Synthesis and Properties of Metal Poly(butyl acrylate)

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Received 20 October 1997; accepted 30 April 1998

ABSTRACT: Butyl acrylate colloids were obtained by codeposition at 77 K of the monomer with several metals such as Pd, Au, Ag, Cu, Zn, Cd, Ga, In, Ge, Sn, Sb, and Bi. The colloids were polymerized with different amounts of an initiator (AIBN) at 65°C for 0.5 h and a wide range of viscosity-average molecular weights (\bar{M}_v , 10⁴–10⁵ g/mol) 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 400°C, with Ga–poly(butyl acrylate) being the most stable at 407°C. The metal content ranged between 0.10 and 1.32% w/w for the highest MW fraction and between 0.11 and 1.09% w/w for the lowest MW fraction. Polymers with several colors were obtained depending on the metal used. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 547–550, 1999

Key words: butyl acrylate colloids; metal clusters; doped polymers; thermal stability

INTRODUCTION

Butyl acrylate (BA) has been used in the paint, coating, and latex industries.^{1,2} Because we have previously studied the properties of doped butyl methacrylates,³ we wanted to determine the same parameters with BA in order to compare metal incorporation and molecular weights. This method, which involves the codeposition of metal atoms with organic monomers at low temperature, can be used with a wide variety of metals and solvents.

EXPERIMENTAL

Metal Colloid

A metal atom reactor was used.^{4,5} In a typical example, a $W-Al_2O_3$ crucible (Osram Sylvania)

and our own crucibles prepared with W wire and alumdum cement were charged with 0.250 g of Ag metal beds (Aldrich, USA).

BA (50 mL) was previously distilled under a vacuum in a ligand inlet tube and freeze-pumpthaw degassed in 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 Ag (0.180 g) and *n*-BA were cocondensed simultaneously over a 1-h period. A heating tape was used around the inlet tube to facilitate the monomers' 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 a vacuum by removal of the liquid nitrogen Dewar for 1.5 h. Upon meltdown, a black sol was obtained. After the addition of nitrogen, the solution was allowed to warm for another 1.0 h at room temperature.

The solution was siphoned off under nitrogen into a flask. A drop of the colloid was placed on a copper grid to measure the particle size by TEM.

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Contract grant sponsor: Fondecyt; contract grant number: 1960621.

Journal of Applied Polymer Science, Vol. 71, 547-550 (1999)

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Based on the Ag evaporated and the monomers used, the approximate concentration could be calculated.

Polymerization

BA–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 azobisisobutyronitrile (AIBN) under a nitrogen flow. The flasks were closed and placed in an isothermal bath at 60°C for 50 min. The content of each flask was poured into beakers with methanol. The black polymers obtained were filtered off and dried under a vacuum (10^{-3} Torr) for 48 h at 40°C. The yield of each polymer fraction was determined.

Molecular Weights

The viscosity-average molecular weight (\bar{M}_v) was calculated by the Mark–Houwink equation.⁶ The intrinsic viscosity was measured at 25°C using an Ostwald viscometer. The polymers were dissolved in 2-butanone at 25°C, K = 6.85 E-3; a = 0.75.⁷ The yields and molecular weights of the metal–PBA are summarized in Table I.

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 2500 atomic adsorption instrument. The results are listed in Table II.

Transmission Electron Microscopy

Electron micrographs were obtained by a JEOL JEM 120 EXII with a 4 Å resolution. A drop of the sample was placed on a carbon-coated copper grid of 100 mesh. Several magnifications were used. A log normal distribution was used to calculate the average particle size.

Thermogravimetric Analyses

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 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

