Synthesis and Properties of Poly(butylacrylate-*co*butylmethacrylate) Doped with Metal Clusters

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ABSTRACT: Butylacrylate/butylmethacrylate (BABMA) colloids were obtained by cocondensation at 77 K of the monomers with several metals such as Au, Pd, Ag, Cu, Cd, Ga, Ge, In, Sn, Sb, Bi, and Zn. The relative stability of the comonomer metal colloids at room temperature was measured. Au-, Pd-, Cd-, and Ge-BABMA colloids are the most stable. The average particle size of these clusters dispersed in the monomers ranges between 19 and 72 Å. On the other hand, the metal clusters in the copolymers range from 32 to 126 Å. The colloids were polymerized with 2,2'-azoisobutyronitrile and dibenzoyl peroxide using 0.1, 0.25, 0.5, and 1.0 mol % initiator at 65°C to obtain poly(butylacrylate-co-butylmethacrylate). The doped copolymers yields are over 52% w/w in most of the MW fractions The viscosity average molecular weights (\bar{M}_v) range between 370,000 and 970,000 g/mol for the highest MW fraction. The copolymers were characterized by means of thermogravimetry, Fourier transform IR, elemental analysis, and conductivity measurements. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1239–1245, 1999

Key words: poly(butylacrylate-*co*-butylmethacrylate); colloids; monomers; copolymers

INTRODUCTION

Several applications using macromolecules with clusters incorporated have been used to generate metal films or bigger metal clusters. A series of studies related to measurements of polymers with electrolyte properties¹ and adsorption ion measurements² have been carried out.

These copolymers are used as agglutinate in adhesives, paints, and artificial leather. Also, there is considerable interest in the synthesis of macromolecules with extended electron systems in the main chain. The delocalization of the electrons in these systems increases the charge carrier concentration in the current transportation.^{3,4} In fact, the low conductivity in polymeric systems has been attributed to bonding systems with impurities.

Our interest is to study the copolymerization of acrylic esters with several metals and their characterization. Several metal clusters will be dispersed in polymeric matrices of butylacrylate and butylmethacrylate.

EXPERIMENTAL

Metal Colloid

A metal atom reactor was used.^{5–7} In a typical example, a W-Al₂O₃ crucible (Osram Sylvania) and our own crucibles prepared with W wire and aluminum cement, were charged with 0.300 g of Ag metal beds (Aldrich, USA).

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Figure 1 Electron micrograph of metal colloids. (a) Au(BA-co-BMA) with 51 \pm 22 Å. (b) Ag (BA-co-BMA) with 72 \pm 19 Å.

Butylacrylate (50 mL) and butylmethacrylate were previously distilled separately under vacuum in a ligand inlet tube and freeze-pumpthaw 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; Ag (0.297 g) and *n*-butylacrylate with *n*-butylmethacrylate were cocondensed using a Y inlet tube simultaneously over a 1 h period. A heating tape was used around the inlet tube to facilitate the monomer's introduction. 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 Dewar for 1.5 h. Upon meltdown a black dispersion was obtained. After addition of nitrogen, the colloidal solution was allowed to warm for another 1.0 h at room temperature.

The dispersion was siphoned off under nitrogen into a flask. A drop of the colloid was placed on a copper grid to measure particle size by transmission electron microscopy (TEM). Based on the Ag evaporated and the monomers used, the approximate concentration could be calculated (0.0275M).

Polymerization

а

b

(Butylacrylate-butylmethacrylate)Ag colloid (10 mL) was placed in each of the four polymerization flasks with 0.1, 0.25, 0.50, and 1.0 mol % of recrystallized AIBN (azobisisobutyronitrile) under nitrogen flow. The flasks were closed and placed in an isothermal bath at 65°C for 50 min. The contents of each flask were poured in beakers with methanol. The black polymers obtained were filtered off and dried under vacuum (10^{-3} Torr) for 48 h at 40°C.

Similarly, another set of polymers using BPO (benzoyl peroxide) and the same concentration initiator were prepared.

Molecular Weights

The viscosity 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, K = 6.85 E-3; a = 0.75,⁹ with an ultrasonic bath Brason 2210.

