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Synthesis and molecular weights of metal polyacrylonitriles

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SUMMARY

Polyacrylonitrile colloids were obtained by codeposition at 77 K of the monomer with several metals such as: Au, Pd, Ge, Ga, In, Sn, Sb and Bi. The colloids after warm up were polymerized with different amounts of initiators (AIBN) at 283 K and a wide range of viscosimetric molecular weights ($\bar{M}v \sim 10^5$) were obtained depending upon the metal involved. The colloid metal dispersions concentrations are reported. The metal composition is ranging between 0.4-7.0 %. The thermal stability and metal microanalysis is also described. The polymers are stable up to 573 K.

INTRODUCTION

We have recently reported the synthesis of colloidal metals in nonaqueous solvents (1-4). The Chemical Liquid Deposition method, which involves deposition of metal vapor with organic solvents at low temperature (77 K) is wide in scope and can be employed with a variety of metals and solvents. In this work we report the synthesis approach to preparing metal clusters trapped in solid organic polymers based on our earlier studies involving the preparation of colloidal metals in nonaqueous solvents. This method, involves deposition of metal vapors (atoms) with organic solvents at low temperature. The colloidal metal dispersions with monomers like styrene and methyl methacrylate (5-7) have been recently reported.

EXPERIMENTAL PART

Metal Colloid. The metal atom reactor has been described (1-3). As a typical example, a W-Al_2O_3 crucible was charged with 0.4 g of Pd metal foil (Alfa Products). Acrylonitrile (100 ml), previously distilled in a ligand inlet tube was freeze-thaw-degassed several cycles. The reactor was pumped down to 1×10^{-4} Torr while the crucible was warmed to red heat. A liquid nitrogen filled Dewar of 5 liters was placed around the vessel, and Pd (0.2g) and acrylonitrile (161 g) were codeposited over a 1 h period. A heating tape was used around the inlet tube to facilitate the introduction of the solvent. The matrix was black at the end of the deposition. The matrix was allowed

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*To whom offprint requests should be sent 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 1.0 h at room temperature. The solution was syphoned out under N_2 into a flask ware. Based on Pd evaporated and acrylonitrile the approximate concentration could be calculated.

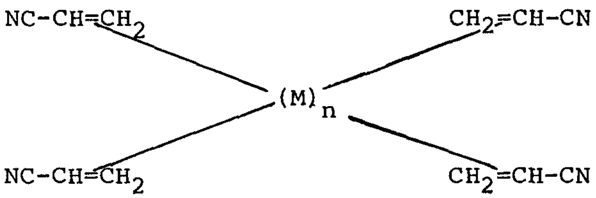
Polymerization. Au colloid (10 ml) was placed in four flask tubes with 0.1, 0.2, 0.5 and 1.0 mol % of AIBN (azobisisobutironitrile) under N_2 flow. The polymerization flasks were closed and placed in an isothermal bath at 333 K for 8 min. The content of each flask was poured in separated beakers with methanol. The purple polymers obtained were filtered off and dried under vacuum for 24 h at 293 K. The yield of each polymer fraction was determined. The molecular weights were determined in toluene at 298 K. Table 2 summarize the M.W. of the 0.1 % mol of AIBN.

Elemental Analysis. The carbon, hydrogen and metal analysis were performed by the Chemistry Department Laboratories (Universiti of Concepción).

Thermogravimetric Analysis. The thermogravimetric data were obtained using a Perkin-Elmer Thermobalance TGS-1 with 5 mg samples heated under nitrogen flow (50 ml min^{-1}) at 283 K min^{-1} from 298 to 873 K.

RESULTS AND DISCUSSION

We have recently reported the first metal colloids stabilized in a nonpolar solvent, styrene and methyl methacrylate (5-7). This must be due to the ligating action of the unsaturated bonds in styrene and methyl methacrylate. Acrylonitrile also exhibited a similar behaviour and the ligating action of the unsaturated bonds in AN probably is like:



During the polymerization the metal clusters tend weakly to agglomerate until solidification eventually traps them. Andrews and Ozin (8) have also reported studies of metal atoms and clusters in liquid polymeric materials.

Values of yields versus molecular weight ($\bar{M}v$) are summarized for metal polyacrylonitriles in Table 1; the yields are similar for Au and Sb. Pd-PAN showed the highest yield in all the fractions. A similar situation was observed for PMMA. This

Table 1. Correlation between Metal Polyacrylonitriles and Molecular Weights.

