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Metal polymers: Synthesis and molecular weights of metal poly(4-methylstyrene)s with AIBN. VIII.

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SUMMARY

4-Methylstyrene colloids were obtained by codeposition at 77 K of the monomer with several metals such as Au, Ag, Cu, Pd, Zn, Ga, In, Ge, Sn, Sb, Bi. The colloids were polymerized with different amounts of initiator (AIBN) at 65°C for 9 h and a wide range of viscosity average molecular weights ($\bar{M}v$, 10^3-10^5) were obtained depending upon the metal used. The metal colloid concentration and stability are reported. The most stable colloids were Au, Pd and Ga being in solution for several months at room temperature. The thermal stability and metal composition are also described. The polymers are stable even at 385°C, being Pd with Ge-poly(4-methylstyrene) the most stable. The metal content is ranging between 0.14 and 0.55 (w/w) with Pd and Sn, respectively.

INTRODUCTION

Another approach in preparing colloidal metals in non-aqueous solvents has been reported (1-3). Metal clusters dispersed in organic monomer such as styrene were prepared (4-6). This method, chemical liquid deposition, involves deposition of metal vapor with organic solvents at low temperature (77 K) followed by controlled accretion of metal atoms. Several solvents and/or monomers and a variety of metals can be used. Polymers with photoconductor properties and better thermal stability can be obtained. In this work, we now report the synthesis of metal clusters trapped in solid 4-methylstyrene polymers.

EXPERIMENTAL PART

Metal Colloid

The metal atom reactor has been described previously (1,2). As a typical example, a W-Al_2O_3 crucible (Sylvania Emissive Product) and/or M_o wire covered with alundum cement (Fischer) was charged with 0.20 g of Sn metal (Alfa Products). 4-Methylstyrene (4-MeS; 100 mL) was previously distilled in a ligand inlet tube and freeze-thaw degassed with several cycles. The reactor was pumped down to 10^{-5} mmHg while the crucible was warmed to red heat. A liquid nitrogen filled Dewar of 5 L was placed around the vessel, and Sn (0.010 g) and 4-MeS (60 mL) were deposited over a period of 1.5 h. A heating tape was placed around the inlet tube to facilitate solvent introduction. The matrix was dark brown at the end of the deposition. The matrix was allowed to warm slowly under

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vacuum by removal of the liquid nitrogen filled Dewar for 1.5 h. Upon the meltdown a dark brown solution was obtained. After addition of gaseous nitrogen, the solution was allowed to warm for another hour at room temperature. The sol was syphoned off under nitrogen into a flask.

Polymerization. Colloid Sn-4-MeS (10 mL) was placed in four polymerization flasks with 0.1, 1.0, 2.5 and 5.0 mol% of 2,2′-azoisobutyronitrile (AIBN) under nitrogen flow. The flasks were closed and placed in an isothermal bath at 65°C for 9 h. The content of each flask was quenched with methanol. The dark brown polymers obtained were filtered off and dried under vacuum at 10^{-3} Torr for 48 h at 40°C. The yield of each polymer fraction was determined.

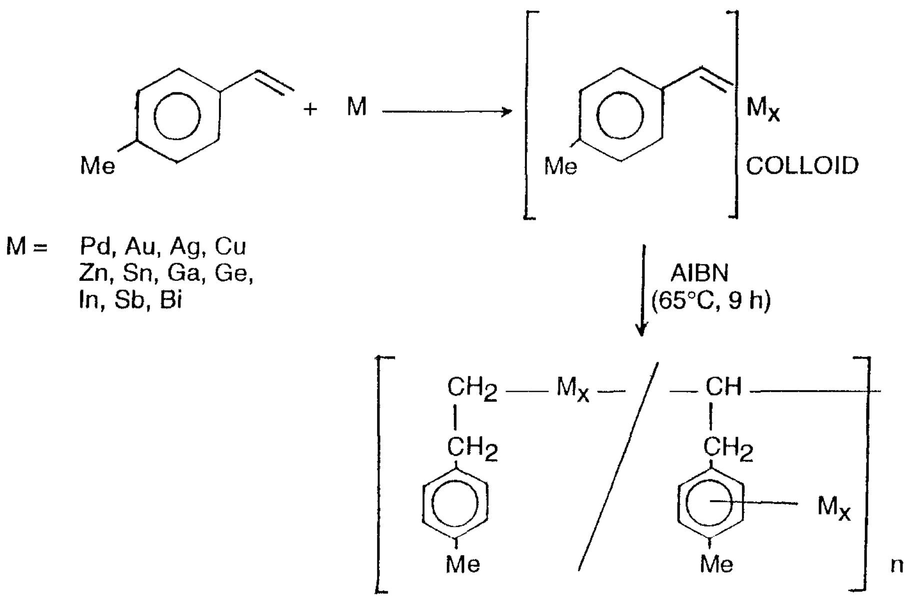
Molecular Weight. The average molecular weight ($\bar{M}v$) was calculated by the Mark-Houwink equation (7). The intrinsic viscosity was measured at 25°C by using an Ostwald viscometer ($K=8.8x10^{-5}$ mL/g; a=0.74). The polymers were dissolved in toluene at 30°C.

