Polymer Bulletin 37, 175–182 (1996)

Polymer Bulletin

# Metal polymers

## XIII. Synthesis and molecular weights of metal poly(styrene-*co*-butyl methacrylate)

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Received: 29 January 1996/Revised version: 8 April 1996/Accepted: 10 April 1996

## SUMMARY

Styrene-co-butyl methacrylate colloids were obtained by codeposition at 77 K of the monomers with several metals such as Pd, Au, Ag, Cu, Zn, Cd, Ga, In, Ge, Sn, Sb and Bi. The colloids were copolymerized with different amounts of initiator (BPO) at 65°C for 3.0 h and a wide range of viscosity average molecular weights ($\bar{M}v$, $10^4$-$10^5$ g/mol) were obtained depending upon the metal used. The metal colloid concentration and stability are reported. A medium particle size of 60-244 Å comonomer colloids was found. The thermal stability and metal composition are also described. The copolymers are stable even at 380°C, Ga- poly(styrene-co-butyl methacrylate) being the most stable with 418°C. The metal content is ranging between 0.10 and 2.26% w/w for the highest MW fraction and between 0.20 and 2.41 % w/w for the lowest MW fraction. Copolymers with different colors were obtained depending on the metal used.

## INTRODUCTION

The design and synthesis of monocomposite materials (1) is a new strategy to prepare materials with complementary behaviour between the polymer and the inorganic clusters interacting at the molecular level. In this approach, the ability of layered inorganic solids to act as host lattices for organic compounds has been applied to obtain polymer intercalation materials (2).

We have studied colloidal metals in organic co-monomers, such as styrene-butyl methacrylate (3,4) styrene-4-methylstyrene (5,6), styrene-methyl methacrylate (7,8), styrene-acrylonitrile, by using our CLD method (9) in which metal vapors are codeposited with organic monomers and solvents at low temperature (77 K). This method has been used for the synthesis of polymers and also copolymers with metal doped. In the present work we report the synthesis of metal clusters incorporated in solid copolymers of styrene and butyl methacrylate.

There are some differences in yield and molecular weight ranges depending upon the radical initiator. Almong (10) and Tseng (11) have used low molecular weight salts as co-stabilizers for the dispersion polymerization of styrene in alcohols. The system produces stabilization of the nuclei that are initially generated, thus preventing their flocculation to give polydisperse particles.

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## EXPERIMENTAL PART

*Metal Colloid.* A metal atom reactor was used (9, 12). In a typical example a W-$Al_2O_3$ crucible (Osram Sylvania) and our crucibles prepared with W wire and alundum cement, were charged with 0.1452 g of Ga metal shots (Fluka).

Styrene (21 mL) and n-butyl methacrylate (29 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 50 $\mu$ 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, Ga (0.1337 g) and styrene and butyl methacrylate were cocondensed simultaneously over a 1.5 h period. A heating tape was used around the inlet Y 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 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 siphoned off under nitrogen into a flask. A drop of the colloid was placed on a copper grid to measure particle size by TEM. Based on the Ga evaporated and the monomers used, the approximate concentration could be calculated.

*Polymerization.* (Styrene-co-butyl methacrylate) Ga colloid (10 mL) was placed in each of the four polymerization flasks with 1.0, 1.5, 3.0 and 5.0 mol% of recrystallized BPO (benzoyl peroxide) under nitrogen flow. The flasks were closed and placed in an isothermal bath at 65°C for 3.0 h. The content of each flask was poured in beakers with methanol. The black copolymers obtained were filtered off and dried under vacuum ($10^{-2}$ 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 (13). The intrinsic viscosity was measured at 25°C by using an Ostwald viscometer. The polymers were dissolved in 2-butanone at 25°C, $K = 5.3 \times 10^{-3}$ ml/g; $a = 0.76$ (14).