Table I Yield and Molecular Weights (\overline{M}_V) of Metal Poly(BA)s

Polymer	Yield ^a (%)	${\rm MW}~(\bar{M}_V~{\rm E3})$	Color
PBA ^b	60.5; 66.1 52.0; 48.8	209,176-153,031 137,829-130,379	White
Pd–PBA	12.2; 49.3 55.2; 51.6	230,244-164,688 137,829-105,154	Black
Cu–PBA	20.5; 72.5 74.2; 84.1	244,421-177,354 136,705-96,826	Yellowish
Ag–PBA	7.2; 55.3 66.1; 49.2	291,794-264,971 180,556-126,694	Brown
Au–PBA	44.9; 51.3 51.5; 78.1	225,990-192,693 168,621-68,487	Purple
Zn–PBA	39.7; 52.3 57.7; 58.8	239,241-159,221 113,649-697,49	Black
Cd–PBA	45.8; 51.9 67.8; 66.1	256,176-184,580 153,031-108,673	Black
Ga–PBA	51.5; 48.1 59.4; 62.1	217,542-156,893 130,379-101,663	Black
In–PBA	39.5; 46.5 41.9; 28.8	273,840-196,782 154,573-140,837	Brown
Ge–PBA	40.1; 51.8 44.3; 51.9	209,176–153,031 112,222–913,72	White
Sn-PBA	37.3; 46.8 53.2; 37.4	269,396–189,031 109,027–681,79	Yellowish
Sb-PBA	44.6; 63.8 61.2; 67.4	220,069-142,726 129,271-102,011	Black
Bi–PBA	55.7; 53.1 71.8; 64.9	296,327-273,840 180,556-126,694	Black

 $^{\rm a}$ Yields correspond to 0.1, 0.25, 0.5, and 1.0 mol % of AIBN. $^{\rm b}$ PBA: poly(butyl acrylate).

increased 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

Metal colloids have been stabilized by organic monomers, for example, methyl,⁸ ethyl,⁹ and butyl methacrylate,¹⁰ and also by comonomers such as styrene–methyl methacrylate¹¹ and styrene– butyl methacrylate.¹² The stabilization mechanism is probably due to the ligating behavior of the unsaturated bonds in BA either from the vinyl group or the carboxylate group, as shown in the following scheme:



M = Pd, Au, Ag, Cu, Zn, Cd, Ga, In, Ge, Sn, Sb, Bi.

From our previous results, the metal clusters should be stabilized by the vinyl group and also with the carbonyl group of the monomer. Au–, Pd–, and Cd–BA are stable for several months at room temperature. The same behavior was observed for the methacrylate series already reported.^{8–10}

The size of metal clusters increases by clustering in the monomeric medium and this process takes place during the warming from 77 K to room temperature. The radical polymerization allows the metal clusters to grow until the viscosity of the dispersion increases and traps them. The metal clusters are incorporated into the polymers and can be observed by high-resolution electron microscopy (HRTEM) and EDAX.

Table II	Elemental	Analysis	of M-PBA
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Polymer ^a	% M	% C	% H
PBA-1 ^b	_	65.1	9.93
Pd–PBA-1	1.32	62.4	9.15
Cu-PBA-1	0.69	63.1	9.27
Ag–PBA-1	0.12	64.8	10.31
Au–PBA-1	0.23	65.4	9.01
Zn–PBA-1	0.14	63.0	9.22
Cd–PBA-1	0.19	64.9	11.72
Ga–PBA-1	0.23	65.0	9.91
In–PBA-1	1.29	63.5	9.56
Ge–PBA-1	0.16	64.7	10.17
Sn–PBA-1	0.43	67.6	9.64
Sb-PBA-1	0.25	63.5	9.81
Bi–PBA-1	0.10	63.9	9.87

^a The balance is most likely oxygen.

^b The fraction 1 corresponds to the highest MW.



Figure 1 TEM micrograph of Au–BA (magnification: $75.000 \times$). Mean particle size of Au clusters: 30 Å, $\sigma = 13$ Å.

In the transmission electron micrograph (TEM), it is possible to see the spherical shape of the Au clusters in the polymers. The average size of the Au-BA is around 30 Å (see Fig. 1). The bigger particles are due to clustering during the warm-up process. A full study of the thermal stability between 25 to 550°C was carried out for the polymers and cluster-doped polymers. The thermograms reveal that the polymers are stable up to 400°C. A slight improvement in the thermal stability for Ga–BA (T_D = 407°C), Ge–BA (T_D = 405°C), Pd–BA (T_D = 402°C) and Au–BA (T_D = 400°). The presence of the cluster in the polymers not only improves their thermal stability but also their mechanic properties, especially their higher impact resistance. The cluster probably avoids the degradation of the carboxylate group. A summary of the other polymers is shown in Table III. The shapes of the thermograms are similar and all the polymers degrade in a single step.

