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Synthesis and molecular weights of metal poly(ethyl methacrylates). IV

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SUMMARY

Ethyl methacrylate colloids were obtained by codeposition at 77 K of the monomer with several metals such as: Au, Ag, Cu, Pd, Zn, Cd, Al, Ga, In, Ge, Sn, Sb and Bi. The colloids were polymerized with different amounts of initiator (AIBN) at 62°C and a wide range of viscosity average molecular weights ($\bar{M}v$; 10^4-10^6) were obtained depending upon the metal used. The metal colloid concentrations and stability are reported. The thermal stability, morphology and metal composition are also described. The polymers are stable even at 300°C and the metal content is ranging from 0.10 to 3.67%.

INTRODUCTION

We have recently reported colloidal metals in organic monomers, such as styrene (1,2,3) and methyl methacrylate (4). This method, Chemical Liquid Deposition, involves deposition of metal vapor with organic solvents at low temperature (77 K).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 monomers and nonaqueous solvents (4,5). 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 (6,7). As a typical example, a W-Al_2O_3 crucible was charged with 0.2 g of Cu metal (Alfa Products). Ethyl methacrylate (80 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 Cu (0.159 g) and ethyl methacrylate (60 mL) were codeposited 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 the liquid nitrogen filled Dewar for 1.5 h. Upon the meltdown a dark blue sol was

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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 flask. Based on Cu evaporated and ethyl methacrylate inlet the approximate molarity, 0.042 M, could be calculated.

Polymerization. Colloid Cu (10 mL) was placed in four polymerization flasks with 0.1, 0.2, 0.5 and 1.0 mol % of AIBN (azodiisobutyronitrile) under N_2 flow. The flask tubes were closed and placed in an isothermal bath at 62°C for 20 min. The content of each flask was poured in beakers with methanol. The dark blue polymers obtained were filtered off and dried under vacuum at 10^{-3} Torr for 24 h at 30°C. The yield of each polymer fraction was determined.

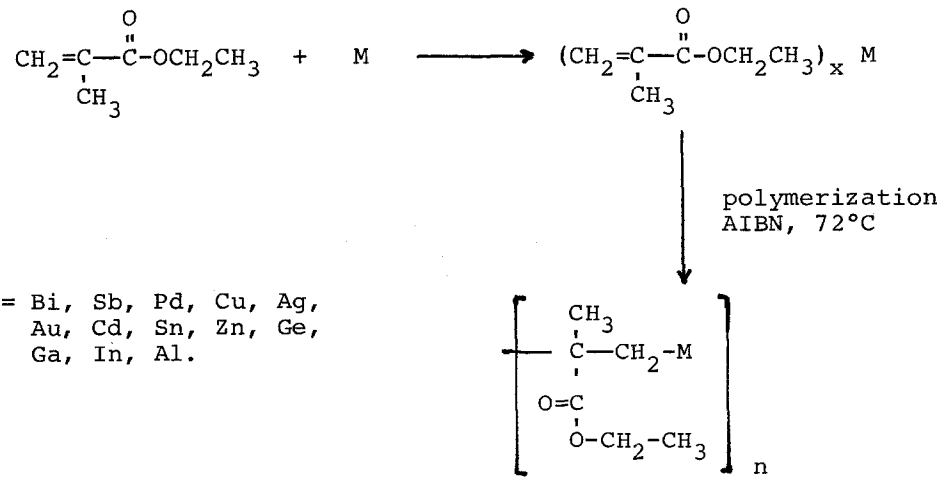
Elemental Analysis. The samples for microanalysis of metals carbon and hydrogen were performed by the Chemistry Department Laboratories (University of Concepción).

Electron Microscopy. Scanning electron microscopy was carried out on a ETEC Autoscan U-1 Model. The surface of the polymers were coated with gold for 4 min to obtain a 150A° thickness using an Edwards S 150 sputter coater.

