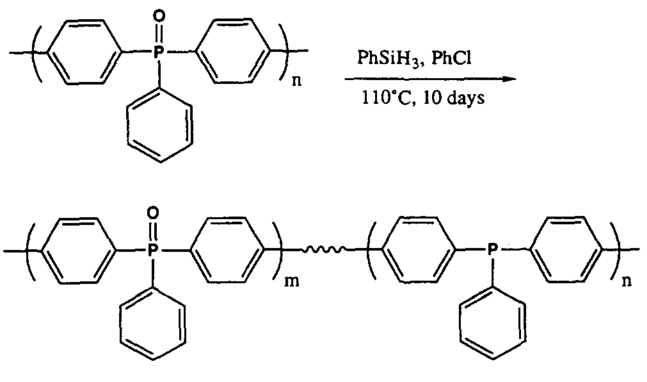


Figure 2 ^{31}P n.m.r. spectrum of PAPO

reaction utilizing a coupling reagent composed of a mixture of a catalytic amount of an anhydrous nickel salt and triphenylphosphine in the presence of an excess of a reducing metal, such as Zn and Mg[3]. From the results of Ueda and coworkers[10,11], it was apparent that the use of highly dry reagents would be required for the successful preparation of high molecular weight PAPO. An efficient synthesis of high molecular weight soluble PAPO has been achieved using the reaction conditions described in the literature[10], as shown in *Scheme 1*. It was found that the addition of dichloro monomer to the activated catalyst mixture produced high molecular weight product, both as deduced by η_{int} (0.39 g dl^{-1}) and g.p.c. The weight average molecular weight ($\bar{M}_w$) using the viscosity detector was in the range 25×10^{-3} with an apparent polydispersity (M_w/M_n) of ≈1.6. In contrast, when the dichloro monomer was added with other reagents at the same time the resulting polymer had a lower molecular weight ($\eta_{\text{int}} = 0.25$ g dl^{-1}, and $\bar{M}_w = 15 \times 10^{-3}$). One might speculate that aging the catalyst is beneficial. *Figure 1* shows the raw g.p.c. chromatograms of two PAPO samples. The polymer was also soluble in DMSO, but only partially in less polar hot chlorobenzene.

The ^1H n.m.r. spectrum of PAPO shows only aromatic protons, as expected, around 7.1–8.8 ppm. The ^{31}P n.m.r. shows one major peak at 25.1 ppm attributed to phosphine oxide groups of the polymer repeat unit and two broad and smaller peaks close to the major peak are assigned to the phosphine oxide end groups as shown in *Figure 2*.



Scheme 2 Reduction of PAPO using phenylsilane

D.s.c. analysis of PAPO showed (*Figure 3*) a very high T_g around 365°C. The polymer exhibited the high thermal stability expected for polyarylenes as shown by the t.g.a. thermogram presented in *Figure 4*. The 5% weight loss upon heating of PAPO in nitrogen or air was detected around 550°C. There was only 65% weight loss at 750°C in air indicating 35% char yield. Phosphorus containing polymers are well known to be flame