Elemental Analysis. Carbon, hydrogen and metal microanalyses were performed by the Faculty of Chemical Sciences Laboratories at the University of Concepción.

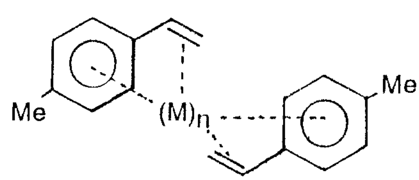
Thermogravimetric Analysis. a Perkin-Elmer Model TGA 7 Thermobalance, with a microprocessor driven temperature control unit and a TA data station was used. The weight of samples were recorded and were generally in the range of 4-6 mg. The sample pan was placed in the balance system and the temperature was raised from 25 to 550°C at a heating rate of 10°C/min. The weight of the sample was continuously recorded as a function of temperature.

RESULTS AND DISCUSSION

The synthesis of polymers with metal incorporated from sols or metal dispersed in monomers was reported by us (5,6). The following scheme summarizes the procedure:



We have reported metal colloids stabilized by a nonpolar solvent, viz. styrene (4). This is probably due to the ligating properties of the unsaturated bonds in methylmethacrylate (9), ethylmethacrylate (10), and vinyl acetate (11). Ligating of the unsaturated bonds in 4-MeS probably occurs as:



The stability of the colloids of Au, Pd, Sb and Ag in 4-MeS can be related to the inherent stability of these metals. Sb and Ag clusters are trapped in the monomer solution and their oxidation can be avoided. Similar behaviour was found for group XI metals with poly(vinyl acetate) (10). Metals with negative E°, such as Zn, Ga, Sn, do not form stable colloids.

We must keep in mind that during the polymerization the metal clusters are able to agglomerate and might be surrounded by the growing polymer. Due to the low amount of metal incorporated in the polymer it is difficult to distinguish shifts in absorption frequencies in the aromatic region. The metal polymers are homogeneous. For Au we obtained from light to deep purple 4-MeS polymers. Table 1 summarizes yields in all polymer fractions and viscosity molecular weights (Mv) of metal poly(4-methylstyrenes).

Table 1. Molecular Weight and yield of metal poly(4-methylstyrene).

Polymer	Yield (%)	Molecular Weight[a,b] ($\bar{M}v$)	Color
P-4-MeS	32.86;49.93 51.14;66.31	92.750;69.700 58.860;31.750	white
Au-(P-4-MeS)	9.78;30.12 46.81;63.53	111.000;66.900 56.300; 9.350	purple
Ag-(P-4-MeS)	43.90;80.85 60.73;78.03	143.400;127.000 53.620; 11.050	brown
Cu-(P-4-MeS)	40.17;34.04 21.81;39.91	98.160; 41.360 38.140; 11.740	yellowish
Pd-(P-4-MeS)	67.72;37.00 67.73;37.51	146.800;123.780 81.000; 42.080	black
Zn-(P-4-MeS)	38.39;44.80 13.39;42.06	121.128; 80.140 33.860; 8.130	black
Ga-(P-4-MeS)	21.76;25.31 42.70;38.26	106.460; 82.640 41.700; 7.670	grey
In-(P-4-MeS)	26.12;99.48 76.74;54.35	83.910; 46.000 41.100; 12.270	black
Ge-(P-4-MeS)	41.29;47.44 74.60;91.32	114.960; 92.750 53.620; 2.740	grey
Sn-(P-4-MeS)	61.74;36.60 18.36;45.40	86.830; 61.530 29.500; 5.590	black
Sb-(P-4-MeS)	29.55;85.58 22.10;99.19	107.900; 81.000 66.950; 27.320	black
Bi-(P-4-MeS)	17.65;42.19 61.84;55.46	120.570; 58.860 53.620; 38.700	black

