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Metal polymers: Synthesis and characterization of metal poly (styrene-*co*-4-methylstyrene) copolymers with benzoyl peroxide. XI

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SUMMARY

Styrene-*co*-4-methylstyrene (S-4-MeS) colloids were obtained by cocondensation at 77 K of the monomers with several metals such as: Pd, Au, Ag, Cu, Zn, Ga, Ge, In, Sn, Sb and Bi. Au, Ga and Ge colloids are stable for months at room temperature. The colloids of these comonomers were polymerized with different amounts of initiator benzoyl peroxide (BPO) at 65°C for 3 h, and a wide range of viscosity average molecular weights ($\bar{M}v$ 10^3-10^5) were obtained depending upon the metal used. Transmission electron microscopy showed clusters of spherical shapes in the comonomer dispersions. The particle size of these clusters displaced in the polymer is around 100 Å. The metal comonomer colloid concentration and stability at room temperature are reported. the thermal stability and metal incorporation are also described. The polymers are stable over 350°C with decomposition temperatures around 400°C. The metal content in the polymers is ranging form 0.05 to 0.77%. The color of the polymers depends upon the metal used, e.g. In-(S-4-MeS) is black and Au-(S-4-Me) is purple.

INTRODUCTION

The effect of initiator type and initiator concentration has received more attention in the literature (1). It should be expected that the concentration of initiator will affect the number of free radicals produced. This would control the number of nuclei that are formed and as a result affects the particle size. In the studies of S-4-MeS copolymers using azobiisobutyronitrile and benzoyl peroxide initiators, several differences were found.

We have studied colloidal metals in organic co-monomers, such as styrene-methyl methacrylate (2,3), styrene-acrylonitrile (4,5) and styrene-4-methylstyrene (6,7). Our CLD method (8) involves codeposition of metal vapor with organic monomers and solvents at low temperature (77 K). The method has been used for the synthesis of polymers as well as copolymers with incorporated metals. In this work we report the synthesis of metal clusters trapped in solid copolymers.

(Styrene-*co*-4-methylstyrene)s. We found some differences in yield and molecular weight ranges depending upon the radical initiator used. This method, which involves deposition of metal atoms with organic monomers at low temperature followed by controlled atom accretion, is wide in scope and can be employed with a variety of metals and solvents. Au-comonomers have been

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tested for NLO properties and copolymers with potential semiconductor and photoconduction properties can be obtained.

In order to control particle size distribution for a range of temperature and initiator compositions Almong (9) and recently Tseng (10) have used low molecular weight salts as co-stabilizers for the dispersion polymerization of styrene in alcohols. The system seems to provide immediate stabilization of the nuclei that are initially formed, thus presenting their flocculation to give polydisperse particles. Peine (11) has reinvestigated these systems and found that there was no effect of these low molecular weight stabilizers on particle size, size distribution or molecular weight, indicating that the co-stabilizer plays no role in these reactions.

EXPERIMENTAL PART

Metal Colloid. The metal atom reactor has been described previously (8, 12). As a typical example, a W-alundum crucible was charged with 0.2 g of Au metal (Aldrich). Styrene (50 mL) and 4-methylstyrene (50 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 5-7 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 and Au (0.105 g) and styrene and 4-methylstyrene were codeposited simultaneously using a Y tube device, over a 1.5 h period. A heating tape was used around the inlet tube to facilitate the monomers flow in the reactor. The matrix was allowed to warm slowly under vacuum by removal of the liquid nitrogen filled Dewar for 1.5 h. Upon meltdown a purple sol was obtained. After addition of nitrogen the solution was allowed to warm for another 1 h at room temperature. The purple dispersion was syphoned out under nitrogen into a flask. Based on Au evaporated and monomers used the approximate concentration could be calculated.

Polymerization. (S-4-MeS)Au colloid (10 ml) was placed in each of the four polymerization flasks with 0.1, 0.5, 1.0 and 2.5 mol% of benzoyl peroxide under nitrogen flow. The flasks were closed and placed in an isothermal bath at 65°C for 3 h. The content of each flask was poured in beakers with methanol. The purple 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 weights ($\bar{M}v$) were calculated by the Mark-Houwink equation (13). The intrinsic viscosity was measured at 25°C by using an Ostwald viscometer. The polymers were dissolved in benzene at 25°C ($K = 8.11 \times 10^{-5}$, $a = 0.75$) (14).

Elemental Analysis. The samples for C, H microanalyses were performed in a Perkin-Elmer 2100 Automatic Analyzer and metals in a Perkin-Elmer 3500 Atomic Absorption by the Faculty of Chemistry Sciences Laboratories (Universidad de Concepción).

Electron Microscopy. Transmission electron microscopy (TEM) was carried out on a JEOL JEM 1200 EXII. The particle size of the comonomer colloids and clusters were determined.

