Synthesis and TEM studies of metal clusters dispersed in polymers

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Summary

Solvated metal atoms were obtained by cocondensation of metals and monomers at 77 K. Stable colloids were formed upon warming. Several colloids using iron and nickel have been prepared with the following monomers: styrene, methyl methacrylate, ethyl methacrylate and butyl methacrylate. The colloids were polymerized with two different initiators, benzoyl peroxide (BPO) and 2,2'-bis-azoisobutyronitrile (AIBN). The metal clusters should be stabilized by styrene between the aromatic ring and the vinyl group, and in the acrylate series between the vinyl and the carbonyl group. The yields of the polymers of Ni-styrene and Fe-styrene range from 10-70% and the molecular weights range from 10.000 to 250.000, even higher than the homopolymer. Electron micrographs were obtained by a Jeol JEM 1200 EX II with 4 Å resolution, for the colloids and the polymers. The colloids exhibited a smaller particle size than the metal clusters in the polymers. The styrene with either Fe or Ni clusters should be around 100 Å colloidal sizes. A dramatic increase in the polymer was observed. Very big clusters in the dope polyacrylate were found. During polymerization particle size growing and size increase were observed.

Introduction

Several methods have been developed for the synthesis of new materials changing the metals and controlling size, distribution and concentration.

The preparation of polymer metal composites are generally oriented on plasma polymer thin films and include simultaneous evaporation of polymer and metal from separate sources, or simultaneous plasma polymerization and metal evaporation from resistibly heated crucibles (1-3).

A method for cationic polymerization of bulk liquid monomers that end with the incorporation of ultrafine metal particles into polymer matrices has been reported. Ultrafine metal particle in polyisobutylene matrix were encapsulated (4). Pulsed-laser vaporization is used to generate energetic meta ions from a metal target (Zn, Ti, Zr, Fe, Al, Sn, Pd and Pt) above the monomer liquid (5). Isobutylene was used because it is known to be polymerized in the bulk by cationic mechanism (6). The SEM micrograph indicates that spherical metal particles are in a size range of 100-200 nm within the polymer matrix. The molecular weight ($\overline{M}w$) of the polymers are as high as 1×10^6 and depending on experimental conditions were determined by GPC.

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In this work, the stabilization of Fe and Ni metal cluster in monomers such as styrene, methyl, ethyl and butyl methacrylate was studied. The metal clusters were produced by resistive heating of the metals and simultaneous codeposition with the monomers at 77 K. The particle size of the cluster in the polymers was determined. The most relevant differences with some other systems previously reported is the incorporation of metal atoms instead of metal ions within the polymer matrix.

Experimental

Metal Colloid
The static metal atom was used (7). As a typical example a W-Al_2O_3 crucible (Ceramic Coating) was charged with 0.250 g of Ni metal shots (Aldrich).

Methylmethacrylate (50 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 5 μm 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 Ni (0.148 g) and methylmethacrylate were codeposited simultaneously over a period of 1 h. The matrix was allowed to warm up to room temperature. Upon meltdown a black colloid was obtained. After addition of nitrogen the solution was allowed to warm for another 1 h at room temperature. The sol was siphoned out under nitrogen into a flask.

Polymerization
Methylmethacrylate Ni-colloid (10 ml) was placed in each of the four polymerization flasks with 0.1, 0.25, 0.50 and 1.0 mol% of benzoyl peroxide (BPO) under nitrogen flow (8). The flasks were closed and placed in an isothermal bath at 65°C for 40 min. The content of each flask was poured in beakers with ethyl ether. The purple polymers obtained were filtered off and dried under vacuum (10^{-3} Torr) for 48 h at 40°C. The yield of each polymer fraction was determined. Similarly, 0.1, 0.5, 1.0 and 5.0 mol% of azoisobutyronitrile (AEBN) was used.