Elemental Analysis

Carbon, hydrogen, and metal microanalyses were performed by the Faculty of Chemical Sciences Laboratories at the University of Concepción. A Perkin Elmer 2100 Automatic Analyzer was used. The metals were determined in a Perkin Elmer Atomic Adsorption, PE 2400 Model.

TEM Studies

Electron micrographs were obtained on a Jeol JEM 1200 EX II with 4 Å resolution. A drop of sample was placed on a carbon coated copper grid of 100 mesh.

Copolymers ^a	1^{b}	2	3	4
Poly(BA-co-BMA)-Ag	234,150	123,050	97,230	55,180
Poly(BA-co-BMA)-Au	746,760	333,080	171,180	32,610
Poly(BA-co-BMA)-Bi	444,250	366,870	237,680	132,065
Poly(BA-co-BMA)-Cd	473,140	229,520	132,065	105,620
Poly(BA-co-BMA)-Cu	582,940	306,000	232,230	101,400
Poly(BA-co-BMA)-Ga	976,300	868,110	575,730	200,380
Poly(BA-co-BMA)-Ge	477,820	329,940	170,030	114,230
Poly(BA-co-BMA)-In	811,510	477,820	254,260	109,900
Poly(BA-co-BMA)-Pd	771,810	421,390	292,150	150,680
Poly(BA-co-BMA)-Sb	632,220	484,630	150,680	114,230
Poly(BA-co-BMA)-Sn	626,760	265,500	179,980	16,500
Poly(BA-co-BMA)-Zn	582,940	311,940	118,620	58,690
Poly(BA-co-BMA)	595,315	300,110	185,010	89,050

Table I Molecular Weights of Poly(BA-co-BMA) with AIBN

^a Copolymers: poly(butylacrylate-co-butylmethacrylate).

^b The values 1, 2, 3, and 4 correspond to 0.1, 0.25, 0.5, and 1.0% mol AIBN.

Statistical Treatment

Each micrograph was divided in 81 squares, those without relevant information (too many clusters or undefined borders) were discarded. For the rest of the squares with the RAN program, only 20% were considered. In these squares, the particles were counted and measured with accuracy. Then with Statgraphics software, the mean and standard deviation of the particles were calculated.

Thermogravimetric Analyses

A Perkin Elmer Model TGA-7 Thermogravimetric System with a microprocessor driven tempera-

ture control unit and a TA data station was used. The mass of the samples was generally in the range of 3-5 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.

Gel Chromatography

A Perkin-Elmer 1200 GPC with refraction index detector with a polystyrene/divinyl benzene column, was used.

Table II Molecular Weights of Poly(BA-co-BMA) with BPO

Copolymers ^a	1^{b}	2	3	4
Poly(BA-co-BMA)-Ag	379,446	262,640	210,836	133,380
Poly(BA-co-BMA)-Au	311,940	216,125	163,276	118,620
Poly(BA-co-BMA)-Bi	336,010	271,180	195,217	132,065
Poly(BA-co-BMA)-Cd	394,440	232,230	190,090	84,040
Poly(BA-co-BMA)-Cu	329,940	243,017	174,980	81,490
Poly(BA-co-BMA)-Ga	385,780	259,860	150,680	114,230
Poly(BA-co-BMA)-Ge	392,150	306,010	141,280	89,050
Poly(BA-co-BMA)-In	417,950	237,680	132,065	61,097
Poly(BA-co-BMA)-Pd	354,430	210,860	155,475	75,290
Poly(BA-co-BMA)-Sb	339,060	190,090	143,610	65,910
Poly(BA-co-BMA)-Sn	404,990	265,500	210,840	109,900
Poly(BA-co-BMA)-Zn	366,870	226,820	143,610	97,230
Poly(BA-co-BMA)	317,905	206,125	132,065	97,230

^a Copolymers: poly(butylacrylate-co-butylmethacrylate).

^b The values 1, 2, 3, and 4 correspond to 0.1, 0.25, 0.5, and 1.0% mol BPO.

Polymers	${ar M}_n{}^{ m a}$	$ar{M}_v$	$ar{M}_w \ M_w/M_n$
Poly(BA-co-BMA)	73,106	89,000	189,389 2.591
Poly(BA)	49,696	130,379	76,351 1.536
Poly(BMA)	138,393	340,012	653,085 4.719

Table III Molecular Weight Distributions

^a The values for 1.0 mol % AIBN were measured.

