Synthesis of poly (buthyl acrylate –*co*- vinyl formamide) copolymer and its importance in designing new materials

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Resumen

Las micelas formadas por los copolímeros en bloque, al ser depositadas para producir películas delgadas, se caracterizan por presentar un tamaño muy reducido (varias decenas de nanómetros) y alta estabilidad, lo que permite su utilización en diversos campos como son: la liberación de fármacos, diagnóstico, nanolitografía, síntesis de nanopartículas, y almacenamiento de información de alta densidad.

En este trabajo se realizó la síntesis de un copolímero de poli (acrilato de butilo-*co*-vinil formamida) empleando el método de polimerización en emulsión. La estructura del copolímero se comprobó mediante FT-IR. Posteriormente se depositaron dentro de la estructura del material orgánico nano-cristales de Pd de forma esférica de ~10 nm, dando origen a un material híbrido que puede ser aplicado en áreas como nanolitografía, catálisis, sensores. Las películas fueron analizadas usando AFM

Palabras clave: Polimerización en emulsión, nano-cristales de Pd, FT-IR.

Abstract

Block copolymer micelles formed in thin films are mainly characterized by their small size (several tens of nanometers) and high stability, leading to their promising applications in fields, such as: drug delivery, diagnosis, nanolithography, nanoparticle synthesis, and high-density information storage media technologies.

Therefore, in this work the synthesis of a poly (buthyl acrylate –*co*- vinyl formamide) copolymer using the emulsion polymerization technique is presented and discussed. The copolymer structure was confirmed by FT-IR. Subsequently Pd nano-crystals of spherical shape of ~ 10 nm were deposited inside the structure of the organic material. The films were analyzed using AFM, giving rise to a hybrid material that could be applied in areas such as nanolithography, catalysis, sensors

Keywords: Emulsion polymerization, Pd nano-crystals, FT-IR.

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I. INTRODUCTION

One approach to prepare organic-inorganic hybrid materials has been combining the advantageous properties of crystalline inorganic solids with those of organic molecules within a molecular-scale composite. The inorganic component forms an extended framework bound by strong covalent or ionic (or both) interactions to provide high carrier mobilities. The organic component facilitates the self-assembly of these materials, enabling hybrids to be deposited by the same sample, at low-cost, using low-temperature processes as the organic materials. [1]

The polymerization method is important to generate the properties of copolymer coatings. Nowadays exist many methods, but the emulsion polymerization [2] provides some advantages, such as good heat transfer, low viscosity, high monomer conversion, direct application and high surface area [3]. In fact, adjustment of the ratio of functional groups in copolymers and fillers is very important to the basic properties and functions of coatings.

In this study, the poly (buthyl acrylate –*co*- vinyl formamide) copolymer was prepared by emulsion polymerization and the nanoparticles of Pd were prepared separately. This hybrid material formed thin films with different structural arrays which could be applied in different areas, i.e. sensors [4], catalysis [5], etc.

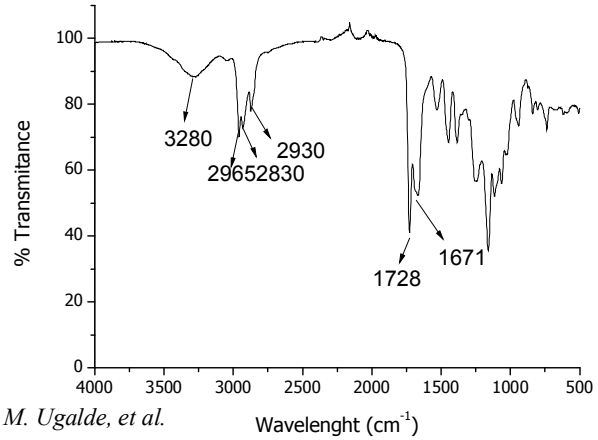
II. EXPERIMENTAL

The emulsion was prepared by dispersing the desired amount of monomers of BA and NVF (from Aldrich), once they were distilled under reduced pressure. The commercially pure Sodium lauryl sulfate (SLS), triton X-305, potassium persulfate (KPS) and distilled water were used according to ref. [6]. The previously treated monomers were mixed with the aqueous SLS, Triton X-305 and distilled water to form a solution with a stechiometric relation 1:2:1 using a rotating stirrer at room temperature. The resulting emulsion was sheared further by sonification with ultrasonic cleaner branson 200 for 20 min at 117 V. The beaker containing the emulsion was immersed in cool water during sonification to maintain the temperature constant.

The emulsion was transferred to a 500-mL, three-neck flask equipped with argon inlet-outlet tube, condenser, and mechanical stirrer. The system was purged with argon for 20 min and heated to 80°C. Agitation was provided by a paddle stirrer at 500 rpm.
The polymerization was started by injection of *20* mL of sodium persulfate. The viscosity and conversion rate were measured during the process. After reaching the standard of emulsion, the mixture was removed and cooled. [6]

The synthesis of the hybrid material, was carried out using, palladium (Pd) nano-crystals. These nano-crystals were prepared by a well Known experimental method. [7] Thin films of PBAtu-*co*-PVFA and the mixture of Pd nanoparticles were prepared by spray coating latex and benzyl alcohol onto silicon substrates. Then the thin films were annealed at 60°C.

