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Metal polymers: Synthesis and molecular weights of metal poly(*n*-butyl methacrylates). VI

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SUMMARY

Butyl methacrylate colloids were obtained by codeposition at 77 K of the monomer with several metals such as Au, Pd, Cu, Ag, Zn, Cd, Al, Ga, In, Ge, Sn, Sb and Bi. The colloids were polymerized with different amounts of initiator (AIBN) at 65°C for 30 min and a wide range of viscosity average molecular weights ($\bar{M}v$, 10^3-10^5) 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 polymers are stable even at 290°C, Pd-poly(n-butyl methacrylates) being the most stable. The metal content is ranging between 0.01 and 0.66%. Polymers with different colors were obtained depending on the metal used.

INTRODUCTION

We have already reported the synthesis of colloidal metals in nonaqueous solvents (1-3). Also, we have been successful in the preparation of colloids by cocondensation of metals and monomers at 77 K (4,5). This method to incorporate metal in polymer is another approach to prepare new colloidal systems. In this work, we report the synthesis to prepare metal clusters trapped or dispersed in n-butyl methacrylates. In previous work, we have studied the series of methyl (6) and ethyl (7) methacrylates. The most relevant difference with those systems is that metal poly(n-butyl methacrylates) were produced in higher yields.

These polymers should have potential semiconductor and photoconductor applications.

EXPERIMENTAL PART

Metal Colloid. A metal atom reactor was used (1,2). As a typical example, a W-Al_2O_3 crucible (Sylvania Emissive) was charged with 0.4 g of Cu metal lumps (Merck). n-Butyl methacrylate (60 ml) was previously distilled under vacuum in a ligand inlet tube and freeze-pump-thaw degassed with several cycles. The reactor was pumped down to 5μ 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 Cu (0.3 g) and n-butyl methacrylate (60 g) were codeposited over a 1.5 h period. A heating tape was used around the inlet tube to facilitate the solvent introduction. A dark blue 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

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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 nitrogen into a flask. Based on Cu evaporated and n-butyl methacrylate used, the approximate concentration could be calculated.

Polymerization. Colloid Cu (10 ml) was placed in each of the four tubes with 0.5, 1.0, 1.25 and 5.0 mol % of recrystallized AIBN (azodiisobutronitrile) under N_2 flow. The flasks were closed and placed in an isothermal bath at 65°C for 30 min. 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.

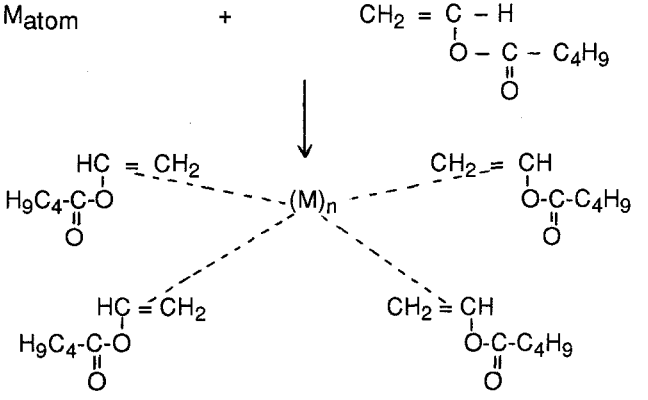
Molecular Weights. The average molecular weight ($\bar{M}v$) was calculated by the Mark-Houwink equation (8). The intrinsic viscosity was measured at 25°C by using an Ostwald viscometer. The polymers were dissolved in 2-butanone at 25°C.

Elemental Analysis. Carbon, hydrogen, and metal microanalyses were performed by the Faculty of Chemical Sciences 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 of 5-10 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 have previously described several metal colloids stabilized with styrene (9), acrylonitrile (10), methyl (6) and ethyl methacrylate (7). This phenomenon is probably due to the ligating action of the unsaturated bonds of the vinyl group:



During the warm up processes and later on during the polymerization process the small metal clusters tend to grow until the polymer traps them. The metal clusters are incorporated in the polymers and this can be observed by FTIR and mass spectrometry.

Table 1 summarizes yields and molecular weights (Mv) of metal poly(n-butylmethacrylates). The yields are higher than for methyl and ethyl methacrylates. The longer hydrocarbon chain is draining electrons in the carbonyl group and allows the polymer to grow and increase conversion. In, Zn, Sn and Sb-PBMA exhibit the highest yield. It is interesting to notice that Ag and Au showed the lowest molecular weights. Probably due to the good stability of the colloids they do not grow much during the reaction. Since small clusters of Ag colloids (Ag_2, Ag_4^{2+}) are stable (11), they compete with the AIBN and stop the polymerization.

In all the sets of polymers a linear correlation was obtained between Mv and $[AIBN^{-1}]^2$ (12). This is in agreement with the fact that molecular weight decreases with the increase of initiator concentration.

Elemental analyses were performed after drying the samples under vacuum at 30°C for several days. Table 2 summarizes the data for metal poly(n-butyl methacrylates).