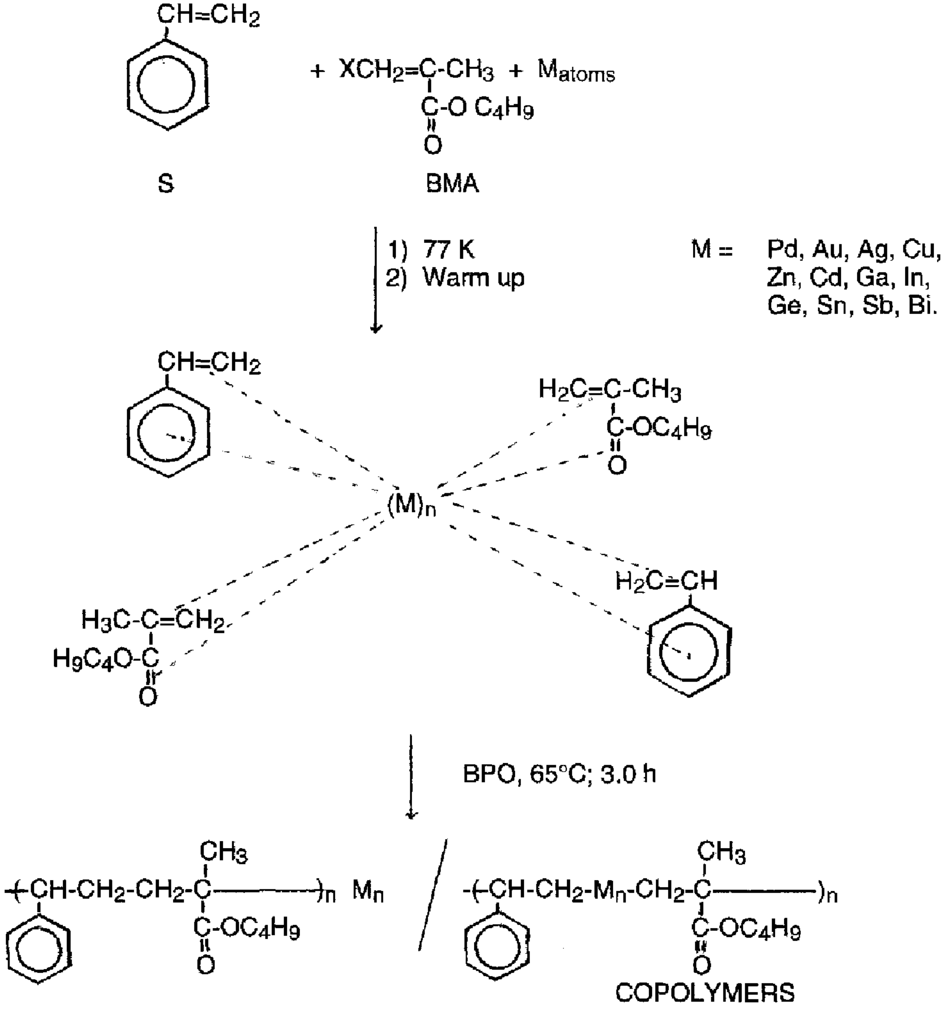
*Elemental Analysis.* Carbon, hydrogen and metal microanalyses were performed by the Faculty of Chemical Sciences Laboratories at the University of Concepción. A Perkin Elmer 2100 Automatic Analyzer was used. The metals were determined in a Perkin Elmer 2500 Atomic Absorption.

*Transmission Electron Microscopy.* Electron micrographs were obtained by a Jeol JEM 1200 EX II with 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 2-3 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

Previously, metal colloids were stabilized by organic monomers, e.g. styrene (15), methyl methacrylate (16), ethyl methacrylate 917) and butyl methacrylate (3). The stabilization process is probably due to ligating of the unsaturated bonds in styrene either from the vinyl group or the aromatic ring, and in butyl methacrylate from the vinyl group, as is shown in the following scheme:



From our previous results, the metal clusters should be stabilized by styrene between the aromatic ring and the vinyl group, and also with the vinyl and carbonyl group of the other monomer. Au, Pd and Ga-SBMA are stable for several weeks at room temperature. These typical properties are similar to previous results on metal styrene-co-acrylonitrile (18), styrene-co-methyl methacrylate (19), styrene-co-4-methylstyrene (20) and styrene-co-ethyl methacrylate (21) copolymers.

The size of metal clusters increases by aggregation in the monomeric medium and this took place during the warming from -196°C to room temperature. During the copolymerization the metal clusters tend to grow until the viscosity of the solution increases and eventually traps them. The metal clusters are incorporated in the copolymers and can be detected by TEM and EDAX.

Table 1 summarizes yield and molecular weights ($\bar{M}v$) of metal poly(styrene-co-butyl methacrylate)s.

Table 1. Correlation between metal (styrene-*co*-butyl methacrylate)s and molecular weights.

| Copolymer | Yield (%)* | MW ($\bar{M}v$ x $10^{-3}$) | Color |
|---|---|---|---|
| SBMA** | 20.6 ; 29.3 | 48 ; 43 | White |
| | 40.2 ; 46.6 | 40 ; 35 | |
| Pd-SBMA | 38.5 ; 50.7 | 118 ; 72 | Black |
| | 74.7 ; 51.5 | 68 ; 44 | |
| Cu-SBMA | 17.6 ; 20.8 | 26 ; 23 | Blue |
| | 30.0 ; 38.4 | 20 ; 42 | |
| Ag-SBMA | 22.4 ; 27.1 | 10.4 ; 8.2 | Black |
| | 44.3 ; 52.9 | 5.3 ; 2.4 | |
| Au-SBMA | 34.4 ; 41.5 | 44 ; 26 | Purple |
| | 48.6 ; 55.9 | 23 ; 13 | |
| Zn-SBMA | 31.7 ; 40.2 | 106 ; 89 | Colorless |
| | 58.8 ; 71.1 | 79 ; 9.3 | |
| Cd-SBMA | 29.8 ; 33.6 | 54 ; 23 | White |
| | 46.4 ; 57.9 | 10 ; 4.2 | |
| Ga-SBMA | 26.4 ; 37.1 | 148 ; 94 | White |
| | 54.4 ; 55.2 | 75 ; 58 | |
| In-SBMA | 26.2 ; 23.8 | 94 ; 51 | White |
| | 41.3 ; 48.8 | 38 ; 32 | |
| Ge-SBMA | 33.2 ; 37.6 | 102 ; 72 | White |
| | 46.7 ; 56.2 | 35 ; 23 | |
| Sn-SBMA | 25.9 ; 42.9 | 152 ; 68 | Colorless |
| | 28.0 ; 39.6 | 41 ; 29 | |
| Sb-SBMA | 26.2 ; 27.4 | 65 ; 51 | Grey |
| | 38.9 ; 57.1 | 61 ; 32 | |
| Bi-SBMA | 27.4 ; 35.4 | 156 ; 75 | Grey |
| | 44.9 ; 59.5 | 41 ; 10 | |

