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Metal polymers: XV Synthesis and molecular weights of metal poly(styrene-*co*-ethyl methacrylates)

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SUMMARY

Styrene-ethyl methacrylate metal colloids were obtained by codeposition at 77 K of the monomers with several metals such as Pd, Au, Ag, Cu, Zn, Cd, Ga, In, Ge, Sn, Sb and Bi. The colloids were polymerized with different amounts of initiator (AIBN) at 65°C for 3.25 h 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 concentration and stability are reported. The thermal stability and metal composition are also described. The copolymers are stable even at 380°C and In-(styrene-*co*-ethyl methacrylate) being the most stable (423°C). The metal content is ranging between 0.12 and 1.22% w/w. Copolymers with several colors were obtained depending on the metal and concentration used.

INTRODUCTION

We have previously reported the synthesis of colloidal metal dispersed in organic monomers, such as styrene (1), ethyl methacrylate (2) and comonomers like styrene-methyl methacrylate (3) and styrene-acrylonitrile (4).

In this method (5,6), the copolymers are doped by direct cocondensation of the metal vapor with both monomers at liquid nitrogen temperature (77 K). This approach allows the synthesis of polymers and copolymers with different amounts of incorporated metal clusters. Alternating copolymers of styrene-*co*-ethyl methacrylate prepared by radical polymerization (AIBN) can be obtained.

EXPERIMENTAL PART

Metal colloid. A metal atom reactor was used (6,7). As a typical example, a W-Al_2O_3 (Osram Sylvania) was charged with 0.3 g of Ag metal beds (Aldrich). Styrene (26 ml) and ethyl methacrylate (24 ml) were previously distilled under vacuum in a ligand inlet tube and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 5 μ of Hg while the crucible was warmed to red heat. Several current intensities were used depending upon the metal. A liquid nitrogen filled Dewar of 5L was placed around the vessel, Ag (0.15 g) and styrene and ethyl methacrylate were codeposited simultaneously over a 1.5 h period. A heating tape was used around the inlet Y tube to facilitate the

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introduction of monomers. A black matrix was formed on the walls of the reactor 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 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 solution was siphoned out under nitrogen into a flask. A drop of the colloid was placed on a copper grid to measure particle size by TEM. Based on Ag evaporated and the monomers used, the approximate concentration could be calculated.

Polymerization. Ag bicolloid (10 ml) was placed in each of the four polymerization flasks with 0.1, 0.2, 0.5 and 1.0 mol% of recrystallized AIBN (azodiisobutyronitrile) under N_2 flow. The flasks were closed and placed in an isothermal bath at 65°C for 3 hours. The content of each flask was poured in beakers with methanol. The black copolymers obtained were filtered off and dried under vacuum for 48 h at 10°C. The yield of each copolymer fraction was determined.

Molecular weights. The viscosity average molecular weight ($\bar{M}_v$) was calculated by the Mark-Houwink equation (8). The intrinsic viscosity was measured at 25°C by using an Ostwald viscometer. The polymers were dissolved in 2-butanone at 25°C. $K = 9.3x10^{-3}$ ml/g; a = 0.72 (9).

Elemental analysis. Carbon, hydrogen and metal microanalyses were carried out by the Faculty of Chemical Science Laboratories at the University of Concepción.

Thermogravimetric analysis. A Perkin Elmer Model TGS-2 Thermogravimetric System, 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 3-5 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.

