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Metal polymers: synthesis and molecular weights of metal poly(styrene-co-acrylonitrile). IX

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SUMMARY

Styrene-co-acrylonitrile colloids were obtained by codeposition at -196°C of the monomers with several metals such as Pd, Au, Ag, Cu, Fe, Ga, Sn, Sb and Bi. The colloids were polymerized with different amounts of initiator (AIBN) at 60°C for 24 h and a wide range of viscosity average molecular weights (Mv, 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 385°C; Ag-poly(styrene-co-acrylonitrile) being the most stable. The metal content is ranging between 0.12 and 1.56% w/w. Copolymers with different colors were obtained depending on the metal used.

INTRODUCTION

Recently, we have reported the synthesis of colloidal metals in organic monomers such as styrene (1), acrylonitrile (2) and others (3, 4, 5). This new approach to incorporate metal clusters is wide in scope. In this work, we report the synthesis to prepare metal clusters trapped and/or dispersed in poly(styrene-co-acrylonitrile). Previously, we have studied the copolymer of styrene and methyl methacrylate (6). The most relevant feature with those systems is that metal poly(styrene-co-acrylonitrile) (SAN) exhibits a good thermal stability.

EXPERIMENTAL PART

Metal Colloid. A metal atom reactor was used (6, 7). As a typical example, a W-Al_2O_3 crucible (sylvania Emissive) and others prepared by us with Mo wire and alundun cement, was charged with 0.174 g of Fe metal shots (Aldrich).

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Styrene (30 ml) and acrylonitrile (30 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, and Fe (0.10 g) and styrene and acrylonitrile were codeposited simultaneously over a 2 h period. A heating tape was used around the inlet tube to facilitate the monomers introduction. A black matrix was formed on the wells 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 syphoned out under nitrogen into a flask. Based on Fe evaporated and styrene and acrylonitrile unused, the approximate concentration could be calculated.

Polymerization. (Styrene-acrylonitrile) Fe Colloid (10 ml) was placed in each of the four tubes with 0.1, 0.2, 0.5 and 1.0 mol% of recrystallized AIBN (azodiisobutyronitrile) under nitrogen flow. The flasks were closed and placed in an isothermal bath at 65°C for 2 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.

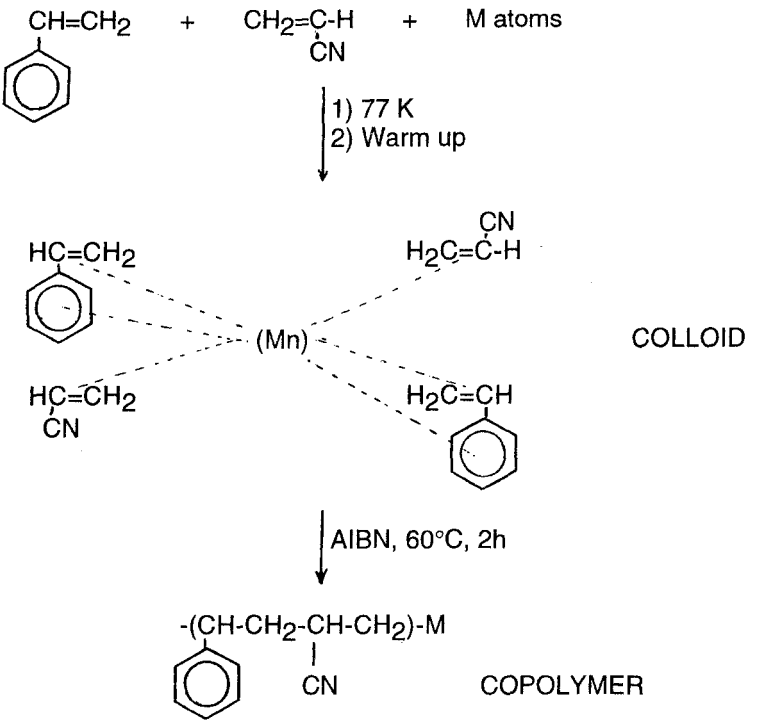
Molecular Weights. The average molecular weight (Mv) was calculated by the Mark-Houwink equation (8). The intrinsic viscosity was measured at 25°C by using an Ostwald viscometer. The polymers were dissolved in toluene at 25°C.

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

Thermogravimetric Analyses. A Perkin-Elmer Model TGA-7 Thermogravimetric System, with a microprocessor driver 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.

RESULTS AND DISCUSSION

We reported the first metal colloids stabilized by organic monomers, styrene (1), methyl methacrylate (3) and acrylonitrile (2). This is most probably due to the ligating action of the unsaturated bonds in styrene either from the vinyl group or the aromatic ring, as is shown in the following scheme:



Another possibility of metal cluster stabilization could be between the aromatic ring and the unpaired electron of the nitrogen of the cyano group. Pd and Au-SAN colloids are stable for several months at room temperature. This feature is coincident with our previous observation on styrene (1) and acrylonitrile (9). During the bulk polymerization the metal clusters tend to agglomerate until solidification eventually traps them. The metals are incorporated in the polymers and can be detected by high resolution mass spectrometry (CIMS).