RESULTS AND DISCUSSION

The synthesis of copolymers with metal incorporated from sols or metal clusters dispersed in monomers is known.¹⁰ The following scheme shows the synthesis of these copolymers.



Table IV Molecular Weight Distributions

Polymers	$\bar{M}_n{}^{\rm a}$	${ar M}_v$	\bar{M}_w	M_w/M_n
Poly(BA-co-BMA)	59,100	97,230	222,538	3.765
Poly(BA)	59,784	130,379	26,825	1.943
Poly(BMA)	6,300	9,632	7,110	1.129

Poly(BA-co-BMA): poly(butylacrylate-co-butylmethacrylate); poly(BA): poly(butylacrylate); poly(BMA): poly(butylmethacrylate).

^a The values for 1.0 mol % BPO were obtained.





b

Figure 2 Electron micrograph of metal clusters in (BA-co-BMA) copolymers. (a) Ag-(BA-co-BMA) with 126 \pm 24 Å. (b) Cu-(BA-co-BMA) with 78 \pm 42 Å.

The stabilization is due to the ligand properties of the unsaturated ligands in the vinyl group and also to the resonance structure of carbonylic group, in agreement with some results already published.¹¹ Ethylmethacrylate,¹¹ butylacrylate,¹² methylacrylate,¹³ butylmethacrylate,¹⁴ and several comono-

(BA-co-BMA) Colloids ^a	μ (Å)	σ (Å)
(BA-co-BMA)-Au	51	22
(BA-co-BMA)-Ag	72	19
(BA-co-BMA)-Cu	25	10
(BA-co-BMA)-Pd	19	6

Table VParticle Size and Standard Deviationof Metal (BA-co-BMA) Colloids

^a (BA-co-BMA): (butylacrylate-co-butylmethacrylate).

mers such as styrene–butylmethacrylate,¹⁵ styrene–ethylmethacrylate,¹⁶ and others.

The generation of colloids by evaporation of the metal at low temperatures with vinyl monomers butylacrylate and butylmethacrylate with metals such as Au, Ag, Bi, Cu, Cd, Ga, Ge, In, Pd, Sn, Sb, and Zn exhibit several advantages: (1) colloidal sols in short periods can be obtained, (2) the uses of a wide variety of different monomers and metals, and (3) due to the absence of water, the interaction with the solvent in aqueous media is avoided.

The stability of the colloids depends either on the redox potential of the metal or on the solvent capacity to stabilize particles in solution. The stability of these comonomeric colloids was compared when half of the metallic dispersion flocculates. It is quite interesting to observe that most of the colloids show stability between 3 and 21 h. But only Au, Ag, and Pd colloids are stable for several months. The same behavior has been found for other metal cluster dispersions.^{17–19}

The colloids prepared with monomers are less stable than with alcohols, ketones, and amides. These colloids can easily react with oxygen to produce metal oxides.^{20,21} However, the noble metals are more stable due to the *d* orbitals in the valence band allowing interaction with vinylic and carboxylic bonds in the monomers. The monomers show a lower capacity to solvate the metal particles in solution, due to the resonance forms of the monomers.

The molecular weight values for doped polymers with metal clusters were obtained by the viscosimetric method. In order to calculate MW, the same parameters K and a for the homopolymers were used in the doped polymers. In all cases, the increase in initiator concentration decreases the MW.

In Table I are summarized the MW for poly(BAco-BMA) with the four fractions of AIBN. Ga, In, Pd, Au, Sb, and Sn showed a higher MW in the copolymer than the nondoped copolymer in most of the fractions.

On the other hand, Table II summarizes the MW for poly(BA-co-BMA) using BPO. It is interesting to

а



Figure 3 Electron micrograph of metal clusters in (BA-co-BMA) copolymers. (a) Pd-(BA-co-BMA) with 32 \pm 10 Å. (b) Au-(BA-co-BMA) with 52 \pm 19 Å.



Figure 4 Thermograms of (a) Ag-(BA-co-BMA), (b) Cu-(BA-co-BMA), (c) Au-(BA-co-BMA), and (d) Pd-(BA-co-BMA) obtained at a heating rate of 10°C/min.

observe that only Au in fraction 1 presents a lower MW; the rest of the doped copolymers exhibit higher MW than the undoped copolymers.

