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Synthesis and molecular weights of metal poly(methyl methacrylates)

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SUMMARY

Methyl methacrylate colloids were obtained by codeposition at 77K of the monomer with several metals such as: Au, Pd, Cu, Ge, Ga, In, Sn, Sb and Bi. The colloids were polymerized with different amounts of initiator (AIBN) at 60°C and a wide range of viscosity average molecular weights ($\bar{M}v$; 10^4-10^5) were obtained depending upon the metal used. The metal colloid concentrations are reported. The thermal stability and metal composition are also described. The polymers are stable even at 350°C and the metal content is 0.7 to 3.1%.

INTRODUCTION

A recent approach in preparing colloidal metals in non-aqueous solvents has recently been described (1,2,3). This method, Chemical Liquid Deposition, involves deposition of metal vapor with organic solvents at low temperature (77K). The method is wide in scope and can be employed with a variety of metals and solvents. In this communication we report the synthesis of metal clusters trapped in solid, organic polymers based on our earlier work on the preparation of colloidal metals in non-aqueous solvents. This method, which involves deposition of metal vapors (atoms) with organic solvents. At low temperature followed by controlled atom accretion, is wide in scope and can be employed with a variety of metals and solvents.

EXPERIMENTAL PART

Metal Colloid. The metal atom reactor was described previously (1,2,3). As a typical example, a W-Al_2O_3 crucible was charged with 0.4 g of Au metal foil (Alfa Products). Styrene (100 ml), was previously distilled in a ligand inlet tube and freeze-thaw-degassed with several cycles. The reactor was pumped down to $1x10^{-3}$ Torr while the crucible was warmed to red heat. A liquid nitrogen filled Dewar of 5 L was placed around the vessel, and Au (0.2g) and styrene (81.9 g) were co-deposited over a 1.5 h period. A heating tape was placed around the inlet tube to facilitate the solvent introduction. The matrix was dark blue at the end of the deposition. The matrix was allowed to warm slowly under vacuum by removal of

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the liquid nitrogen filled Dewar for 1.5 h. Upon meltdown a purple sol was obtained. After addition of nitrogen, the solution was allowed to warm for another 1.0 h at room temperature. The solution was syphoned off under N_2 into a Schlenk flask. Based on Au evaporated and styrene inlet,the approximate molarity could be calculated.

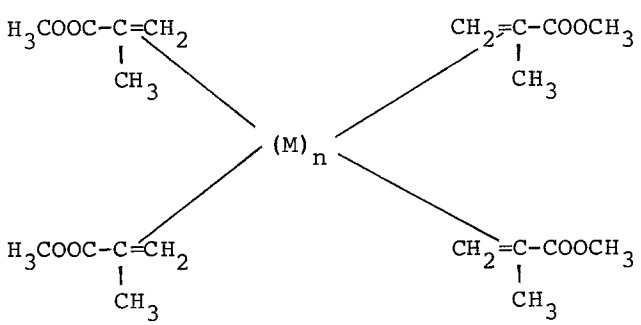
Polymerization. Colloid Au (10 ml) was placed in four Schlenk tubes, with 0.1, 0.2, 0.5 and 1.0 mol % of AIBN (azodiisobutyronitrile) under N_2 flow. The Schlenk tubes were closed and placed in an isothermal bath at 60°C for 20 min. The content of each Schlenk flask was poured in beakers with methanol. The purple polymers obtained were filtered off and dried under vacuum for 24 h at 20°C. The yield of each polymer fraction was determined.

Elemental Analysis. The samples for microanalysis of Pd and Sb were handled by Galbraith Laboratories (U.S.A.). The carbon, hydrogen and other metals were performed by the Chemistry Department Laboratories (University of Concepción).

Thermogravimetric Analysis. The thermogravimetric data were obtained using a Thermobalance TGS-1, Perkin Elmer with 2-6 mg samples heated under nitrogen flow (50 ml min^{-1}) from 25 to 550°C.

RESULTS AND DISCUSSION

We have recently reported the first metal colloids stabilized by a nonpolar solvent, styrene (4,5). This must be due to the ligating action of the unsaturated bonds in styrene. Methyl methacrylate behaves similarly; the ligating action of the unsaturated bonds in MMA is probably as follows:



During polymerization the metal clusters tend to weakly agglomerate until solidification eventually traps them. The metal is apparently incorporated in the polymers and can be detected by high resolution mass spectrometry, CIMS.