During the warmup process, metal atoms will undergo some accretion and agglomeration to generate the metal clusters.

Table 1 summarizes yields and molecular weights (Mv) of metal poly(styrene-co-acrylonitrile). We can observe that the yields are low for the highest Mv fractions and only Fe and Sn-SAN exhibit good yields. In the case of Cu-SAN, we found that their molecular weights are the lowest in this set. Similarly, Cu-PSMMA also exhibit the same behaviour (10). The green color of the copolymer is an indication that some oxidation is occurring during the polymerization and copper radicals will compete with AIBN.

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

Copolymer	Yield (%)*	M.W. (Mv)x10^{-3}	Color
SAN	7.65 ; 12.16	794 ; 621	White
	25.04 ; 40.94	326 ; 198	
Pd-SAN	3.8 ; 8.7	334 ; 216	Black
	16.5 ; 26.0	184 ; 140	
Cu-SAN	11.7 ; 18.5	208 ; 165	Light-green
	29.3 ; 55.2	136 ; 127	
Ag-SAN	11.7 ; 15.0	601 ; 392	Brown
	27.7 ; 52.6	330 ; 216	
Au-SAN	10.7 ; 15.3	252 ; 230	Purple
	2.7 ; 38.9	210 ; 202	
Fe-SAN	26.5 ; 32.3	330 ; 226	Brown
	68.3 ; 77.7	167 ; 107	
Sn-SAN	12.9 ; 17.6	441 ; 419	Grey
	81.7 ; 91.8	212 ; 22	
Sb-SAN	8.6 ; 17.8	519 ; 492	Black
	19.4 ; 30.7	256 ; 183	
Bi-SAN	9.6 ; 13.0	750 ; 523	Black
	20.7 ; 41.6	306 ; 230	

*Yields correspond to 0.1, 0.2, 0.5 and 5 mol% of AIBN

In all the samples, it is possible to obtain a linear correlation between Mv and $(AIBN)^{-1/2}$ (8). This is in agreement with the fact that molecular weight decreases with the increase of initiator concentration.

The monomer reactivity values for styrene and acrylonitrile are $r_1 = 0.40$ and 0.01 at 60°C. The monomers alternate regularly along the chain regardless of the composition of the monomer feed (11). Thus, an equimolar ratio of reactants would produce a copolymer with three styrene units for every two acrylonitrile units.

The analysis of copolymerization mechanisms using copolymer composition data and/or comonomer unit sequence distribution data has recently been published. A model which utilizes reactivity ratios has seldomly been used for styrene and acrylonitrile copolymers (12).

Table 2. Correlation between copolymers and content composition.

Copolymer	%M	%C	%H	%N
SAN-1	-	83.39	7.14	7.17
SAN-4	-	83.62	7.15	7.06
SAN (ratio.3:2)	-	86.17	6.38	7.44
Pd-SAN-1	3.47	83.42	7.10	7.17
Pd-SAN-4	0.42	83.67	7.05	7.09
Cu-SAN-1	0.45	82.93	7.01	7.26
Cu-SAN-4	0.07	83.10	7.10	7.79
Ag-SAN-1	1.12	82.74	7.03	7.54
Ag-SAN-4	0.13	83.20	6.98	7.78
Au-SAN-1	1.33	83.30	6.65	7.13
Au-SAN-4	0.39	84.04	7.10	7.28
Fe-SAN-1	1.56	83.15	7.94	6.88
Fe-SAN-4	0.44	83.10	7.50	8.80
Ga-SAN-1	8.84	82.66	7.06	7.06
Ga-SAN-4	0.05	78.89	6.77	11.10
Sn-SAN-1	1.34	83.06	7.39	9.22
Sn-SAN-4	0.23	83.01	7.12	7.74
Sb-SAN-1	0.12	82.86	7.10	7.06
Sb-SAN-4	0.04	83.10	7.06	6.63
Bi-SAN-1	0.86	25.28	7.28	6.74
Bi-SAN-4	0.17	85.20	7.11	6.36

* The balance is most likely oxygen.

Due to the different polymerization rates of styrene and acrylonitrile, these monomers will preferently produce alternate copolymers.

Copolymer analyses were performed after drying the samples at 10^{-3} Torr for 48 h. Table 2 summarizes the data of metal poly(styrene-co-acrylonitrile). It seems that metal clusters have been incorporated in all the copolymer samples. The amount of metal incorporated is ranging from 0.12 to 3.47% (w/w for Sb and Pd respectively). The samples exhibit different colors depending on the metal incorporated.

A complete study of thermal stability between 25 to 550°C was carried out with metal copolymers (13). The thermograms reveal that the copolymers are stable up to 395°C, exhibiting only one decomposition curve. On the other hand, acrylonitrile showed two decomposition stages at around 270 and 390, respectively.

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