Polymer	Yield(%)*	M.W. ($\bar{M}v$)	Polymer Color
Au-PAN	15.0;16.0	1.311,600; 460,000	Grey
	48,0;49.7	325,600; 207,000	
Pd-PAN	25.8;26.8	1.800,300;1.067,200	Grey
	34.0;40.2	178,000; 89,400	
Ge-PAN	7.4;20.2	687,500; 505,600	White
	44.1;48.5	468,000; 352,400	
Ga-PAN	2.8;13.4	544,100; 448,800	White
	40.3;41.4	228,300; 186,500	
Sb-PAN	13.4;13.7	608,700 487,800	Grey
	37.1;40.6	325,800; 173,800	
In-PAN	0.4; 1.3	408,920; 254,500	Brown
	15.5;35.4	54,200; 34,300	
Bi-PAN	8.9;26.4	408,900; 255,900	White
	37.8;39.2	232,600; 149,300	
Sn-PAN	1.4; 6.2	1.677,800; 678,000	White
	13.2;43,2	445,200; 257,200	
PAN	10.6;12.6	727,500; 443,000	White
	22.0;34.9	215,400; 131,000	

*This yields correspond to 0.1, 0.2, 0.5 and 1.0 mol % of AIBN, respectively.

is probably due to the higher stability of this metal-monomer dispersion. Au, Pd and Sn are the most stable dispersions exhibiting the highest set of molecular weights.

In all the metals, it is possible to obtain a linear correlation between $\bar{M}v$ versus $[\mathrm{AIBN}]^{-\frac{1}{2}}$ (8). The molecular weight decreases with the increase of initiator concentration.

The analyses of the polymers were carried out after drying at 10^{-3} Torr for 24 h. Table 2 summarizes some data for metal polyacrylonitriles. The metals are incorporated in the polymers, the amount is ranging between 0.4 and 7.0 % depending upon the metal.

Table 2. Correlation Between Metals, Microanalysis and Molecular Weights*.

Polymer	%M	%C	%H	%N	M.W. ($\bar{M}$vx10^{-4})
Au-PAN	1.3	66.48	6.53	26.06**	131.1
Pd-PAN	7.0	65.56	6.31	22.50	180.3
Ge-PAN	2.7	65.93	6.35	25.44	68.7
Ga-PAN	1.9	66.70	8.49	25.61	54.4
Sb-PAN	3.9	68.76	7.11	21.97	60.8
In-PAN	7.0	65.56	6.31	22.50	40.8
Bi-PAN	1.5	70.19	5.99	26.35	40.9
Sn-PAN	1.4	66.58	6.40	24.46	167.8
PAN	-	68.83	6.26	26.47	72.7

*The 0.1 mol % AIBN was considered.

**Oxygen is the probably missing percentage.

PAN = polyacrylonitrile

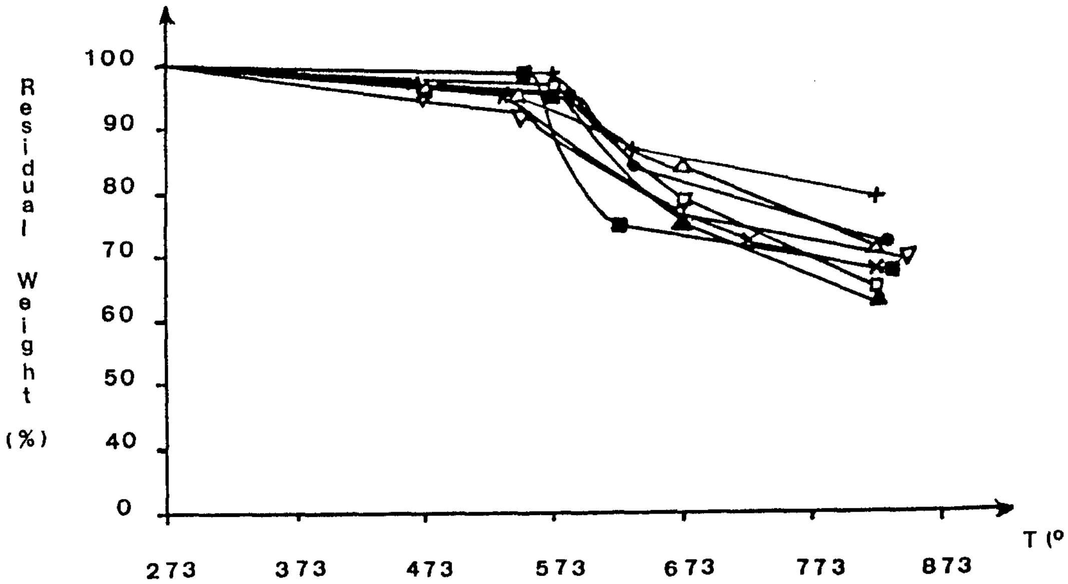


Figure 1. Thermogravimetric curves of metal polyacrylonitriles at heating rate of 283 K min^{-1}: ✚ Ge-PAN, ● Ga-PAN, ▲ Au-PAN, × Sn-PAN, □ Sb-PAN, ■ Bi-PAN, ▽ In-PAN, △ Pd-PAN.

A study of the thermal stability was performed between 273 and 873 K for the metal polyacrylonitriles (10). The thermograms reveal that polymers are stable up to 573 K. For Ge-PAN a 20% weight loss was observed. The other polymers showed higher degradation, up to 35%, and Bi-PAN was the most stable with 40% total weight loss (See Fig. 1).

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