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Synthesis and molecular weights of metal (styrene-methyl methacrylate) copolymer. III

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SUMMARY

Styrene-methyl methacrylate colloids were obtained by codeposition at -196°C of the monomer with metals, such as: Au, Pd, Cu, Ga, In, Sn and Bi. The colloids were polymerized with various amounts of initiator (AIBN) at 60°C and a wide range of viscosity average molecular weights ($\bar{M}v$; $2.0x10^4$ - $1.9x10^5$) were obtained depending upon the metal used. The metal colloid concentrations are reported. The thermal stability and metal composition are also described. The copolymers of Au, Ge, Pd and Sn are stable even at 300°C. The metal content is 0.9 to 11% with an exception of 22% for Au.

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 (-196°C). The method is wide in scope and can be employed with a variety of metals and organic solvents. In this work we report the synthesis of metal clusters trapped in solid, organic polymers based on our earlier paper 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 is followed by controlled atom accretion has been recently reported (4,5).

EXPERIMENTAL PART

Metal Colloid. The metal atom reactor was described previously (1,2,3). As a typical example, a W-Al_2O_3 crucible (Sylvania Emissive) was charged with 0.3 g of Pd metal lumps (Alfa Products). Styrene (50 ml) and methyl methacrylate (50 ml), were previously distilled in a ligand inlet tube and freeze-thaw-degassed with several cycles. The styrene was distilled over the methyl methacrylate. The reactor was pumped down to $1x10^{-4}$ Torr while the crucible was warmed to red heat. A liquid nitrogen filled Dewar of 5 L was placed around the vessel, and Pd (0.36 g) and the mixture of styrene-methyl

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methacrylate (176.2 g) were codeposited over a 1.0 h period. A heating tape was placed around the inlet tube to facilitate the solvent introduction. The matrix was black at the end of the codeposition. The matrix was allowed to warm slowly under vacuum by removal of the liquid nitrogen filled Dewar for 1.5 h. Upon meltdown a black sol was obtained. After addition of nitrogen, the solution was allowed to warm for another 1.0 h at room temperature. The dispersion was syphoned off under nitrogen atmosphere into a flask ware. Based on Pd evaporated and the monomers inlet, the approximate concentration could be calculated.

Polymerization. Pd colloid (10 ml) was placed in each of the four polymerization flasks, with 0.1, 0.2, 0.5 and 1.0 mol % of AIBN (azodiisobutyronitrile) under N2 flow. The flasks were closed and placed in an isothermal bath at 65°C for 1 h. The content of each flask was poured in beakers with methanol. The black copolymers obtained were filtered off and dried under vacuum for 24 h at 20°C. The yield of each polymer fraction was determined.

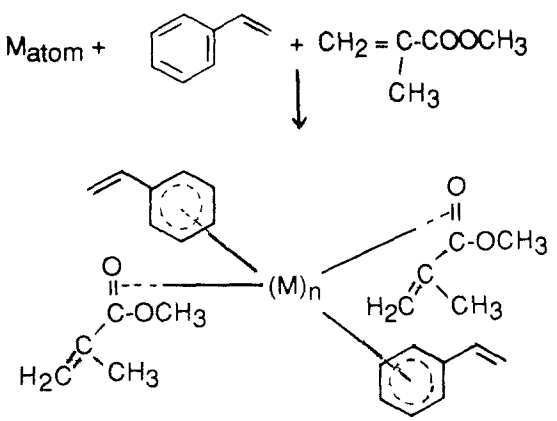
Molecular Weights. The average molecular weight ($\bar{M}v$) can be calculated with Mark-Houwink equation. The intrinsic viscosity was measured at 25°C by using an Ostwald viscometer. The copolymers were dissolved in 2-butanone at 25°C.

Elemental Analysis. The carbon, hydrogen and metals microanalysis 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 2-5 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 nonpolar solvents, styrene and methyl methacrylate (6,7). This is probably due to the ligating action of the unsaturated bonds in styrene and methyl methacrylate, perhaps as shown here:



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 (styrene-methyl methacrylate) copolymers. As we can see the yields are similar for several metals: Sn, In, Ge and Ga. The higher yields correspond to Cu, Pd and Au. It is interesting to note that the colloids with this metals are the most stable. Ge, Ga , Pd and Au-PSMMA showed the highest set of molecular weights. However, it is difficult to explain the $\bar{M}v$ of Cu. There is a good chance that

Table 1. Correlation between metal (styrene-methyl methacrylate) copolymers and molecular weights.