Molecular Weights
An Ostwald viscometer was used. The values of intrinsic viscosity were used in the Kuhn-Mark-Houwink equation (9). The polystyrene were dissolved in toluene and the acrylates in 2-butanone.
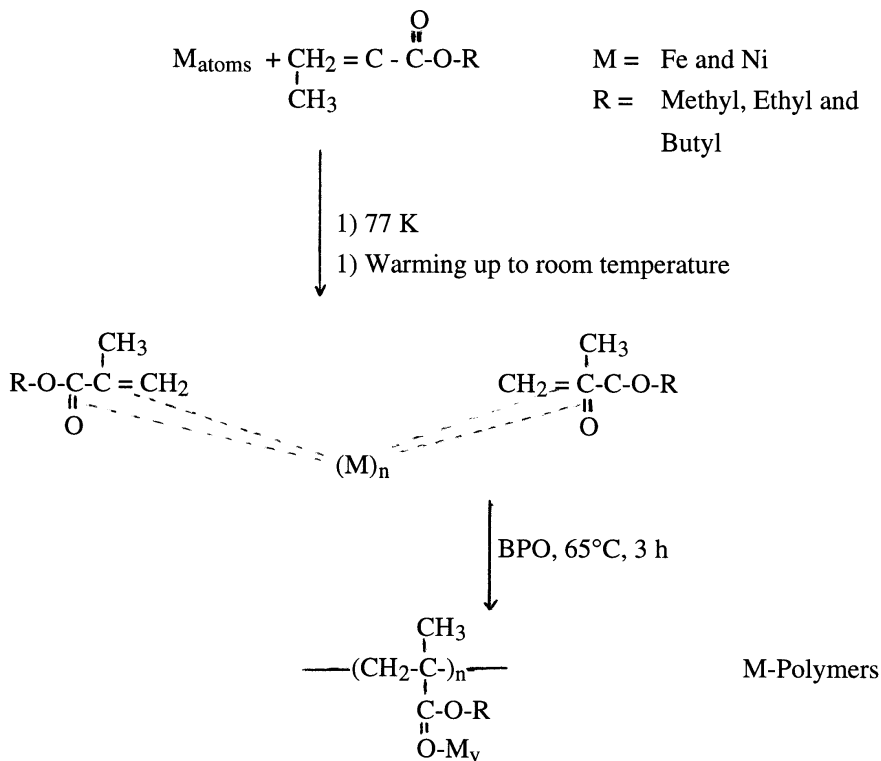
Elemental Analysis
The samples for C, H microanalyses were performed in a Perkin-Elmer 2100 Automatic Analyzer and metals in a Perkin-Elmer 3500 Atomic Absorption Spectrometer by the Faculty of Chemical Sciences Laboratories (Universidad de Concepción).

Electron Microscopy
Transmission electron microscopy (TEM) was carried out in a Jeol JEM 1200 EXII. The particle size of the colloids were determined. The samples of colloids were placed in a copper grid with carbon films of 5 μg/cm^2 from ACF metals. The polymers were included in araldite and an Ostwald ultramicrotome was used to obtain 400 Å slices of the doped polymers. Images were obtained at a direct magnification of x 4, x12, x120 and x250 K.

Results and Discussion

Several polystyrenes, polymethyl-, ethyl and polybutylmethacrylates doped with Fe and Ni clusters were prepared by cocondensation of the monomers with the metal vapors. The following scheme summarizes the process for acrylate series.

$$M_{atoms} + CH_2 = \underset{\underset{CH_3}{|}}{C} - \overset{\overset{O}{\|}}{C} - O - R$$

M = Fe and Ni

R = Methyl, Ethyl and Butyl

1) 77 K

1) Warming up to room temperature

$$R-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C} = CH_2 \qquad\qquad CH_2 = \underset{\overset{CH_3}{|}}{C}-\underset{\overset{O}{\|}}{C}-O-R$$

(M)$_n$

BPO, 65°C, 3 h

$$--(CH_2-\underset{\underset{\overset{C-O-R}{\|}}{|}}{\overset{\overset{CH_3}{|}}{C}})_n--$$
O-M$_y$

M-Polymers

Similar method and properties using styrene with other metals have been previously reported (10).

The size of metal clusters found in the polymers was studied by TEM. On Table 1 we can observe that most of the colloids exhibited a smaller size than the metal clusters in the polymers. This is due to the clustering process during the polymerization. These values are quite larger than those reported for Au and Ag clusters in poly(styrene-*co*-ethyl methacrylate) (11).

Table 1. Mean particle size of colloids and polymers

Samples	Mean size (Å)	σ (Å)
Ni-styrene	105	10
Fe-styrene	90	10
Ni-PS	500	863
Ni-PMMA	5069	1470
Ni-PEMA	5455	1864
Fe-PEMA	9216	3422

The amount of metal clusters incorporation by microanalysis was obtained.

The metal elemental analysis for the polymers obtained using benzoyl peroxide (BPO) and azoisobutyronitrile (AIBN) is not quite different which can be observed in Table 2. Also, a comparison with the molecular weights for the highest and lowest molecular weight fraction has been achieved.

The metal concentration is low in the polymers, the Fe series exhibited between 0.2 and 2.2 metal % w/w. On the other hand, the Ni series ranges from 0.15-2.0 metal % w/w. The C/H are in the normal values very similar to the theoretical values.