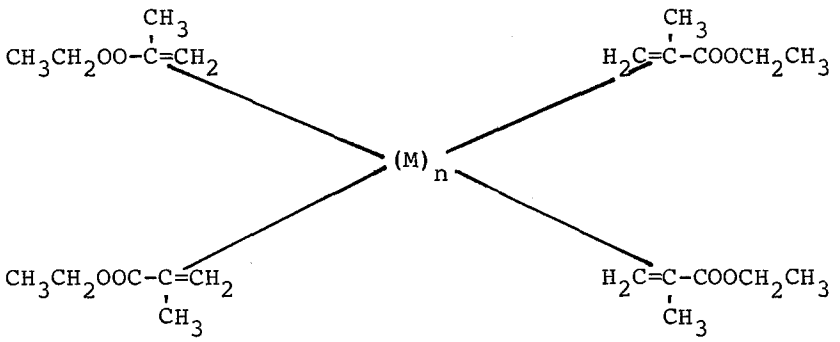
Thermogravimetric Analysis. The thermogravimetric data were obtained using a Thermobalance TGA 7, Perkin-Elmer with 2-6 mg samples heated under nitrogen flow (50 mL min^{-1}) at 10°C min^{-1} from 25 to 550°C.

RESULTS AND DISCUSSION

The synthesis of polymers with metal incorporated from sols or dispersed metals in monomers is relatively new (8). The following scheme is summarizing the synthesis of this polymers.



We have recently reported the first metal colloids stabilized by a nonpolar solvent, styrene (1,2,3). This must be due to the ligating action of the unsaturated bonds in styrene. Ethyl methacrylate behaves similarly and the ligating action of the unsaturated bonds in MMA is probably as follows:



The stability of this colloids was related with the normal oxidation potential of the metal. The stability of the colloids decreases with the increase of the oxidation potential. In fact, the most stable colloids were with metals of the IX group (Cu, Ag and Au) and also Pd. This interaction was also favored for the presence of d electrons able to interact with the Π electrons of the vinyl bond of the ethyl methacrylate.

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 spectroscopy.

Table 1 summarizes yields and molecular weights ($\bar{M}v$) of metal poly(ethyl methacrylates). The higher yields are similar for several metals: Zn and Ag. Zn-PEMA showed the highest yield in all the fractions and is very similar to pure PEMA.

Of particular interest is the fact that IX group elements exhibit higher molecular weights polymers. This is due mainly to the higher stability of the colloid sols. These molecular weights are higher than that reported for PMMA (4). However, the $\bar{M}v$'s of Ge are again the lowest of the metals. This behaviour is similar for Ge-PS (1); probably some AIBN initiator was trapped by the metal and the polymerization stopped (9).

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

Polymer	Yield(%)*	M.W. ($\bar{M}v$)	Polymer Color
PEMA	12,15-20,03 31,49-95,03	705.054-416.810 274.415- 86.052	White
Al-PEMA	10,19-12,51 17,29-23,83	1.186.369-750.033 424.274-274.033	Yellowish
Ge-PEMA	8,96-12,28 27,18-73,77	455.266-390.574 274.462- 79.302	Light brown
Pd-PEMA	7,42-13,91 19,99-37,74	593,584-305.843 237.784-168.001	Black
Cu-PEMA	9,25-14,82 36,24-89,15	615.405-424.274 250,425- 91.606	Brown
In-PEMA	8,14-12,32 17,16-31.93	668.256-524.999 427.064-257.202	Dark brown
Ga-PEMA	9,28-13,46 22,42-36,31	789.258-645.102 350.928-173.617	Brown
Cd-PEMA	7,63-11,56 18,52-34,30	967.393-622.912 431.084-275.557	Black
Au-PEMA	11,4 -14,78 24,13-36,18	708.405-600.888 302.673-213.965	Purple
Zn-PEMA	15,03-23,94 27,94-95.77	557.347-397.265 312.202- 88.980	Black
Ag-PEMA	11,79-15,42 26,34-64,80	689.961-507.442 364.044- 98.885	Black
Sn-PEMA	9,39-12,79 21,23-47,58	622.912-430.810 252.551- 91.601	Grey
Ga-PEMA	11,17-16,29 25,05-87,37	564.556-390.574 255.985- 93.905	Brown
Cd-PEMA	8,28-11,46 15,58-24,27	979.533-750.735 377.260-262.301	Black
Ag-PEMA	10,28-14,40 22,98-31,74	947.230-682.441 486.234-271.402	Black

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

In all the experiments, it is possible to obtain a linear correlation between $\bar{M}v$ and $(AIBN)^{-½}$ (10). 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. Tables 2 and 3 summarize the composition of metal poly(ethyl methacrylates). It is clear that metals has been incorporated in the polymers in all the samples. The amount of metal incorporated is ranging between 0.10 to 3.67% and the samples showed different colors depending of the metal.

Table 2. Correlation between polymer, composition and concentration*.

