

## Preparation and Characterisation of Noble Metal Solid Sols in Poly(methyl methacrylate)

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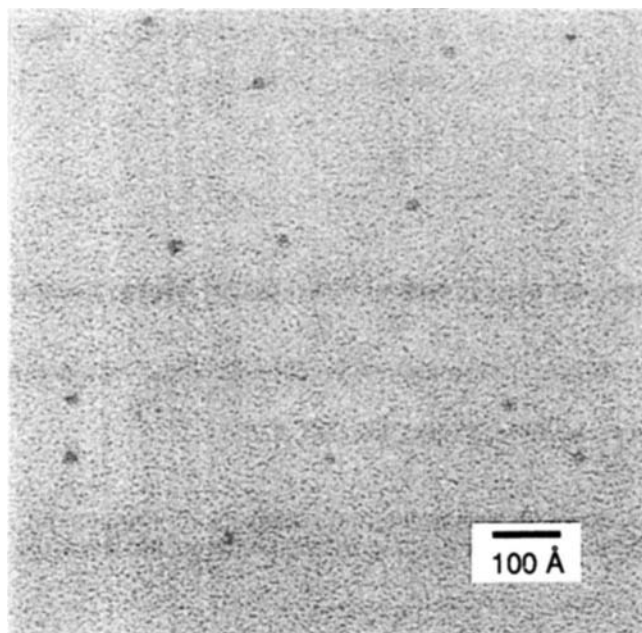
Novel solid sols of palladium, platinum, silver and gold in poly(methyl methacrylate) have been prepared and characterised by both visible spectroscopy and transmission electron microscopy.

Since medieval times gold has been utilized to produce red coloured glasses, which were useful for glass wares and stained glass windows.<sup>1</sup> For this purpose chloroauric acid is dissolved in molten glass. After cooling, the mixture is heated again at temperatures ranging from 600 to 900 °C; the glass becomes red during the heating period. It is now known that such

coloured glass is a gold solid sol, *i.e.*, a colloidal dispersion of very fine gold particles in a solid medium, which absorb visible light of a characteristic wavelength (*ca.* 520 nm) owing to plasma oscillations of the conduction electrons. In recent years, such glasses coloured with gold have been reevaluated as a nonlinear optical material,<sup>2</sup> and very recently a new

**Table 1** Preparation and properties of solid sols of noble metals in PMMA by process A

Noble metal compound		Min. temp. of post-heating/°C	Solid sol of noble metals	
Name	Conc./ $\mu\text{mol g}^{-1}$		Colour	Size of colloid/Å
Pd-AA	0.5	140	Brown	15–20
	5	120	Dark-brown	
	50	120	Black	10–20
Pt-AA	0.5	140	Light-brown	15–20
	5	140	Brown	
	50	120	Dark-brown	10–20
Ag-CN-STMA	0.5	140	Yellow	20–40
Au-Cl-STMA	0.5	120	Red	80–100

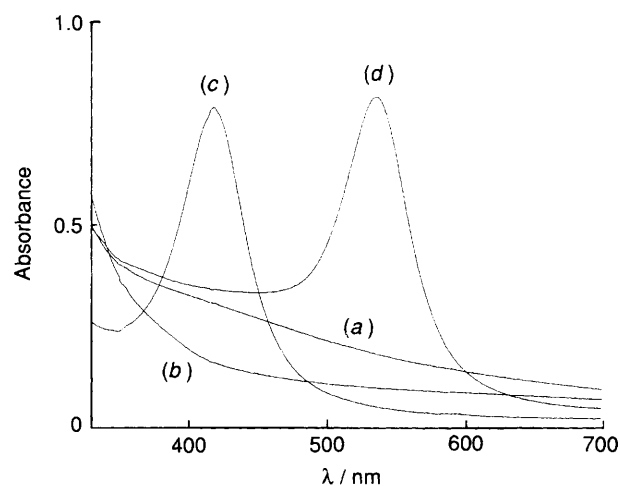
**Fig. 1** Transmission electron micrograph (TEM) of the coloured PMMA sample prepared by process A using Pd-AA (50  $\mu\text{mol per g}$  of PMMA)

preparative method has been reported.<sup>3</sup> On the other hand, some reports have been made on the conversion of noble metal salts dissolved in polyimide to the metallic state to give electrically conductive polymer-noble metal systems.<sup>4</sup> However, in those systems, the noble metals are present in a much higher content and can not be in a well-dispersed colloidal state.

We have succeeded in preparing new types of organic solid sols of noble metals including gold in poly(methyl methacrylate) (PMMA). In this report we describe the preparative procedures and some characteristics of the solid sols.

