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Metal polymers

XII. Synthesis and molecular weights of metal poly(styrene-*co*-ethyl methacrylate)

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SUMMARY

Styrene-*co*-ethyl methacrylate 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 (BPO) at 65°C for 3.5 h and a wide range of viscosity average molecular weights ($\bar{M}_V$, 10^4-10^5 g/mol) were obtained depending upon the metal used. The metal colloid concentration and stability are reported. The medium particle size of In comonomer colloids was 49 Å. The thermal stability and metal composition are also described. The copolymers are stable even at 310°C; Pd-poly(styrene-*co*-ethyl methacrylate) being the most stable. The metal content ranging between 0.11 and 3.76% w/w for the highest MW fraction and between 0.08 and 0.96% w/w for the lowest MW fraction. Copolymers with different colors were obtained depending on the metal used.

INTRODUCTION

Several syntheses of colloidal metals dispersed in organic monomers, such as styrene (1), ethyl methacrylate (2) and comonomers like styrene-methyl methacrylate (3) and styrene-acrylonitrile (4) have been reported.

Musco (5) has recently reported the coordination of a chiral ligand to a Pd(II) complex which may switch chain end control to an enantiomorphic site control to yield an optically active isotactic alternating copolymer. The alternating copolymerization of carbon monoxide with styrene and 4-methylstyrene yields a highly isotactic polymer.

In our system, the CLD method (6) involves the cocondensation of metal vapor with both organic monomers simultaneously at liquid nitrogen temperature (-196°C). The method allows the synthesis of polymers and copolymers with incorporated metal clusters. It is possible to obtain alternating copolymers of styrene-*co*-ethyl methacrylate with certain tacticity due to other influences of the metal clusters in bulk.

EXPERIMENTAL PART

Metal colloid. A metal atom reactor was used (7,8). As a typical example a W-Al_2O_3 crucible (Osram Sylvania) and others prepared by us with W wire and alundun cement, was charged with 0.142 g of Ge metal shots (Aldrich).

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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 5 L was placed around the vessel, Ge (0.112 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 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 Ge evaporated and the monomers used, the approximate concentration could be calculated.

Polymerization. (Styrene-*co*-ethyl methacrylate) Ge colloid (10 mL) was placed in each of the four polymerization flask with 0.1, 0.2, 0.5 and 1.0 mol% of recrystallized BPO (benzoyl peroxide) under nitrogen flow. The flasks were closed and placed in an isothermal bath at 65°C for 3.5 h. 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 40°C. The yield of each polymer fraction was determined.

Molecular Weights. The average molecular weight ($\bar{M}_V$) was calculated by the Mark-Houwink equation (9). The intrinsic viscosity was measured at 25°C by using an Ostwald viscometer. The polymers were dissolved in 2-butanone at 25°C, $K = 9.3 \times 10^{-3}$ ml/g; $a = 0.72$ (10).

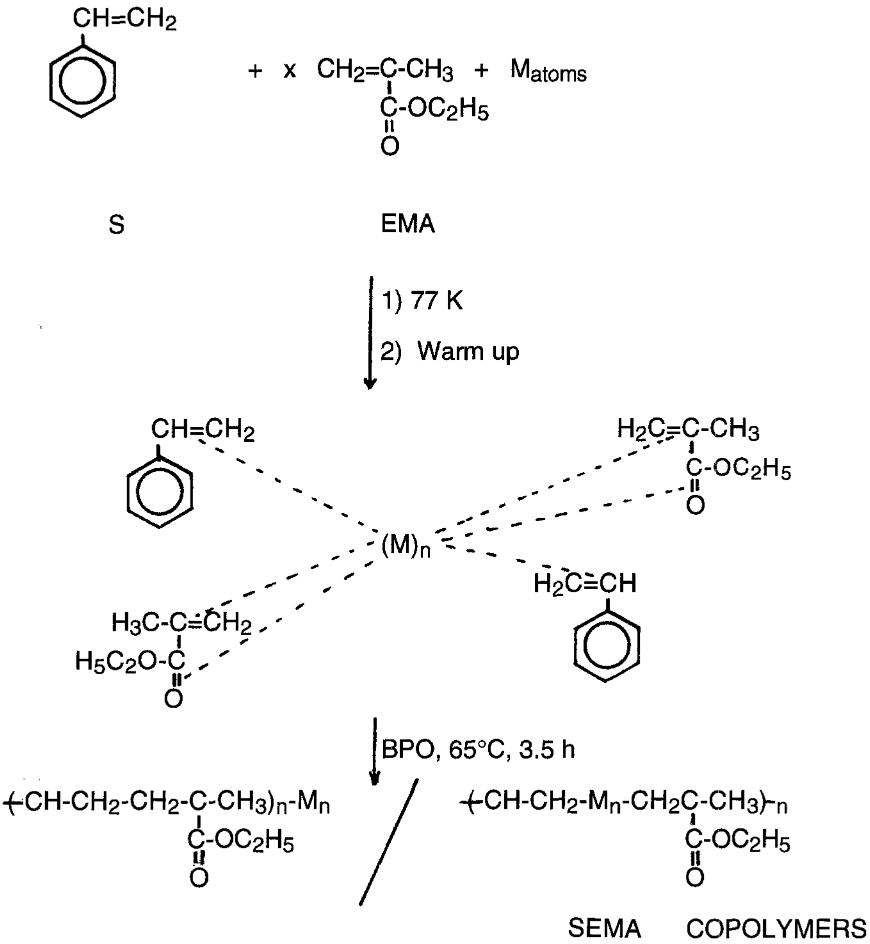
Elemental Analysis. Carbon, hydrogen and metal microanalysis were performed by the Faculty of Chemical Sciences Laboratories at the University of Concepción.