The metals are incorporated in the polymers as indicated by different colors depending on the metal used. The amount of metal incorporated is fairly low, but enough to increase the thermal stability. The amount of metal incorporated is ranging from 0.01 and 0.86% for Bi and Cd, respectively. From Table 2 we can conclude that the 0.5% mol AIBN polymers exhibit a higher metal concentration, most probably due to the lower radical initiator concentration. Furthermore, in fraction 4 (5.0% mol) the AIBN concentration is higher and they compete with the metal. As a result, a lower metal incorporation in the polymers is observed.

A study of thermal stability between 25 to 550°C was carried out for the metal polymers (13). The thermograms reveal that the polymers are stable up to 280°C and for Pd-PBMA even at 386°C thermal degradation was not observed. The homopolymer exhibits one degradation step in the four MW fractions. In contrast, all the polymers with metals incorporated are showing two steps, being the first one the most important. The second step ranges between 5-6 kJ/mol which is irrelevant from the kinetic point of view.

Table 1. Correlation between metal poly(n-butyl methacrylates) and molecular weights.

Polymer	Yield	(%)*	MW (Mv)		Polymer color
Pd-PBMA	40.40;	58.64	279.400;	184.800	black
	80.50;	73.27	69.300;	2.500	
Cu-PBMA	16.14;	84.43	340.000;	170.300	green
	63.86;	76.12	103.800;	31.000	
Ag-PBMA	71.25;	60.10	64.000;	44.200	brown
	70.21;	59.31	39.800;	13.100	
Au-PBMA	75.16;	88.30	79.400;	52.900	light-purple
	83.69;	90.79	39.700;	23.100	
Zn-PBMA	78.77;	90.90	217.700;	177.000	dark-blue
	97.63;	90.88	163.200;	91.800	
Cd-PBMA	55.74;	95.63	149.300;	129.100	white
	88.18;	66.29	122.700;	69.300	
Al-PBMA	52.37;	35.32	856.900;	296.300	colorless
	49.70;	23.94	271.000;	23.100	
Ga-PBMA	39.73;	39.57	576.300;	313.500	white
	8.17;	47.49	226.300;	103.800	
In-PBMA	93.32;	93.04	149.300;	122.700	brown
	92.84;	31.69	97.800;	4.600	
Ge-PBMA	78.11;	74.54	257.600;	207.300	white
	78.90;	97.33	142.500;	31.000	
Sn-PBMA	91.38;	89.80	214.900;	149.300	yellow
	91.94;	34.50	74.800;	7.000	
Sb-PBMA	92.70;	89.03	628.000;	358.000	black
	87.66;	58.92	313.500;	85.700	
Bi-PBMA	70.15;	81.85	512.200;	423.300	black
	71.97;	20.06	331.100;	199.700	
PBMA	67.00	69.00	230.500;	122.700	colorless
	77.40	52.50	110.000;	22.000	

*The yields are corresponding to 0.5, 1.0, 1.25 and 5.0 mol% of AIBN.

Table 2. Correlation between monomer, composition and concentration.

Polymer	Concentration Colloidx1xE-3	% M	% C	% H
Pd-PBMA-1*	5.07	0.72	65.24	9.73**
Pd-PBMA-4		0.24	67.49	10.18
Cu-PBMA-1	8.53	0.85	65.31	9.97
Cu-PBMA-4		0.43	65.82	10.02
Ag-PBMA-1	1.76	0.50	66.58	9.92
Ag-PBMA-4		0.16	67.75	10.04
Au-PBMA-1	8.53	0.04	65.00	9.36
Au-PBMA-4		0.08	66.18	9.53
Zn-PBMA-1	24.20	0.16	65.26	4.61
Zn-PBMA-4		0.10	67.17	10.12
Cd-PBMA-1	1.00	0.86	67.22	9.93
Cd-PBMA-4		0.09	64.28	10.28
Al-PBMA-1	5.44	0.20	66.17	10.24
Al-PBMA-4		0.04	68.33	10.24
Ga-PBMA-1	1.23	0.06	62.73	9.62
Ga-PBMA-4		0.03	65.98	10.03
In-PBMA-1	1.46	0.12	67.89	10.52
In-PBMA-4		0.28	67.59	10.24
Ge-PBMA-1	8.52	0.08	65.66	9.76
Ge-PBMA-4		0.10	67.48	10.07
Sn-PBMA-1	2.77	0.23	67.14	10.08
Sn-PBMA-4		0.30	67.82	10.23
Sb-PBMA-1	3.52	0.04	67.58	10.36
Sb-PBMA-4		0.07	67.46	9.54
Bi-PBMA-1	6.22	0.01	67.72	10.27
Bi-PBMA-4		0.08	67.62	10.44
PBMA	---	---	66.00	9.10

* 1,4 correspond to the higher and lower MW fraction
** The balance is the likely oxygen.
PBMA = poly(n-butyl methacrylate)

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