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# Morphological characterization of poly(phenylacetylene) nanospheres prepared by homogeneous and heterogeneous catalysis

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**Scanning electron microscopy characterization of the materials obtained by homogeneous and heterogeneous catalytic polymerization of phenylacetylene is described. The catalysts used are $\beta$-dioxygenato rhodium(I) complexes. The effects of the reaction medium, presence of a cocatalyst and the type of catalysis (homogeneous or heterogeneous) on the morphology of the polymers obtained have been studied and discussed. Using a supported complex at 0 °C, nanoparticles with a diameter distribution as narrow as 30 to 70 nm were obtained. Polymer nanopowders were found to be unaffected by ageing. Copyright © 2003 John Wiley & Sons, Ltd.**

**KEYWORDS:** polymer microstructure; nanospheres; poly(phenylacetylene); scanning electron microscopy

## INTRODUCTION

Polymer nanospheres find applications in different fields, such as orally delivered controlled-release therapeutic agents,[1–5] nanosphere lithography,[6] confined-reaction vessels,[7] silica particles coating for pigments,[8] luminescent materials.[9] When speaking of nanospheres the size range is very wide, from a few to two or three hundred nanometres. Hollow or bulk nanospheres can be prepared from several polymers like poly-$\varepsilon$-caprolactone, polylactic acid ethyl acetate, hybrid polymers with acrylated polyurethane dispersions, polystyrene, poly(methyl methacrylate) and poly(benzyl methacrylate).[10]

A common preparation route is to produce the polymer nanoparticles from microdroplets of dilute polymer solution. Particle size is controlled by droplet size and weight fraction of polymer in solution. The control on particle size and particle size distribution is still one of the bottlenecks of the technology.

Poly(phenylacetylene) (PPA) is an interesting material because of its physical properties[11–14] and because of the fact that the polymerization catalysts used are tolerant to a wide variety of substituents on the phenyl group thus permitting the obtainment of several functional polymers. In our laboratories we have developed the first rhodium(I) heterogeneous catalyst[15] for the synthesis of PPA and we have evaluated the properties of PPA obtained using ionic liquids as innovative solvents.[16] Despite the growing interest in PPA[17–19] little attention has been paid to its morphology, which may influence the properties of the final material.

Based on our experience, and knowing that PPA can adopt a microspherical morphology,[20] we have confidently started to investigate the possibility of achieving nanosized PPA spheres.

The available literature on PPA morphology is limited to scanning electron microscopy (SEM) observation of free-standing films obtained with several rhodium(I) catalysts in methylene chloride[21] or in compressed carbon dioxide.[22]

Since the morphology of the polymer is a preliminary step towards the final applications of the material, in this paper we report the influence of experimental parameters upon the morphology and particle size distribution of the powders obtained by Rh(I)-$\beta$-dioxygenato-catalysed phenylacetylene polymerization. The experimental parameters

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taken into account were the nature of the solvent, the type of catalyst, the presence of a cocatalyst and the temperature.

## EXPERIMENTAL

PPA samples were prepared by the catalytic procedure described elsewhere[15] using (cod)Rh(acac), (nbd)Rh(acac), (cod)Rh(AAEMA) and Rh-pol (cod = 1,5-cyclooctadiene, acac = acetylacetonate, nbd = norbornadiene); AAEMA is the deprotonated form of 2-(acetoacetoxy)-ethylmethacrylate and Rh-pol is the supported metal complex obtained by thermal copolymerization of (cod)Rh(AAEMA). After catalysis, the polymer was obtained by evaporating the solvent and then dissolving it in chloroform. The samples were prepared by slow addition of methanol to the chloroform solution kept under vigorous stirring.

SEM (Philips, SEM XL 30, $LaB_6$ source) was performed on the as-prepared samples after being glued with silver suspension on an aluminium stub. Gold coating was necessary to prevent charging. Images were taken at 5 to 10 kV acceleration voltage.

Particle size distribution and average particle size were determined statistically by using image elaboration software UTHSCSA Image Tool, ver.3.00, after manual contrast enhancement. Data were compared with the manually elaborated image for comparison. Software results are hereafter reported in the plots as 'autom'.

## RESULTS AND DISCUSSION

Table 1 presents selected experimental details regarding conditions under which the polymers subject to morphological analysis have been obtained. Several effects that may influence the morphology of the PPA obtained have been investigated.