PEMA	Concentration Colloid*1*E-3	Metal(%)	Carbon(%)	Hydrogen(%)**
Pd-PEMA	15	2,57	58,55	8,84
Pd-PEMA	30	3,67	50,64	7,9
Cu-PEMA	42	0,10	61,18	8,77
Ag-PEMA	4,5	0,45	62,94	9,03
Ag-PEMA	29	1,08	61,84	9,23
Au-PEMA	9,4	0,62	59,67	8,94
Zn-PEMA	35	0,63	55,47	8,86
Zn-PEMA	48	0,42	63,13	8,83
Cd-PEMA	22	1,08	61,97	9,09
Cd-PEMA	19	0,19	42,91	7,9
Al-PEMA	16	0,13	58,1	8,66
Ga-PEMA	26	0,13	62,37	9,15
Ga-PEMA	17	0,18	62,51	9,3
In-PEMA	14	0,26	44,26	9,14
In-PEMA	15	0,26	32,07	8,64
Ge-PEMA	12	0,39	63,28	8,75
Ge-PEMA	42	1,15	51,18	8,82
Zn-PEMA	17	0,52	53,37	7,66

* Data for 0.1 mol% AIBN.

** The balance is the likely oxygen.

PEMA= poly(ethyl methacrylate).

Table 3. Correlation between polymer, composition and concentration*.

PEMA	Colloid Concentration* 1*E-3	Metal (%)	Carbon (%)	Hydrogen** (%)
Pd-PEMA	15	0,24	61,73	9,2
Pd-PEMA	30	0,72	61,91	9,1
Cu-PEMA	42	0,01	62,33	9,23
Ag-PEMA	4,5	0,15	63,05	9,22
Ag-PEMA	29	0,16	62,67	9,22
Au-PEMA	9,4	0,25	60,11	9,12
Zn-PEMA	35	0,38	58,15	8,58
Zn-PEMA	48	0,25	63,13	8,83
Cd-PEMA	22	0,07	61,69	8,87
Cd-PEMA	19	0,05	55,02	8,31
Al-PEMA	16	0,4	77,43	9,06
Ga-PEMA	26	0,1	61,05	9,31
Ga-PEMA	17	0,14	62,81	9,21
In-PEMA	14	0,09	62,94	9,25
In-PEMA	15	0,08	55,96	8,49
Ge-PEMA	12	0,11	63,17	8,46
Ge-PEMA	42	0,24	61,91	9,11

*Data for 1.0 mol% AIBN.

** The balance is the likely oxygen.

From tables 2 and 3 we can conclude that the 1.0 % mol AIBN polymers exhibit a lower metal concentration, most probably due to the radical concentration. The probability to react with the metals is higher and the incorporation in the polymer decreases. More stable sols such as Pd-PEMA increase the metal concentration in the polymer and the C,H decrease. On the other hand, metals like Cu and Zn with a high afinity for oxygen showed a low metal concentration.

In the transmission electron micrograph (TEM) it is possible to observe the approximate size of the clusters. Figure 1 shows the size and shape of the Pd clusters in PEMA. Most of the clusters are spherical with around 2000 metal atoms in it.

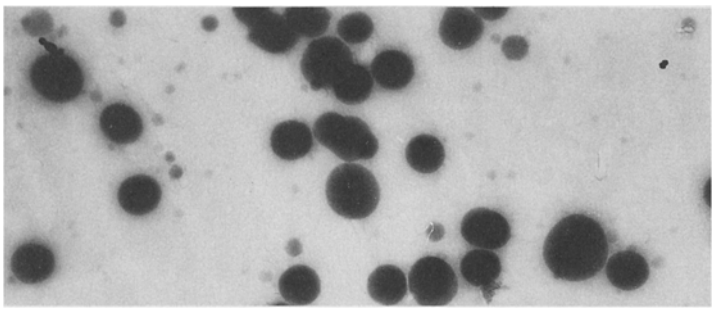


Figure 1. Electron micrograph (TEM) of Pd-PEMA (fraction #4 in M.W.), 63200x

A study of thermal stability between 25 to 550°C was carried out for the metal polymers (11). The thermograms reveal that polymers are stable up to 200°C and for Pd and Au even at 300°C did not lose weight. Cd and Sn-PEMA exhibit a first T_D at 160 and 161°C and a second one at 410 and 424°C, respectively. Pd-PEMA is also stable with a T_D at 410°C. Their residual weights are very low, ranging from 0.5-5% in most of them (11). These polymers are less thermally stable than the PMMA series (4).

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