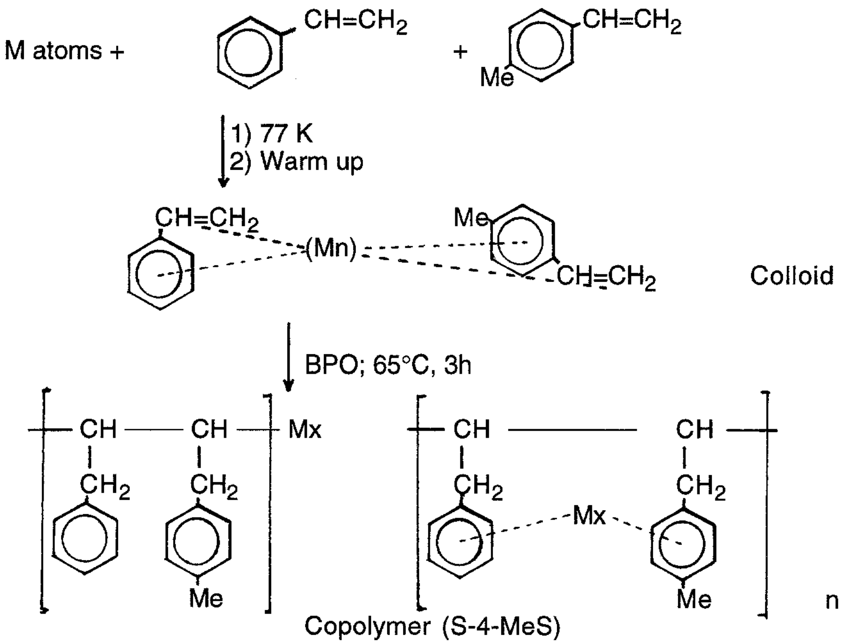
Thermogravimetric Analysis. A Perkin-Elmer Model TGA-7 Thermogravimetric System, with a microprocessor driven temperature control unit and a TA data station, was used. The mass of these samples was generally in the range of 2-5 mg. The sample pan was placed in the balance system equipment and the temperature 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.

FTIR. KBr pellets were prepared with each sample of the higher and lower MW fractions. The samples were recorded in a Nicolet Magna 550 FTIR Spectrometer with 2 cm^{-1} resolution. An average of 128 scans were accumulated for all the samples.

RESULTS AND DISCUSSION

The Au, Pd, Ga and Ge (S-4-MeS) colloids have been stabilized for several months without any salts and/or low molecular weight stabilizers.

We have previously described several metal colloids stabilized with other monomers such as styrene (15), vinyl acetate (16) and (4-methylstyrene) (17). As an extension of our research on these systems on the copolymers with metal clusters, we have stabilized styrene and 4-methylstyrene probably due to the bonding capacity of the unsaturated monomers. The monomers are stabilized as shown in the following scheme:



After the cocondensation and during the warm up process, the small metal clusters will grow until the increased polymer traps them either in the aliphatic and/or aromatic portion of monomers. FTIR showed that the metal clusters have been incorporated in the polymers based on the band displacement in the aromatic region.

Table 1 summarizes yields and molecular weights ($\bar{M}$v) of metal poly(S-4-MeS)s copolymers. The yields of the copolymers prepared either with AIBN or BPO are quite similar. However, the most important difference is the molecular weights. The copolymers obtained with BPO exhibited lower MWs than those

Table 1. Correlation between the metal poly(styrene-*co*-4-methylstyrene) copolymers and molecular weights.

Copolymers	Yield (%)	MW ($\bar{M}$v)	Color
S-4-MeS	20.79 - 5.94 24.21 - 65.49	26.760 - 39.920 24.740 - 6.250	White
Pd-(S-4-MeS)	14.90 - 12.02 30.27 - 16.51	87.610 - 37.140 24.120 - 3.870	Black
Cu-(S-4-MeS)	5.81 - 16.29 28.78 - 15.08	95.330 - 40.600 30.890 - 21.300	Yellow
Ag-(S-4-MeS)	13.50 - 40.96 47.42 - 53.94	160.720 - 80.330 53.420 - 21.500	Brown
Au-(S-4-MeS)	13.34 - 32.52 44.23 - 47.59	121.410 - 62.350 37.830 - 26.400	Purple
In-(S-4-MeS)	19.17 - 15.24 26.73 - 11.7	107.350 - 62.870 57.200 - 42.480	Black
Ga-(S-4-MeS)	16.61 - 13.32 5.22 - 39.41	143.190 - 72.680 37.600 - 33.090	White
Ge-(S-4-MeS)	11.04 - 37.94 21.42 - 51.62	107.060 - 75.660 44.860 - 31.770	White
Zn-(S-4-MeS)	16.20 - 25.77 50.56 - 45.27	140.960 - 78.400 63.390 - 28.520	Black
Sn-(S-4-MeS)	23.69 - 42.89 57.10 - 71.09	148.240 - 109.490 24.740 - 10.810	White
Sb-(S-4-MeS)	15.21 - 9.18 38.15 - 47.89	162.370 - 73.490 64.960 - 1.990	Black
Bi-(S-4-MeS)	4.28 - 14.57 44.48 - 2.03	125.260 - 74.300 27.030 - 5.870	Black

* The yields are corresponding to 0.1, 0.5, 1.0 and 2.5 mol% BPO

prepared with AIBN. On the other hand, Cu, Ag and Au (S-4-MeS) copolymers prepared with BPO showed higher MW than with AIBN. This is probably due to the more reactive radicals obtained of BPO at the same temperature. Also, in the Ga, In and Fe, Sn series, similar results were obtained,.