The thermal decomposition kinetics of the thermogravimetric weight loss data were assumed to follow a kinetic equation¹³ that relates the fraction of the sample weight reacted at time t and k. The reaction rates were calculated using a differential technique with a heating rate (10°C/min) incorporated directly into the data of the temperature versus the sample weight fraction, according to the method developed by Wen and

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Polymer	n	T_D (°C)	E_a (kJ/mol)	Temperature Range (°C)
BA-1	0	397	28.46 ± 1.44	295-430
BA-4	0	397	26.68 ± 1.38	305 - 440
Ga-1	0	407	50.91 ± 4.14	357 - 436
Ga-4	0	389	38.94 ± 2.05	339 - 426
Ge-1	0	405	54.12 ± 2.74	354 - 437
Ge-4	0	404	44.14 ± 1.97	348 - 430
Pd-1	0	402	48.03 ± 3.89	372 - 443
Pd-4	0	398	32.86 ± 2.71	341 - 450
Bi-1	0	402	53.05 ± 1.81	349-424
Bi-4	0	374	36.01 ± 2.42	332 - 420
Au-1	0	400	55.89 ± 3.42	356 - 434
Au-4	0	398	39.58 ± 1.04	336-420
Sb-1	0	401	50.05 ± 0.86	325 - 410
Sb-4	0	395	40.52 ± 1.65	293 - 440
Cu-1	0	401	52.68 ± 3.35	330-440
Cu-4	0	399	35.34 ± 1.82	325 - 435
Cd-1	0	399	31.67 ± 0.95	310-420
Cd-4	0	394	27.05 ± 1.33	305 - 420
Ag-1	0	398	37.28 ± 0.71	310 - 420
Ag-4	0	392	28.55 ± 0.96	310 - 430
Zn-1	0	397	41.36 ± 0.68	345 - 420
Zn-4	0	395	32.27 ± 1.10	330 - 415
In-1	0	398	46.36 ± 2.02	298 - 404
In-4	0	392	44.06 ± 3.47	288 - 415
Sn-1	0	380	41.03 ± 3.69	330 - 425
Sn-4	0	366	37.05 ± 1.10	320-405

Table IIIKinetic Parametersfor Metal Poly(BA)s

 T_D = decomposition temperature (first derivative TGA).

Lin.¹⁴ The specific rates, k_n , were obtained from the Arrhenius equation, that is, the following logarithmic expression:

$$\beta = \ln[-(d\alpha/dT)_{6}/(1-\alpha)^{n}] = \ln A - E/RT$$

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and -A from a linear least-squares fit of the data in a semilogarithmic plot of β versus 1/T. Table III shows the kinetic data obtained according to the above method and the temperature range used to calculate the parameters. On the other hand, the activation energy of the decomposition reaction is found in all the polymers with clusters incorporated higher than the homopolymer. Ga-, Ge-, Au-, Sb-, Bi-, Cd-, and Cu-BA exhibit the highest E_a which are also in correlation with their good stabilities.

The most relevant feature of this work was the increase in the values of MW and in the activation energies of the poly(BA) doped with metal clusters. Also, the determination of the cluster particle size in the polymers is extremely important to demonstrate the incorporation into the bulk.

The authors would like to acknowledge the financial support from Fondecyt (Grant 1960621).

REFERENCES

- 1. Levy, L. B. J Polym Sci Polym Chem Dev 1985, 23, 1505.
- Levy, L. B. J Polym Sci Part A Polym Chem 1992, 30, 569.
- 3. Levy, L. B. J Appl Polym Sci 1996, 60, 2481.
- Cárdenas, G.; Ponce, A. Colloid Polym Sci 1996, 274, 788.
- 5. Cárdenas, G.; Oliva, R.; Klabunde K. J Eur J Solid State Inorg Chem 1996, 15, 1135.
- Levy, L. B. J Polym Sci Polym Chem Ed 1985, 23, 1505.
- Bandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; Wiley: New York, 1989; Vol. VII, p 35.
- Cárdenas, G.; Retamal, C.; Klabunde, K. J. Polym Bull 1981, 25, 315.
- 9. Cárdenas, G.; Salgado, E. Polym Bull 1992, 21, 1.
- Cárdenas, G.; Salgado C., E. Polym Bull 1993, 31, 23.
- 11. Cárdenas, G.; González, M. Polym Bull 1996,37, 175.
- Cárdenas, G.; Acuña, J. Int J Polym Mater 1996, 34, 153.
- Wen, W. Y.; Lin, J. W. J Appl Polym Sci 1976, 22 2285.