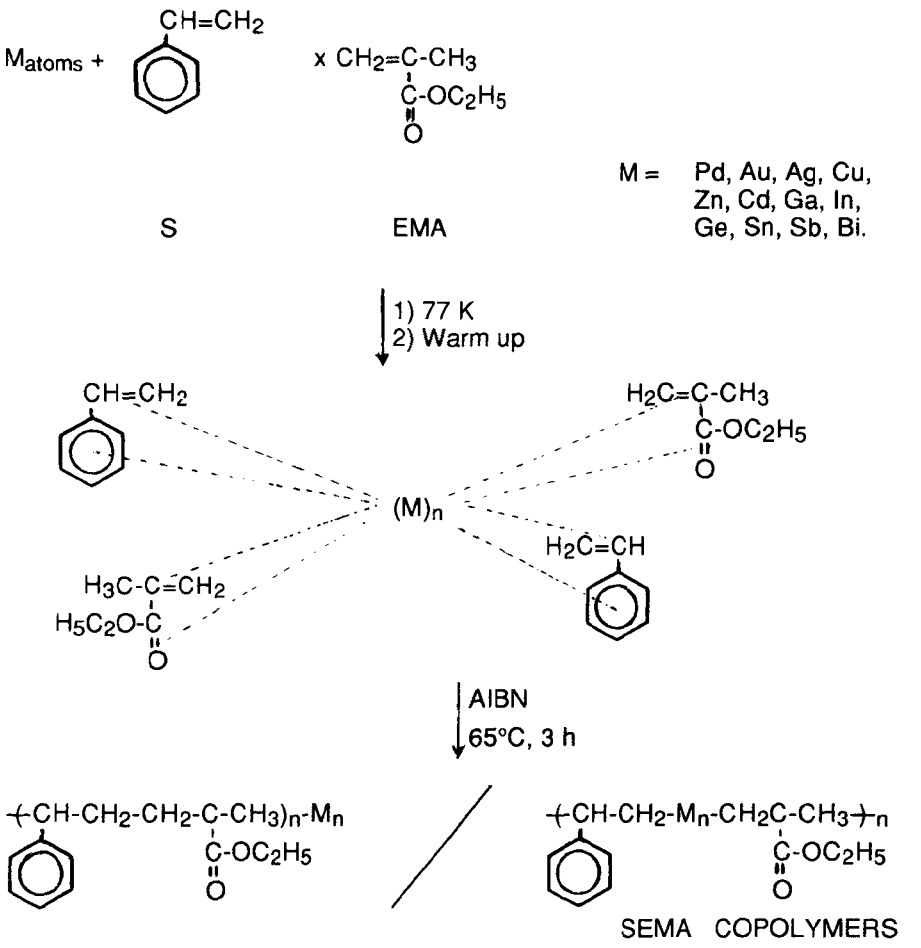
RESULTS AND DISCUSSION

We reported previously metal colloids stabilized by organic monomers, styrene (1), ethyl methacrylate (2) and butyl methacrylate (10). Stabilization is most probably due to the ligating action of the unsaturated bonds in styrene either from the vinyl group or the aromatic ring, and from the unsaturation in the ethyl methacrylate as follows.

The metal clusters should be stabilized between the π-electrons of the aromatic ring and the vinyl group and also with the vinyl and carboxylate group of the ethyl methacrylate. Au, Ge and Ga-SEMA are stable for several months at room temperature. This behavior is similar to previous results on metal styrene-*co*-acrylonitrile (4b), styrene-*co*-methyl methacrylate (3a), styrene-*co*-4-methyl styrene (11) and SEMA copolymers prepared with benzoyl peroxide (12).

The size of metal atoms increases by aggregation in the monomeric medium, and this process took place upon warming from -196°C to room temperature. During the bulk polymerization the metal clusters tend to grow until the viscosity of the solution increases and eventually traps them. The metals are incorporated in the copolymers and can be detected by EDAX and MS.

Table 1 summarizes yields and molecular weights ($\bar{M}_v$) of metal poly(styrene-*co*-ethyl methacrylate). We can observe that the yields are low for



most of the highest $\bar{M}_v$ fractions and only Pd, Au and In-SEMA exhibit the best yields. For Sn and Bi-SEMA, we found that their molecular weights are the lowest in this set. Furthermore, the copolymers Pd, Ag, Cd, Sb and Au-SEMA showed higher molecular weight set than the other copolymers but lower than the undoped SEMA. The most stable metal will produce stable colloids and the initiator allows them to grow faster than others like Bi and Sn. On the other hand, SEMA copolymers prepared with AIBN showed higher $\bar{M}_v$ ranges than those obtained with BPO.

The monomer reactivities of styrene and ethyl methacrylate are $r_1 = 0.55$ and $r_2 = 0.36$ at 60°C (10b). The monomers alternate regularly along the chain regardless of the composition of the monomer feed (13). Thus, an equimolar ratio of reactants would produce a copolymer with two styrene units for every ethyl methacrylate unit, the same as for the BPO series already reported (12).

Table 1. Metal poly(styrene-*co*-ethyl methacrylate)yields, molecular weights and colors.

Copolymer	Yield (%)*	$\bar{M}_v$(g/mol)	Polymer color
SEMA**	29.80; 18.85	359.300; 288.600	White
	27.58; 13.16	209.100; 92.700	
Pd-SEMA	32.40; 38.90	300.200; 188.300	Black
	19.86; 27.93	110.500; 42.400	
Cu-SEMA	29.18; 10.65	292.000; 209.700	Yellow
	22.19; 11.97	120.700; 73.600	
Ag-SEMA	12.63; 32.21	302.200; 196.400	Brown
	20.29; 25.19	112.500; 80.600	
Au-SEMA	29.60; 20.40	312.500; 193.700	Purple
	21.01; 25.17	107.890; 78.100	
Zn-SEMA	16.15; 13.66	290.500; 193.700	Black
	25.59; 30.97	109.000; 47.300	
Cd-SEMA	22.30; 24.17	338.600; 205.000	Black
	27.73; 29.30	115.200; 41.300	
Ga-SEMA	18.70; 14.73	293.000; 195.000	Yellow
	14.84; 19.53	117.900; 55.000	
In-SEMA	34.52; 30.28	288.000; 212.000	Brown
	20.17; 27.94	118.300; 59.500	
Ge-SEMA	23.31; 20.01	295.100; 201.800	Yellow
	13.73; 18.76	119.500; 56.000	
Sn-SEMA	21.79; 24.38	285.500; 192.300	Yellow
	29.49; 26.19	117.100; 54.100	
Sb-SEMA	13.71; 13.92	328.600; 206.400	Black
	22.27; 24.18	114.000; 63.100	
Bi-SEMA	13.57; 20.08	290.500; 189.200	Black
	19.03; 24.06	99.500; 51.900	