P-4-MeS = poly(4-methylstyrene)

[a]The viscosimetric molecular weights correspond to 0.1, 1.0, 2.5 and 5.0 mol% of AIBN.

[b]Bulk polymerization at 65°C for 9 h.

Table 2. Correlation between monomer, composition and concentration.

Polymer	Concentration Colloid x 1xE-3	%M	%C	%H
Pd-(4-MeS)-1*	1.05	0.14	89.95	8.71 **
Pd-(4-MeS)-4		0.65	89.90	8.53
Cu-(4-MeS)-1	9.34	0.37	89.35	8.76
Cu-(4-MeS)-4		0.18	89.67	8.64
Ag-(4-MeS)-1	8.87	0.13	90.27	8.73
Ag-(4-MeS)-4		0.34	90.35	7.95
Au-(4-MeS)-1	1.03	0.41	89.45	8.03
Au-(4-MeS)-4		0.71	89.87	8.28
Zn-(4-MeS)-1	1.24	0.27	89.80	8.16
Zn-(4-MeS)-4		0.23	89.60	8.50
Ga-(4-MeS)-1	3.66	0.34	89.85	8.60
Ga-(4-MeS)-4		0.32	89.74	8.40
In-(4-MeS)-1	0.24	0.21	90.19	8.42
In-(4-MeS)-4		0.43	90.51	8.19
Ge-(4-MeS)-1	2.24	0.17	91.26	8.09
Ge-(4-MeS)-4		0.32	91.52	8.51
Sn-(4-MeS)-1	3.36	0.55	88.98	8.56
Sn-(4-MeS)-4		0.40	89.11	8.71
Sb-(4-MeS)-1	0.84	0.23	90.00	8.78
Sb-(4-MeS)-4		0.61	88.97	8.02
Bi-(4-MeS)-1	4.62	0.24	88.74	8.91
Bi-(4-MeS)-4		0.51	88.60	8.76
P-(4-MeS)-1	--	--	88.77	8.80
P-(4-MeS)-4			88.69	8.68

* -1 and -4 correspond to the higher and lower MW fractions, respectively.
** The balance is likely oxygen.
P-(4-MeS) = poly(4-methylstyrene).

Ag- and Ge-4MeS exhibit higher yields in all polymer fractions than the homopolymer. It is interesting to observe that few metals (In, Sn and Cu) show lower molecular weights than the homopolymers. Most of the other metals exhibited higher $\bar{M}v$ than poly(4-methylstyrene), Pd-4MeS being the highest set. For all polymers a linear correlation between $\bar{M}v$ and $[AIBN]^{-1/2}$ was found. This is in agreement with the observation that molecular weights decrease with an increase of initiator concentration (7).

Table 2 summarizes the composition of metal poly(4-methylstyrenes) prepared with 0.1 and 5.0 mol% AIBN, respectively. It is evident that metal is incorporated in the polymer matrix in all the samples. The color of the polymers depends on the metal cluster incorporated. The amount of metal incorporated is fairly low but enough to increase the thermal stability. The thermal decomposition temperature (T_D) was obtained from the first derivative curve of the thermogram. The four P-4-MeS fractions behave similarly with 384, 387, 389 and 387°C, respectively. The thermograms reveal that these polymers degrade in one stage. In all the metal polymers fraction 1 always showed a higher T_D than fraction 4. Pd, Cu, Zn, Ga, Ge and Bi-P-4-MeS exhibit higher T_D than the homopolymer; for example, Zn and Ge colloid exhibit 406 and 392°C, respectively (12).

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