Preparative procedures were as follows. Reagents of acetylacetonato palladium(II) (Pd-AA) and acetylacetonato platinum(II) (Pt-AA), and ion pairs of silver and gold synthesized in the following manner were used as the starting noble metal compounds. The ion pair of silver (Ag-CN-STMA) was synthesized by the reaction of equimolecular amounts of potassium dicyanoargentate  $\{\text{K}^+[\text{Ag}(\text{CN})_2]^{-}\}$  and stearyltrimethylammonium chloride  $\{[\text{C}_{18}\text{H}_{37}(\text{Me})_3\text{N}]^+\text{Cl}^-\}$  in aqueous solutions. The ion pair of gold (Au-Cl-STMA) was obtained from chloroauric acid  $(\text{H}^+[\text{AuCl}_4]^{-})$  and stearyltrimethylammonium chloride in a similar manner. The molecular structures of Ag-CN-STMA and Au-Cl-STMA were identified to be  $[\text{C}_{18}\text{H}_{37}(\text{Me})_3\text{N}]^+[\text{Ag}(\text{CN})_2]^{-}$  and  $[\text{C}_{18}\text{H}_{37}(\text{Me})_3\text{N}]^+[\text{AuCl}_4]^{-}$ , respectively, by elemental analysis.

One of the noble metal compounds (1.5, 15 and 150  $\mu\text{mol}$ ) and benzoyl peroxide (BPO) (15 mg), as an initiator for

**Fig. 2** Visible spectra of coloured PMMA plates prepared by process B using (a) Pd-AA, (b) Pt-AA, (c) Ag-CN-STMA and (d) Au-Cl-STMA

polymerization, were dissolved in methyl methacrylate (MMA, 3 g). The polymerization of MMA was carried out by heating at fixed temperatures in a polypropylene test tube (process A) or in a glass mould (process B). In A, the solution was heated at 60 °C for 6 h in an oil bath, resulting in the formation of a bullet-shaped solid sample of PMMA which contained the noble metal compound. In B, a solution of the noble metal compound (0.5  $\mu\text{mol g}^{-1}$ ) and BPO in MMA was first heated at 70 °C for 30–60 min. The resulting viscous solution was then transferred into a mould which consisted of two 4 × 6 cm glass plates and a Teflon frame (2 mm thickness), and heated again at 45 °C for 24 h to complete polymerization. After removal from the mould, a clear PMMA plate (2 mm thickness) containing the noble metal compound was obtained.

The PMMA samples or PMMA plates thus prepared were then further heated for 1 h each, at 100, 120 and 140 °C (post heating). In some cases, they became coloured on heating. (The coloured PMMAs were just noble metal solid sols as stated later.)

Table 1 summarises the results for the preparation of solid sols by process A. This shows that the colouration of the sample depends on the temperature of post-heating. In the cases of Pd-AA and Pt-AA, clear coloured samples can be obtained over their concentrations ranging from 0.5–50  $\mu\text{mol g}^{-1}$  and the minimum temperature of post-heating to give colouration tends to become lower with increasing their concentration in PMMA. At those temperatures of colouration, PMMA becomes slightly softened. Polymerization of MMA containing Ag-CN-STMA or Au-Cl-STMA of concentrations of more than 5  $\mu\text{mol g}^{-1}$  caused the deposition of needle crystals or Au metal, respectively.

A typical TEM of the coloured PMMA sample containing Pd is shown in Fig. 1, which indicates the existence of

well-dispersed ultrafine particles of palladium. The diameters of the colloidal particles of noble metals in the PMMA samples measured in the TEMs are also given in Table 1. All the particles of Pd and Pt were found to be extremely fine and not larger than 20 Å, while those of Ag and Au were somewhat larger.

When the noble metal compounds were heated alone, their decomposition to metallic states required much higher temperatures than those used for colloid formation. Therefore, it is considered that the reduction of the noble metal ions is greatly accelerated by PMMA and/or BPO. The colours of the PMMA plates prepared by process B and successive post-heating at 140 °C were quite similar to those of hydrosols of the corresponding noble metals.<sup>5</sup> As shown in Fig. 2, a maximum was found at 418 or 535 nm in the spectra of PMMA plates containing Ag or Au, respectively, while no maximum was present in those containing Pd or Pt.

In general, noble metal particles are formed very rapidly in the preparation of hydrosols.<sup>5</sup> In the present cases, the

particles are considered to be formed very slowly and do not aggregate with each other presumably because PMMA has an extremely high viscosity.

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