These values are in the same ranges than those obtained for other doped series using Au, Ag, Cu and other semiconductor metals, such as methyl (12), ethyl- (13) and butylmethacrylates (14). Also, some copolymers of styrene-*co*-ethylmethacrylates (11), styrene-*co*-4-methylstyrene (15), styrene-*co*-butyl methacrylate (16), have been already reported.

Table 2. Elemental analysis and $\overline{M}_v$ of polymers doped with Fe and Ni.

Polymer	% metal (BPO)	% Metal (AIBN)	$\overline{M}_v \times 10^{-3}$ (BPO)	$\overline{M}_v \times 10^{-3}$(AIBN)
PS -Fe 1	0.46	0.96	251	144
-Fe 4	0.22	0.34	11	35
PS -Ni 1	0.74	0.57	235	109
-Ni 4	0.16	0.21	24	7
PMMA -Fe 1*	1.18	0.41	189	115
-Fe 4	0.30	0.20	12	37
PMMA -Ni 1	0.46	0.97	146	145
-Ni 4	0.24	0.17	64	12
PEMA -Fe 1	0.54	3.96	464	265
-Fe 4	0.26	0.68	68	58
PEMA -Ni 1	0.77	2.05	270	225
-Ni 4	0.16	0.25	45	51
PBMA -Fe 1	0.35	2.24	201	461
-Fe 4	0.19	0.28	116	53
PBMA -Ni 1	0.89	0.85	447	350
-Ni 4	0.28	0.36	163	93

PMMA = poly(methylmethacrylate); poly(ethylmethacrylate); PBMA = poly(butylmethacrylate).
* 1 and 4 are corresponding to the lower and higher initiator concentrations.

On Figure 1a we can see the metal clusters corresponding to Ni-styrene colloids showing a similar size to Fe-styrene colloids (Fig. 2). The particle size of the particles in the agglomerate are quite similar in the Ni-styrene colloids. However, in Figure 1b a polymer slice exhibits a 500 Å particle size. The size increase in the cluster is most probably due to clustering process during the temperature increase in the radical polymerization.

Ni clusters dispersed in poly(methylmethacrylate) showed bigger cluster size mostly spherical, but ten times much bigger than Ni-polystyrene (Fig. 3). The increase in one carbon from methyl- to ethyl-MA also induces an increase in cluster size in the polymers (see Fig. 4). The Ni-PMMA increases their size from 5069 Å to Ni-PEMA with 5455 Å.
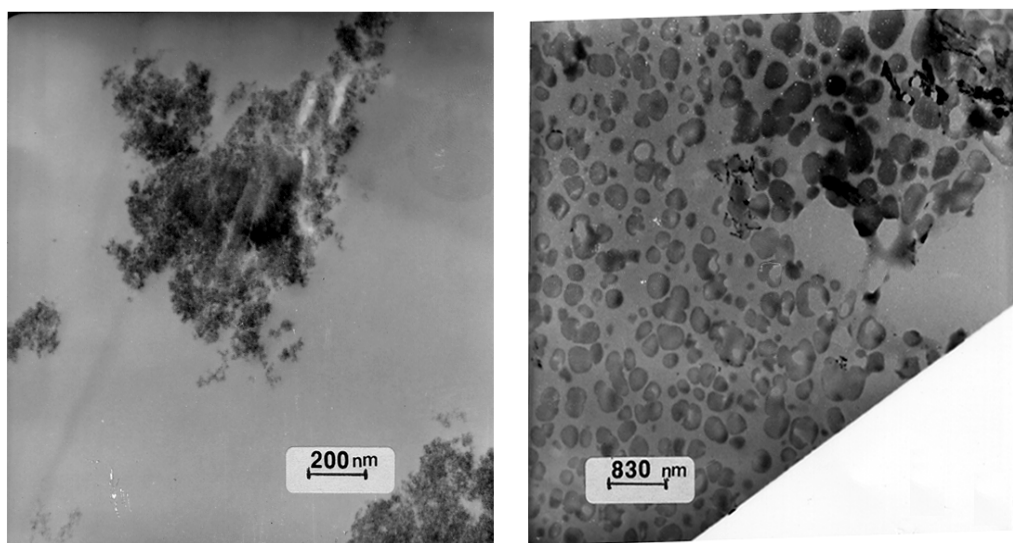
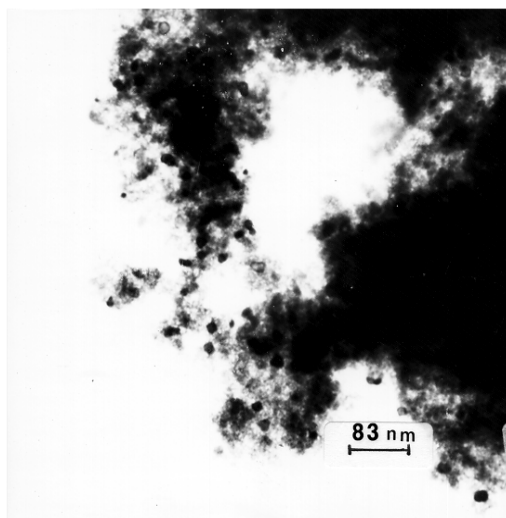**Fig. 1**. Electron micrograph: a) Ni-styrene colloid (50 K); b) Ni-polystyrene cluster (12 K).