**Table 1.** Experimental details of PPA samples under investigation. All samples except A and G were prepared from the THF-soluble fraction of the materials obtained at $T = 22\,°C$ with a substrate/catalyst ratio of 200 mol $mol^{-1}$, in 5 ml solvent; reaction time: 1 h

| Sample name | Figure no. | Catalyst | Reaction solvent |
|---|---|---|---|
| **A**[a] | **1a** | (cod)Rh(AAEMA) | THF |
| **B** | **2** | (cod)Rh(AAEMA) | THF |
| **C** | **3** | (cod)Rh(AAEMA) | $C_6H_6$ |
| **D, E** | **5a and b** | (cod)Rh(AAEMA) | DCE |
| **F**[b] | **7** | (nbd)Rh(acac) | THF |
| **G**[a] | **1b** | (nbd)Rh(acac) | THF |
| **H**[b,c] | **8** | (nbd)Rh(acac) | THF |
| **I** | **9** | (nbd)Rh(acac) | THF |
| **L** | **11** | Rh-pol | THF |
| **M**[d] | **13** | Rh-pol | THF |

[a] THF-insoluble fraction.
[b] Solvent volume: 13 ml.
[c] Cocatalyst: $NEt_3$ ($NEt_3$/cat = 10 : 1).
[d] Reaction temperature, 0 °C.

### Soluble and insoluble fractions

The catalytic procedure followed for the synthesis of PPA leads invariably to materials made up of tetrahydrofuran (THF)-soluble and THF-insoluble fractions.

Insoluble polymers show a bulk structure with cavities and a reduced number of spherical particles still adherent at the surface (Fig. 1a). A second microstructure could also be found (Fig. 1b), where isolated cell-like structures of 4–5 μm