Transmission Electron Microscopy. Electron micrographs were obtained on a JEOL JEM 1200 EX II with 4 Å resolution. A drop of the sample was placed on a carbon coated copper grid of 100 mesh. Several magnifications were employed. A log normal distribution to calculate the average particle size was used.

Thermogravimetric Analyses. A Perkin-Elmer Model TGA-7 Thermogravimetric System, with a microprocessor driven temperature control unit and a TA data station, was used. The mass of these samples was generally in the range of 2-3 mg. The sample pan was placed in the balance system equipment and the temperature was raised from 25 to 550°C at a heating rate of 10°C/min. The mass of the sample pan was continuously recorded as a function of the temperature.

RESULTS AND DISCUSSION

We reported previously metal colloids stabilized by organic monomers, styrene (11), ethyl methacrylate 92) and butyl methacrylate (12). 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 aromatic ring and the vinyl group and also with the vinyl and carboxylate group of the other monomer. Au, Pd, Ge and Cd-SEMA are stable for several months at room temperature. This behavior is similar with previous results on metal styrene-*co*-acrylonitrile (4b), styrene-*co*-methyl methacrylate (3a) and styrene-*co*-4-methyl styrene (13) copolymers.

The size of metal atoms increases by aggregation in the monomeric medium, and this 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, Zn and Cd-SEMA exhibit the best yields. For Bi-SEMA, we found that their molecular weights are the lowest in this set. Furthermore, the copolymers Pd, Ag and Au-SEMA showed higher molecular weight set than the copolymers SEMA. The most stable metal will produce stable colloids and the initiator allows them to grow faster than others like In and Cd. On the other hand, Zn, Sn and Sb-SEMA copolymers are very similar in the $\bar{M}_V$ ranges with the undoped copolymers.

Table 1. Correlation between metal (styrene-*co*-ethylmethacrylate) and molecular weights.

Copolymer	Yield (%)°	M.W ($\bar{M}_V$)x10^{-3}	Color
SEMA**	16.7; 16.5	266 ;188	White
	51.0; 19.5	153; 80	
Pd-SEMA	34.7; 52.2	319; 164	Black
	47.2; 58.2	114; 73	
Cu-SEMA	18.1; 26.2	253; 171	Light-green
	14.2; 24.3	98; 64	
Ag-SEMA	19.8; 44.1	320; 141	Black
	28.6; 11.8	112; 78	
Au-SEMA	12.7; 14.2	293; 202	Purple
	24.3; 27.3	120; 83	
Zn-SEMA	37.7; 40.3	276; 173	Black
	52.3; 75.8	87; 75	
Cd-SEMA	36.2; 28.1	242; 180	Black
	23.4; 24.3	103; 64	
Ga-SEMA	31.2; 19.2	261; 127	Grey
	16.2; 18.7	95; 70	
In-SEMA	17.7; 29.3	251; 156	Black
	31.3; 27.9	101; 66	
Ge-SEMA	21.3; 12.1	269; 155	Grey
	15.0; 22.7	94; 74	
Sn-SEMA	28.9; 25.5	271; 182	Black
	61.8; 25.4	106; 82	
Sb-SEMA	28.7; 55.6	273; 186	Black
	40.8; 99	96; 71	
Bi-SEMA	21.1; 13.7	237; 177	Black
	32.4; 27.0	145; 71	

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

** SEMA = poly(styrene-*co*-ethylmethacrylate).

The monomer reactivity values for 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 (14). Thus, an equimolar ratio of reactants would produce a copolymer with two styrene units for every ethyl methacrylate unit.