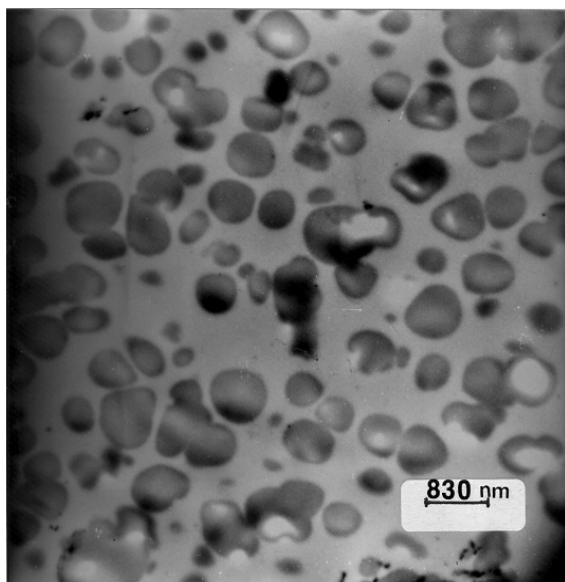**Fig. 2**. Electron micrograph Fe-styrene colloid (120 K)

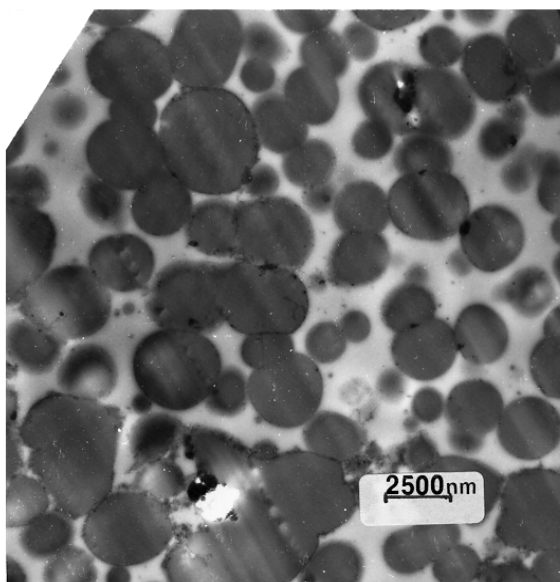**Fig. 3**. Electron micrograph Ni-poly(methylmethacrylate) cluster (12 K).

Fig. 4. Electron micrograph Ni-poly(ethylmethacrylate) cluster (4 K).

Finally, on Figure 5 we can see the TEM of Fe-poly(ethylmethacrylate). The presence of the clusters in similar monomers with analogous particle sizes is indicative of the influence in the distribution and agglomerate dispersity.
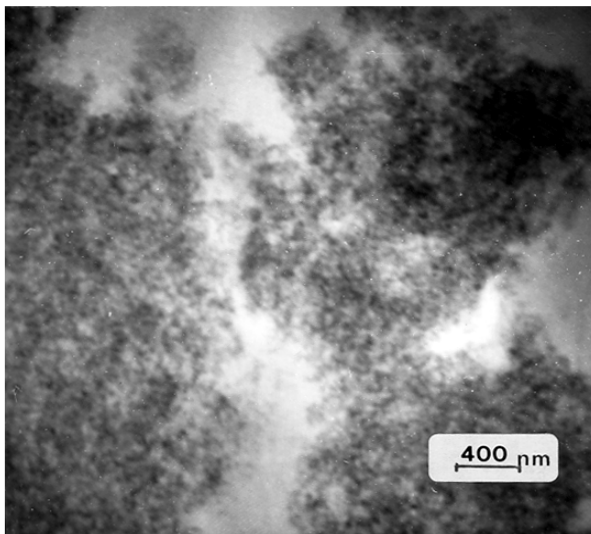
Fig. 5.   Electron micrograph Fe-poly(ethylmethacrylate) cluster (250 K).

Acknowledgements

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