Polymer	Yield (%)*	M.W. ($\bar{M}v$)	Polymer Color
In-PSMMA	2.59 ; 4.65 7.46 ; 11.24	144,400 ; 132,200 70,000 ; 65,700	White
Bi-PSMMA	4.21 ; 4.86 9.73 ; 11.78	155,000 ; 82,200 53,000 ; 19,900	Grey
Cu-PSMMA	5.29 ; 6.60 8.76 ; 15.90	85,000 ; 74,000 66,400 ; 51,400	Light-yellow
Sn-PSMMA	2.38 ; 4.54 7.24 ; 10.48	142,500 ; 71,400 53,300 ; 31,000	White
Ga-PSMMA	3.89 ; 10.81 6.92 ; 9.08	175,000 ; 134,400 107,300 ; 103,500	White
Ge-PSMMA	2.70 ; 3.45 5.51 ; 8.11	187,000 ; 138,000 107,700 ; 89,500	White
Pd-PSMMA	4.00 ; 5.19 9.29 ; 16.43	162,500 ; 102,300 86,000 ; 58,700	Grey
Au-PSMMA	3.67 ; 5.38 8.65 ; 17.30	160,000 ; 141,300 117,400 ; 104,800	Purple
PSMMA	2.71 ; 4.00 6.05 ; 6.91	210,500 ; 175,400 121,500 ; 106,900	White

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

copper radicals can compete with the initiator in a similar situation that was already reported for Ge-PS (6) and Ge-PMMA (8). The AIBN was trapped by the metal and the copolymer stopped growing (9).

In all the experiments, it is possible to obtain a linear correlation between $\bar{M}v$ and $(AIBN)^{-1/2}$ (10). This is in agreement with the fact that molecular weight decreases with the increase of initiator concentration.

The monomer reactivity values for methyl methacrylate and styrene are $r_1 = 0.44$ and $r_2 = 0.50$. This indicates that the styrene would be consumed almost at the same rate than the methyl methacrylate. The copolymer equation may be used to show the effect of the composition of the feed on composition of the copolymer (1).

Thus, as shown in the following illustration, an equimolar ratio of reactants would produce a copolymer with one styrene for each methyl methacrylate unit.

$$n = \frac{r_1 X + 1}{(r_2/X)+1} = \frac{0.44(1) + 1}{(0.50/1)+1} = 0.96$$

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

Copolymer	%M	%C	%H	$\bar{M}v \times 10^{-3}$
In-PSMMA	3.2	74.45	8.2	144
Bi-PSMMA	2.1	74.35	2.1	155
Cu-PSMMA	0.9	69.96	7.4	85
Sn-PSMMA	11.0	69.88	8.1	142
Ga-PSMMA	5.9	75.24	8.1	175
Ge-PSMMA	4.4	75.40	8.3	187
Pd-PSMMA	22.0	69.97	7.7	162
Au-PSMMA	6.8	75.15	8.1	160
PSMMA	---	76.00	7.8	240

* Data for 0.1 mol % AIBN.

** The balance is most likely oxygen, PSMMA = metal poly (styrene-methyl methacrylate) polymers.

Besides, due to polymerization rate difference between styrene and methyl methacrylate they will produce preferently an alternate copolymer. This fact is also in agreement with their q values.

Copolymer analyses were performed after drying the samples at 10^{-3} Torr for 24 h. Table 2 summarizes some data of metal (styrene-methyl methacrylate) copolymers. It seems evident that metal has been incorporated in all the copolymer samples. The amount of metal incorporated is ranging between 0.9 to 11.0 %, with the exception of Au which becomes very concentrated (22.0 %). The samples showed different colors depending on the metal (12).

A study of thermal stability between 25 to 550°C was carried out for the metal polymers (8). The thermograms reveal that the polymers are stable up to 250°C and for In the decomposition starts at 200°C. Ge-PSMMA is the most stable with a residual weight of 85 %. Cu and Bi-PSMMA show the lowest residual weight (2%). In fact, these copolymers are less stable than polystyrene (350°C) and poly(methyl methacrylate) (320°C).

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