* Obtained with 0.1, 0.2, 0.5 and 1.0 mol% of AIBN
** SEMA = poly(styrene-*co*-ethyl methacrylate).

All the systems yield a linear correlation between $\bar{M}_v$ and $(AIBN)^{-1/2}$ (8). This is in agreement with previous results in other doped copolymers (3a, 4b, 11).

Transmission electron micrograph (TEM) shows spherical Ag clusters in the copolymer. The average diameter of the colloid is around 22 Å. Some crystalinity can be observed in the silver metal clusters.

Table 2. Copolymers and their composition

Copolymer*	% M	% C	% H
SEMA-1	-	77.23	9.18
SEMA-4	-	76.65	8.87
Pd-SEMA-1	0.32	77.53	9.16
Pd-SEMA-4	0.10	76.53	9.12
Cu-SEMA-1	0.26	76.98	9.23
Cu-SEMA-4	0.77	75.36	9.21
Ag-SEMA-1	0.67	77.29	8.85
Ag-SEMA-4	0.14	77.67	9.39
Au-SEMA-1	0.15	76.11	9.29
Au-SEMA-4	0.21	74.94	9.20
Zn-SEMA-1	0.13	77.41	9.20
Zn-SEMA-4	0.10	77.66	9.10
Cd-SEMA-1	0.31	78.50	9.08
Cd-SEMA-4	0.14	76.64	8.95
Ga-SEMA-1	0.86	77.57	8.98
Ga-SEMA-4	0.47	77.36	8.95
In-SEMA-1	0.12	75.98	8.98
In-SEMA-4	0.18	77.76	9.16
Ge-SEMA-1	0.28	75.03	9.41
Ge-SEMA-4	0.15	74.92	9.48
Sn-SEMA-1	1.22	75.93	8.83
Sn-SEMA-4	0.84	77.86	9.17
Sb-SEMA-1	0.36	75.62	8.75
Sb-SEMA-4	0.10	76.45	8.66
Bi-SEMA-1	0.13	73.85	8.19
Bi-SEMA-4	0.10	76.91	8.59

* The balance is most likely oxygen.

A complete study of thermal stability between 25 to 550°C was carried out for the copolymers and doped copolymers (14). The thermograms reveal that the SEMA copolymers are stable up to 368°C, exhibiting only one decomposition. This is further evidence for the presence of metal copolymers.

Furthermore, polystyrene showed one decomposition at 400°C (1a) and poly(ethyl methacrylate) exhibited one decomposition at 375°C (15).

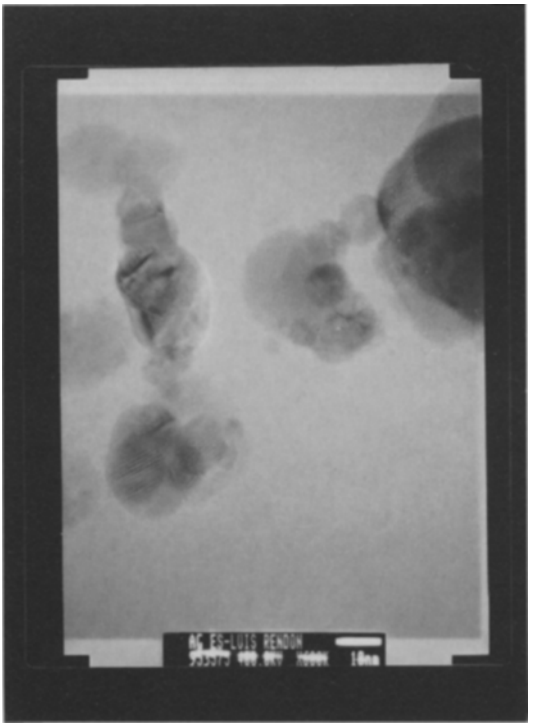


Figure 1. Electron micrograph (TEM) of Ag-SEMA at X600 K magnification.

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