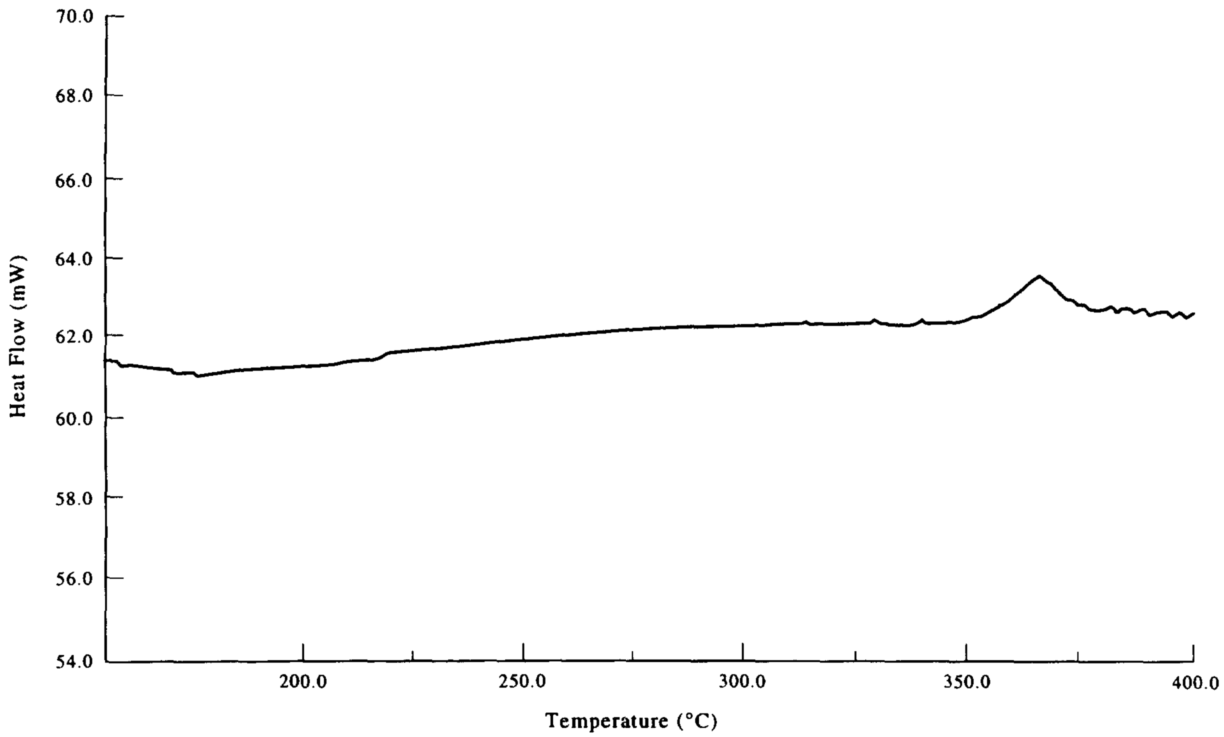


Figure 3 D.s.c. thermogram of PAPO

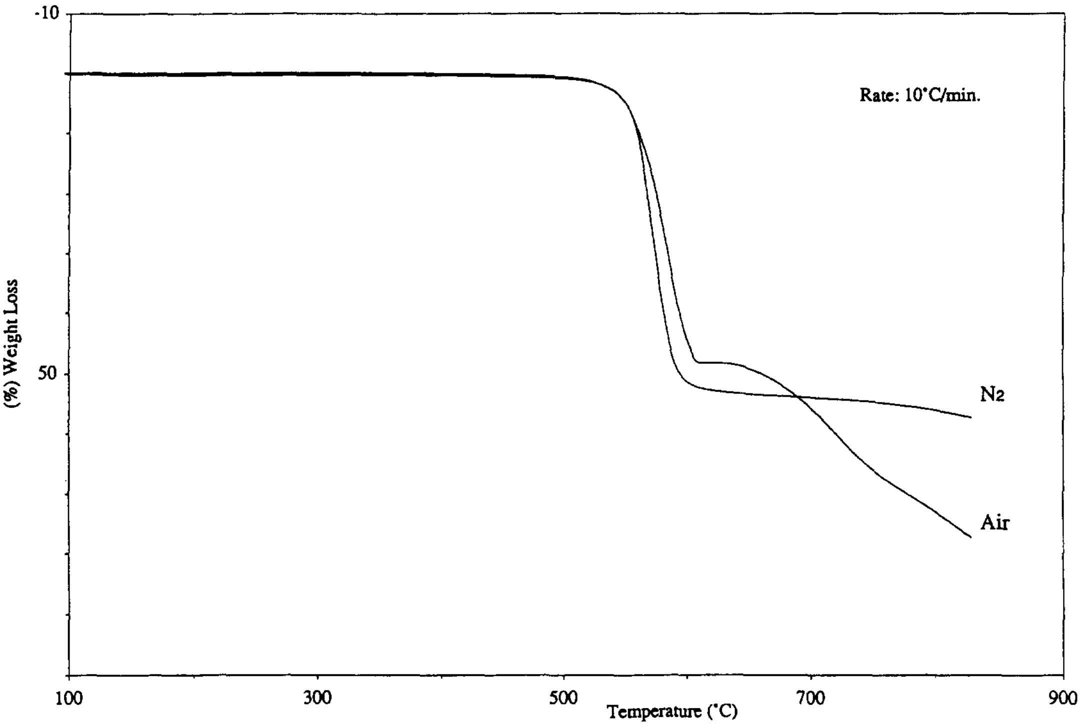


Figure 4 T.g.a. thermogram of PAPO in nitrogen and air

retardant and to demonstrate high char yield at high temperatures[13–18].

The reduction of phosphine oxide groups in PAPO to phosphine was accomplished using phenylsilane as a reducing agent based on a procedure described previously (*Scheme 2*)[20,21]. The poor solubility of PAPO in chlorobenzene only allowed for about 35% reduction. The reduction of soluble poly(arylene ether phosphine oxide)s under the same condition was shown to be quantitative. A very distinct colour change from white to yellow and then brownish red was observed during the course of reaction. The intense colour of partially reduced PAPO is possibly due to formation of an inter- or intra-molecular donor–acceptor complex between the electron withdrawing phosphine oxide and the electron donating phosphine groups.