Table 1 summarizes yields and molecular weights ($\bar{M}v$) of metal poly(methyl methacrylates). As we can see the yields are

Table 1. Correlation between Metal Poly(methyl methacrylates) and Molecular Weights.

Polymer	Yield(%)*	M.W. ($\bar{M}v$)	Polymer Color
Au-PMMA	0.57 ; 0.77	298,000 ; 242,000	Purple
	13.80 ;23.60	108,600 ; 72,600	
Pd-PMMA	13.00 ;17.40	501,400 ; 256,000	Black
	28.15 ;94.30	168,400 ; 90,100	
Cu-PMMA	3.38 ; 6.87	358,300 ; 261,100	Light-Brown
	15.30 ;66.40	150,500 ; 59,300	
Ge-PMMA	4.53 ; 6.22	272,000 ; 231,600	White
	12.50 ;96.00	155,000 ; 33,600	
Ga-PMMA	2.80 ; 5.84	396,100 ; 268,300	Black
	11.45 ;35.90	150,700 ; 52,000	
In-PMMA	3.62 ; 8.57	502,500 ; 277,400	White
	13.87 ;24.06	161,800 ; 114,000	
Sb-PMMA	0.84 ; 2.46	507,200 ; 357,000	Black
	6.00 ; 8.83	231,300 ; 166,100	
Sn-PMMA	4.77 ; 8.17	340,600 ; 296,600	Green
	15.24 ;32.90	151,900 ; 88,000	
Bi-PMMA	1.51 ; 4.60	423,200 ; 306,500	Black
	7.81 ;39.40	150,200 ; 90,000	
PMMA	0.66 ; 1.05	161,300 ; 154,400	White
	6.83 ;23.60	118,600 ; 103,600	

*Yields correspond to 0.1, 0.2, 0.5 and 1.0 mol % of AIBN.

similar for several metals: Cu-Ge, Sn-In. Pd-PMMA showed the highest yield in all the fractions. Of particular interest is the fact that Au, Pd and In are the most stable colloids. Au-PMMA and pure PMMA gave similar yields. Pd, Sb and In showed the highest molecular weights. However, is not easy to explain the $\bar{M}v$ of Ge. This behaviour is similar for Ge-PS (4), probably some AIBN initiator was trapped by the metal and the polymerization stopped (6).

In all the experiments, it is possible to obtain a linear correlation between $\bar{M}v$ and $(AIBN)^{-\frac{1}{2}}$ (7). This is in agreement with the fact that molecular weight decreases with the increase of initiator concentration.

Polymer analyses were performed after drying the samples at 10^{-3} Torr for 24 h. Table 2 summarizes some data of metal poly(methyl methacrylates). It is clear that metal has been incorporated in the polymers in all the samples. The amount of metal incorporated is ranging between 0.7 to 3.1% and the samples showed different colors depending of the metal.

Table 2. Correlation between monomer, content, composition and molecular weight.

Polymer	%M	%C	%H	$\bar{M}v \times 10^{-3}$
Au-PMMA	3.0	58.60	8.21**	298
Pd-PMMA	1.4	61.05	8.28	501
Cu-PMMA	1.8	58.38	7.77	358
Ge-PMMA	0.7	74.05	8.54	272
Ga-PMMA	3.1	58.02	7.16	396
In-PMMA	1.4	58.84	7.66	502
Sb-PMMA	1.6	59.52	8.07	507
Sn-PMMA	3.1	58.05	8.62	340
Bi-PMMA	2.8	58.06	7.71	423
PMMA	-	57.92	6.72	161

* Data for 0.1 mol% AIBN. ** The balance is most likely oxygen. PMMA= poly(methyl methacrylate).

A study of thermal stability between 25 to 550°C was carried out for the metal polymers (8). The thermograms reveal that polymers are stable up to 300°C and for Sb and Bi even at 330°C did not lose weight. Sb is the most stable with a residual weight of 35%. The other stable polymers are Cu and Ge with 28 and 18%, respectively. In-PMMA shows the lowest residual weight (2%).

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