The series of AIBN showed higher MW than the BPO series. Even BPO radicals are more stable than AIBN; most probably the last one produces less radicals.

The reactivity parameters²² are $r_{\rm BMA} = 2.2$ and $r_{\rm BA} = 0.3$, respectively. An alternate copolymer with a ratio 2BA/5BMA was most probably formed.

The presence of the clusters in the copolymers does not allow us to measure Mv and MW by gel permeable chromatography (GPC). The molecular weight distribution of the undoped polymers and copolymers using AIBN and BPO are summarized in Tables III and IV, respectively. The copolymers with metal clusters incorporated cannot be measured by GPC due to the reactivity with the gel in the column. To simplify the analysis, the 1.0 mol % initiator was used. The polydispersity is higher in the BPO polymers—in fact, 3.76 against 2.59 in the AIBN copolymers—showing a wide distribution.

The particle size of the metal clusters grows slowly during the bulk polymerization. The col-

Table VI	Particle Size and	Standard	Deviation
of Metal C	lusters Dispersed	in	
(BA-co-BM	(A) Copolymers		

(BA-co-BMA) Colloids ^a	μ (Å)	σ (Å)
(BA-co-BMA)-Au	52	19
(BA-co-BMA)-Ag	126	24
(BA-co-BMA)-Cu	78	42
(BA-co-BMA)-Pd	32	10

^a (BA-co-BMA): (butylacrylate-co-butylmethacrylate).

loids of Au(BA-co-BMA) are the smaller with 51 Å [Fig. 1(a)] and Ag(BA-co-BMA) being the larger with 72 Å mostly spherical [Fig. 1(b)]. Table V summarizes the particle sizes and standard deviation of the metal clusters in the comonomers solution.

The average particle size of these clusters dispersed in the comonomers ranges from 19 to 72 Å (Table V). However, the clusters' particle size dispersed in the copolymers show an increase, e.g., Ag increases to twice its particle size [Fig. 2(a)], Cu increases three times [Fig. 2(b)] and Pd around twice [Fig. 3(a)]. It is interesting to observe that Au clusters [Fig. 3(b)] remain at the same size in the colloidal dispersion and in the polymeric matrix. Pd clustering is the lowest due to the stability of the metal. However, Ag (126 Å) and Cu (78 Å) due to their higher reactivity agglomerate and increase their particle size during the polymerization process. Table VI summarizes the particle size clusters in the copolymers. Sizes are quite similar to those already reported for styrene-co-ethyl methacrylate.²³

The stability of the doped polymers was studied by thermogravimetry. The single step decomposition in the thermograms is further evidence (Figs. 4) for the presence of an alternating copolymer. The copolymer Ag-(BA-co-BMA) exhibits a $T_D = 392^{\circ}$ C) while Cu-(BA-co-BMA) exhibits a $T_D = 341^{\circ}$ C (see Fig. 4a, b). In the case of Au-(BA-co-BMA) the $T_D = 393^{\circ}$ C and Pd-(BA-co-BMA) gives a $T_D = 403^{\circ}$ C [see Fig. 4(c,d)]. The copolymers of the same MW fraction exhibit a $T_D = 401^{\circ}$ C.

CONCLUSIONS

By cocondensation at 77 K colloids of butylacrylate-butylmethacrylate and metal clusters of Pd, Au, Ag, Bi, Cd, Cu, Ga, Ge, In, Sn, Sb, and Zn were obtained.

The most stable colloids are of Au, Pd, Cd, and Ge. The copolymers prepared with AIBN exhibit the higher viscosimetric molecular weights ranging from 3.7×10^5 to 9.7×10^5 g/mol. The GPC analysis of the undoped copolymers indicates that polydispersity is greater than 1 but the AIBN series showed the narrower MW distribution.

The electrical conductivity {(0.095–-0.596) \times $10^{-6}[\Omega^{-1}~cm^{-1}]$ } measurements gave isolating materials.

An increase in the particle size of the copolymers doped with silver and copper clusters was observed. The authors would like to thank Fondecyt (Grant 1960621) for financial support and D.I. Universidad de Concepción.

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