Sb and Ag(S-4-MeS) copolymers showed the highest molecular weights on fraction 1. Most of the metal exhibited MW over 10^5, with Pd being the lowest, most probably due to the higher stability of the metal. A linear correlation between $\bar{M}v$ and $[BPO]^{-1/2}$ was achieved (18). Transmission electron microscopy showed spherical particles due to the Au clusters dispersed in S-4-MeS colloids (Figure 1).

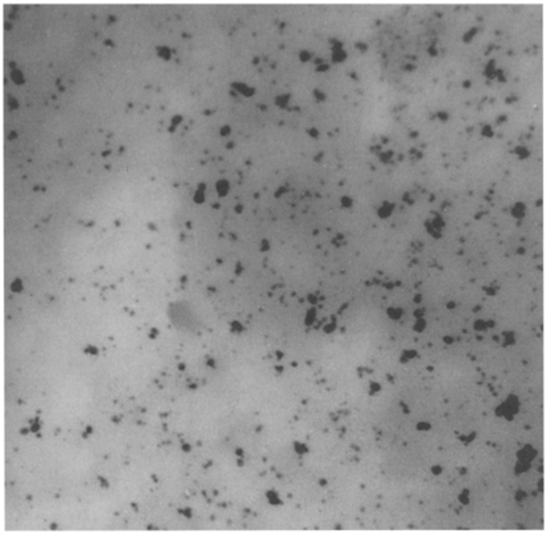


Figure 1. Transmission electron micrographs of Au(S-4-MeS) copolymer at 10^5 x magnification. Particle size 100 Å.

Elemental analyses were carried out after drying the samples under vacuum at 10°C and 10^{-3} Torr for several days. Table 2 summarizes the data for metal poly(S-4-MeS).

The metals are incorporated in the copolymers as indicated by different colors depending upon the metal. The amount of metal in the copolymers is very low, but is enough to change properties such as thermal stability. The metal incorporation ranges from 0.16 to 0.74% for Bi and Ga in fraction 1, respectively. The lowest MW fraction was characterized by their low amount of metal, most probably due to the short copolymer chain. Due to their similar reactivity ratios we should obtain an alternating copolymer. A full study of thermal stability between 25 and 550°C was carried out for the metal-S-4-MeS copolymers. The thermograms reveal that copolymers are stable up to 350°C and the decomposition starts after 400°C. Sb and In-S-4-MeS copolymers are the most stable with decomposition temperature of 424 and 418°C, respectively. The non-doped copolymer showed a T_D around 400°C.

Table 2. Correlation between metal copolymers and composition

Copolymers	% M	% C	% H*
S-4-MeS-1**	-	-	-
S-4-MeS-4	-	-	-
Pd(S-4-MeS)-1	0.35	90.79	8.06
Pd(S-4-MeS)-4	0.26	87.52	7.77
Cu-(S-4-MeS)-1	0.32	88.98	7.91
Cu(S-4-MeS)-4	0.11	87.26	7.95
Ag-(S-4-MeS)-1	0.18	90.62	8.55
Ag-(S-4-MeS)-4	0.35	88.97	8.14
Au-(S-4-MeS)-1	0.17	90.61	8.64
Au-(S-4-MeS)-4	0.08	87.32	7.81
In-(S-4-MeS)-1	0.67	83.86	8.04
IN-(S-4-MeS)-4	0.24	87.72	7.93
Ga-(S-4-MeS)-1	0.74	91.66	8.61
Ga-(S-4-MeS)-4	0.40	88.97	8.09
Ge-(S-4-MeS)-1	0.16	90.89	8.65
Ge-(S-4-MeS)-4	0.14	87.79	7.98
Zn-(S-4-MeS)-1	0.38	91.13	8.67
Zn-(S-4-MeS)-4	0.16	87.30	8.04
Sn-(S-4-MeS)-1	0.43	90.89	8.68
Sn-(S-4-MeS)-4	0.29	87.82	8.09
Sb-(S-4-MeS)-1	0.20	90.46	8.63
Sb-(S-4-MeS)-4	0.05	89.21	8.17
Bi-(S-4-MeS)-1	0.16	90.96	8.67
Bi-(S-4-MeS)-4	0.15	89.20	7.85

* The balance is most probably oxygen.

** 1,4 correspond to the higher and lower MW fraction.

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