* Yields correspond to 1.0, 1.5, 3.0 and 5.0 mol % of BPO

** SBMA : (styrene-co-butyl methacrylate) copolymer.

Ga, Sn and Bi (SBMA) copolymers prepared with BPO showed higher molecular weights than the undoped copolymers. On the other hand, very reactive metals such as copper can be easily oxidized and their copolymer clusters showed lower MW than the undoped copolymers. Au- and Cd-SBMA exhibited similar MW ranges as the undoped copolymers, most probably due to the low reactivity of Au.

Elemental analyses were carried out after drying the samples under vacuum at 40°C and $10^{-3}$ Torr for several days. Table 2 summarizes the data for metal poly(SBMA).

The metals are incorporated in the copolymers as indicated by different colors depending upon the metal. The amount of metal in the copolymers is very low, but is enough to change their thermal and mechanical properties. The metal incorporation ranges from 0.10 to 1.66% for Ge and Ga, respectively. Only Sn and Cu showed higher metal incorporation, 2.26 and 3.20, respectively.

Table 2. Correlation between SBMA copolymers and content composition.

| Copolymer* | % M | % C | % H |
|---|---|---|---|
| SBMA-1 | - | 78.3 | 9.84 |
| SBMA-4 | - | 78.5 | 9.08 |
| Pd-SBMA-1 | 0.35 | 78.0 | 9.87 |
| Cu-SBMA-1 | 3.20 | 74.3 | 8.84 |
| Ag-SBMA-1 | 0.27 | 77.4 | 9.69 |
| Au-SBMA-1 | 0.42 | 77.1 | 9.87 |
| Zn-SBMA-1 | 0.51 | 76.8 | 8.83 |
| Cd-SBMA-1 | 1.15 | 78.6 | 8.42 |
| Ga-SBMA-1 | 1.66 | 78.4 | 8.62 |
| In-SBMA-1 | 0.21 | 77.0 | 9.73 |
| Ge-SBMA-1 | 0.10 | 78.0 | 9.65 |
| Sn-SBMA-1 | 2.26 | 77.4 | 9.84 |
| Sb-SBMA-1 | 0.44 | 76.9 | 9.72 |
| Bi-SBMA-1 | 0.20 | 77.8 | 9.52 |

* The balance is most likely oxygen.

An alternating copolymer with one unit of butyl methacrylate for each two units of styrene should be obtained according to the copolymerization rates ($r_1$(BMA) = 0.310; $r_2$(S) = 0.56).

We obtained a linear correlation between $\overline{M}v$ and $(BPO)^{-1/2}$. This fact is in agreement with previous results in other doped copolymers (15, 16, 17).

In the transmission electron micrograph (TEM) it is possible to see the spherical shape of the In clusters in the comonomer sols. The average size of the Au colloid is around 61 Å (see Fig. 1) and the other doped copolymers are ranging from 60 to 244 Å.

A complete study of the thermal stability between 25 to 550°C was carried out for the copolymers and doped copolymers (22).

The thermograms reveal that the SBMA copolymers are stable up to 380°C. A significant improvement occurs in the thermal stability of Ga-SBMA with a decomposition temperature of 418°C.

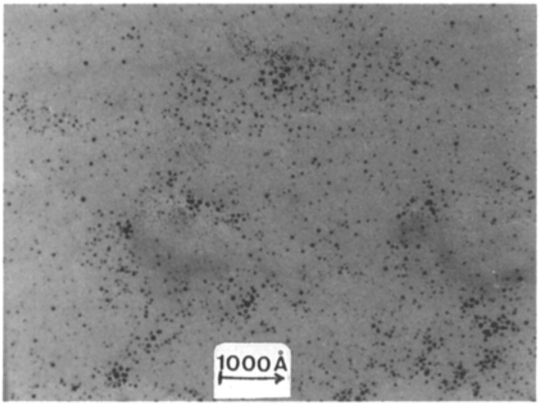


Figure 1. Electron micrograph (TEM) of Au-SBMA at 100 x $10^3$ X magnification.

## ACKNOWLEDGEMENTS

The authors would like to thank Dirección de Investigación from Universidad de Concepción (Grant 95.2407-1.2).

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