Table 2. Correlation between copolymers and content composition

Copolymer*	% M	% C	% H
SEMA-1	-	79.01	8.47
SEMA-4	-	77.80	8.44
Pd-SEMA-1	1.04	78.04	8.86
Pd-SEMA-4	0.97	78.88	8.79
Cu-SEMA-1	1.14	78.35	8.35
Cu-SEMA-4	1.07	78.11	8.40
Ag-SEMA-1	3.76	74.86	8.29
Ag-SEMA-4	0.96	76.38	8.80
Au-SEMA-1	1.44	77.84	8.42
Au-SEMA-4	0.61	77.97	8.38
Zn-SEMA-1	0.51	76.85	8.83
Zn-SEMA-4	0.84	77.66	8.30
Cd-SEMA-1	1.15	78.60	8.42
Cd-SEMA-4	1.03	77.95	8.25
Ga-SEMA-1	1.66	78.40	8.62
Ga-SEMA-4	0.10	78.20	8.45
In-SEMA-1	0.29	72.93	8.54
In-SEMA-4	0.43	77.28	8.22
Ge-SEMA-1	0.24	77.52	8.21
Fe-SEMA-4	0.37	77.15	8.05
Sn-SEMA-1	0.22	77.18	8.86
Sn-SEMA-4	0.74	77.04	8.70
Sb-SEMA-1	0.11	77.54	8.94
Sb-SEMA-4	0.70	76.40	9.02
Bi-SEMA-1	0.49	79.75	8.48
Bi-SEMA-4	0.10	79.79	8.54

* The balance is most likely oxygen.

In all the systems under study, it is possible to obtain a linear correlation between $\bar{M}_v$ and $(BPO)^{-1/2}$ (15). This fact is in agreement with previous results in other doped copolymers (3a, 4b, 13).

In the transmission electron micrograph (TEM) it is possible to see the spherical shape of the In clusters in the comonomer sols. The average diameter of the colloid is around 49 Å and the others are ranging from 50 to 100 Å.

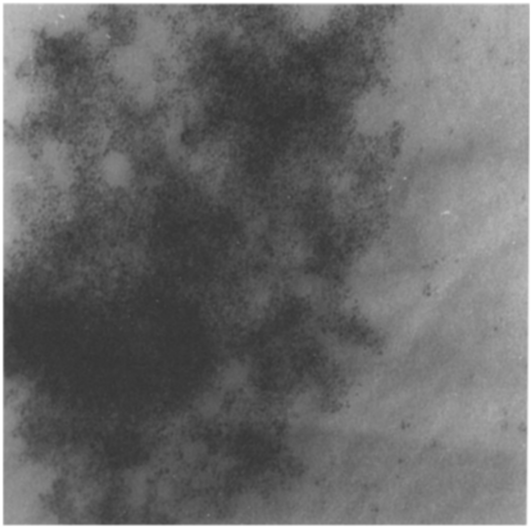


Figure 1. Electron micrograph (TEM) of In-SEMA at 120×10^3 X magnification.

A complete study of thermal stability between 25 to 550°C was carried out for the copolymers and doped copolymers (16). The thermograms reveal that the SEMA copolymers are stable up to 368°C, exhibiting only one decomposition (Fig. 2). This is another evidence of the presence of alternating metal copolymers.

Furthermore, polystyrene showed one decomposition at 400°C (1a) and poly(ethyl methacrylate) exhibited one decomposition at 375°C (17), respectively.

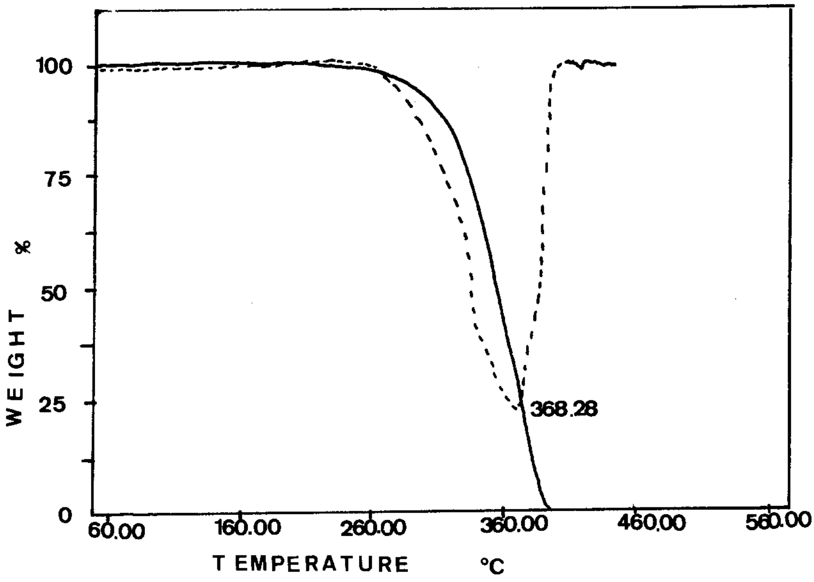


Figure 2. Thermogravimetric curve of poly(styrene-*co*-ethyl methacrylate) (0.1 mol % BPO fraction).

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