The structure of the copolymer was analyzed using a, Thermo Scientific Nicolet 6700 FT-IR spectrometer. The surface morphology of the thin films was studied by AFM Jeol-4210 Scanning probe microscope; operate at 2V, 7 kHz. The size and morphology of nanoparticles was analyzed by high resolution transmission electron microscopy (HRTEM) JEOL JEM-2200FS operating at 200 KV. The material was dispersed in isopropyl alcohol by an ultrasonic washer and deposited on the carbon-grid.



III. RESULTS AND DISCUSSION

The structure of the copolymer was confirmed by infrared spectra. In Figure 1 the typical band of amide group correspond to PVFA (N-H at 3280 cm^{-1}), the ester signal correspond to (C=O stretching, at 1728 cm^{-1}) from PABut, the band of PVFA corresponds to ketone (1621 cm^{-1}, C=O stretching), and the others bands that correspond to aliphatic chain (C-H stretching at 2965, 2830 y 2930 cm^{-1}) were observed.

FIGURE 1. IR spectra of the copolymer PABut-co-PVFA

The images "a" and "b" in Figure 2, showed the bright field images obtained by HRTEM of Pd nano-crystals that were synthesized and which were used to produced the hybrid material. Figure 2a showed that it was possible to obtain nano-crystals with an average of 5 nm. It was also confirmed that the synthesized Pd material showed a final spherical shape and that they tend to form clusters.

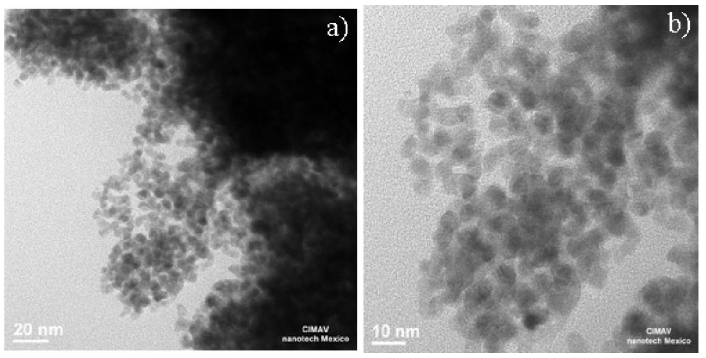


FIGURE 2. TEM micrographs of Pd nano-spheres, synthesized by the sol-gel method, polymerized with acrylamide [ref.7].

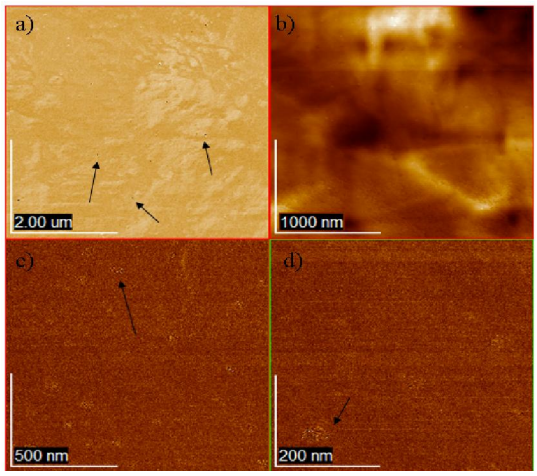


FIGURE 3. a) AFM height image of a thin film of copolymer poly(BuA-*co*-VFAm), b) approach of small holes shown in the image, (a), (c) and (d) Image of the hybrid thin film (copolymer-nano-Pd).

Figure 3 shows the AFM images obtained from the thin films of the copolymer (a and b) and the images (c and d) showed the hybrid material (co-polymer nano-Pd).

When analyzing the images, a smooth surface and the formation of few holes were observed (Figure 2a). However, at higher magnifications, the formation of the aforementioned holes was certainly observed (Figure 2b). Finally in Figures 2c and d, the formation of Pd nano spherical clusters inside those holes was confirmed.

From these results the use of this polymerization technique, resulted in obtaining a copolymer, which could be randomly in nature, having a hydrophilic part and groups with free electron pairs that formed those small holes where Pd nano spheres were hosted.

It is worth noting that Hidenori Mizuno, et al. [8] also used a block copolymer (polystyrene-block poly-2-vinylpyridine, PS-b-P2VP) as a template to deposit nano metals with diameters of 10-70 nm (Au, Ag, Pd, Pt).The results reported by Mizuno, agreed well with the results presented and discussed in this work. In summary, not only the block copolymers can act as templates for fixing metallic nanoparticles, and that be proven at synthesizing copolymers with specific characteristics, such as those mentioned above.

IV. CONCLUSION

This work has demonstrated that subnanometer Pd spherical clusters can be formed in polymer holes. Although the synthesized copolymer resulted in a random structure, it was able to trap metals because it contains a hydrophilic structure and groups free electron pairs, so is possible to trap other metals in random copolymers, taking into account the containing functional groups in that organic structure.

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