The ultraviolet–visible (u.v.–vis) spectrum of the PAPO in DMSO showed an absorption with $\lambda_{max} \sim 280$ corresponds to π–π transition in biphenyl groups (*Figure 5*). It was expected that a new absorption

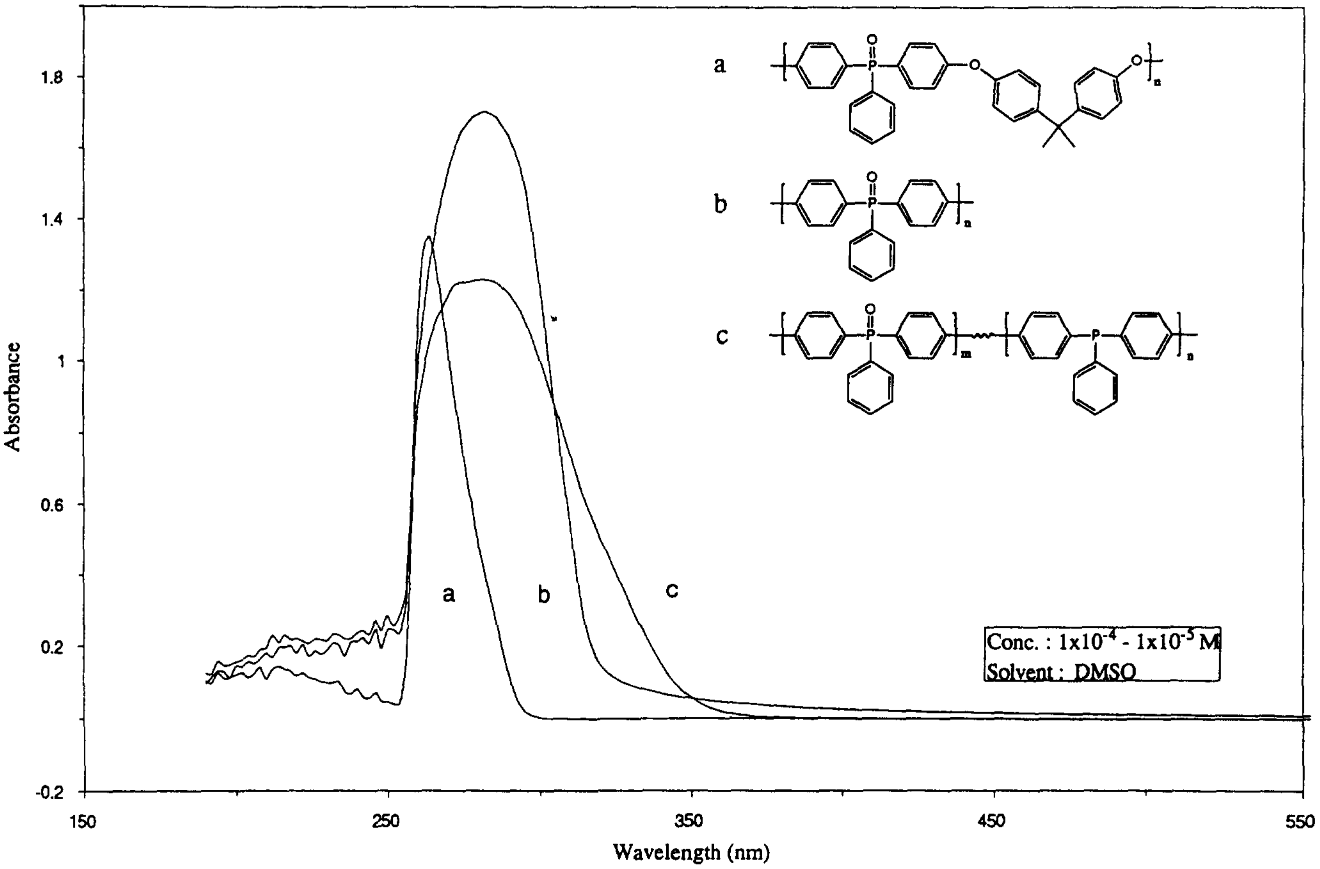


Figure 5 U.v.-vis spectra of PAPO compared with a poly(arylene ether phosphine) oxide and partially reduced PAPO in DMSO solution

band would appear in the visible region for the partially reduced PAPO due to the proposed donor–acceptor complex, which would explain the brownish colour of the polymer. However, only a red-shift was observed to around 300 nm. Quite likely, the phosphine in the partially reduced PAPO was oxidized to phosphine oxide during the prolonged heating of the material in DMSO. Interestingly, the partially reduced PAPO was insoluble in most solvents.

Conclusions

PAPO was successfully prepared by the nickel-catalysed carbon–carbon coupling reaction of bis(4-chlorophenyl)phenylphosphine oxide. In addition to a very high T_g, around 365°C, this material exhibited high thermal stability as judged by dynamic t.g.a. The 5% weight loss in air and nitrogen was detected around 550°C and the material leaves substantial amount of char after heating to 750°C in air. The phosphine oxide groups in PAPO was also partially reduced to phosphine which afforded very intense colour.

Acknowledgements

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