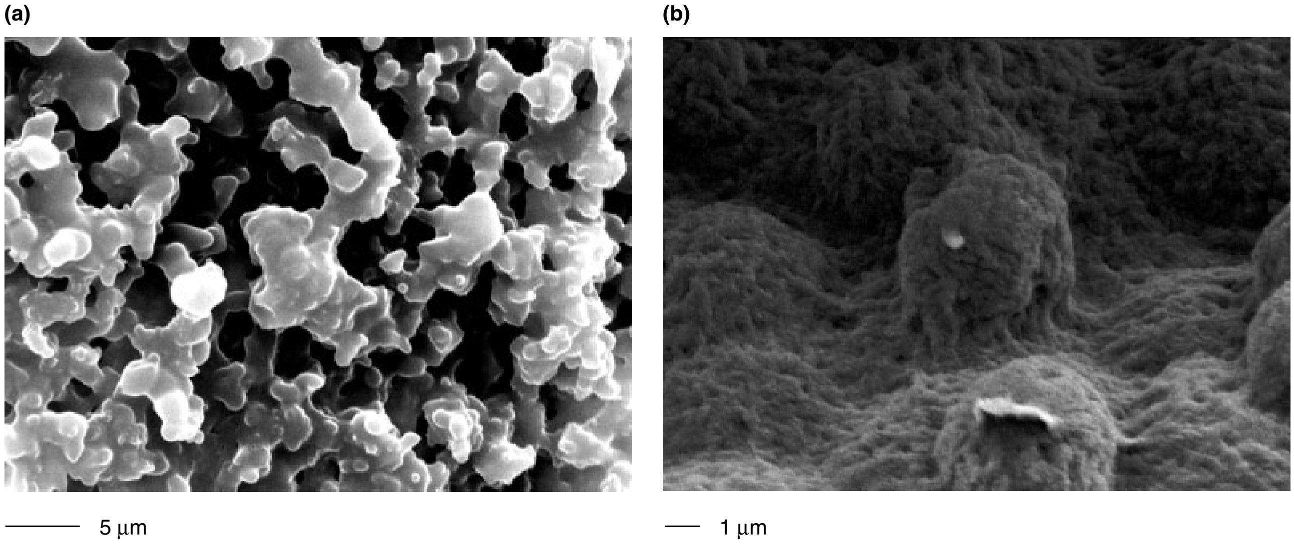

**Figure 1.** SEM micrographs of the THF-insoluble polymer: (a) sample A; (b) sample G.

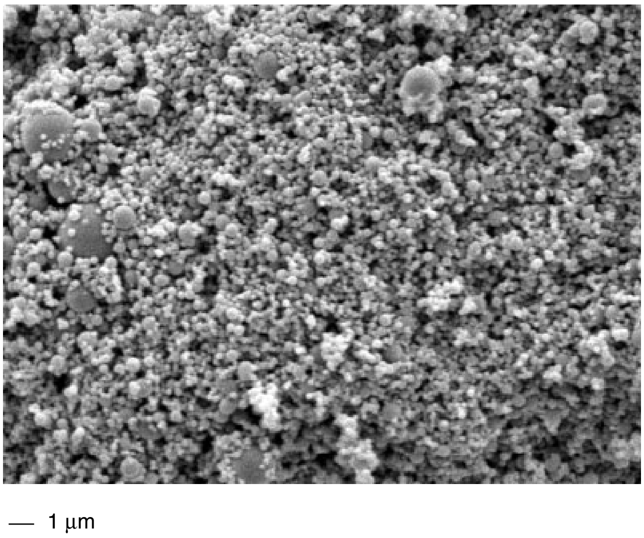

**Figure 2.** SEM micrograph of the THF-soluble sample B.

in size are uniformly dispersed at the polymer surface. Such a structure has already been observed in microsized PPA materials, as reported in Refs 20 and 21. The THF-soluble fraction is a finely dispersed spherical powder of submicrometre size (Fig. 2). The following microstructural characterization refers to the THF-soluble fraction of the PPA obtained, which presented nanosized powders.

## Solvent effect

The effect of the reaction solvent on PPA microstructure can be deduced by comparing samples B, C and D, obtained respectively in THF, benzene and 1,2-dichloroethane (DCE).

SEM observation of sample B (Fig. 2) showed very well dispersed spherical particles with some particles larger in diameter than those of sample C (Fig. 3). Unfortunately, sample C shows an incipient sintering phenomenon, which renders impossible the identification of a number of isolated particles large enough to reproduce statistically the particle size distribution. Such a phenomenon can be probably related to the molecular weight effect, as well as to the less efficient dispersant action of benzene,[23] as evidenced by the higher agglomeration level present in Fig. 3 with respect to Fig. 2.

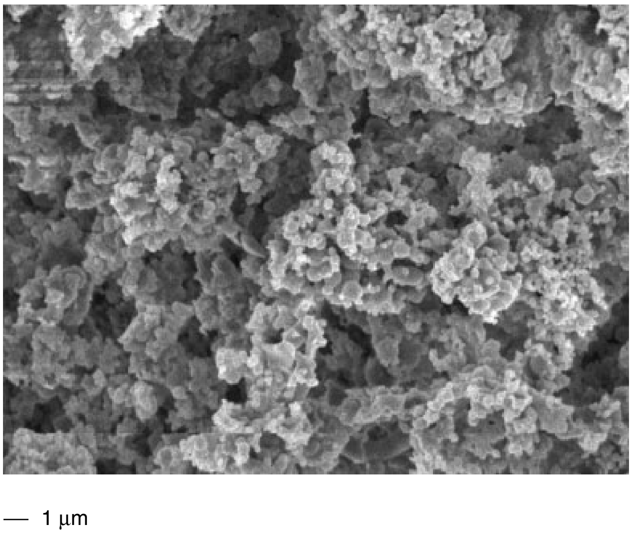

**Figure 3.** SEM micrograph of sample C.

The particle size distribution from sample B, as derived from the image in Fig. 2, is presented in Fig. 4. Both experimental methods used to determine the particle size distribution result in a bimodal distribution, with the first maximum localized at 20 nm and the second being at about 40 nm.

In order to verify the reproducibility of the synthesis and work-up procedures, we examined the morphology of samples D and E, which were prepared at different times. Figure 5a and b shows the SEM micrographs of the as-obtained nanopowders: the average diameter of sample D is higher than in sample B showing a bimodal distribution with the first maximum around 40–50 nm and a second at approximately 110 nm. The sample from the second test (Fig. 5b) shows a higher agglomeration, which hides the typical bimodal distribution (Fig. 6) already observed in samples B and D.

The reaction carried out in DCE allowed the preparation of larger particles (compare Fig. 5 with Figs 2 and 3 or compare Fig. 4 with Fig. 6). As in the case of benzene as reaction medium, a coalescence phenomenon is present.

## Effect of the cocatalyst and of the dilution

Two experimental parameters to be controlled in the catalytic synthesis of PPA are the presence of amine cocatalyst and the volume of the solvent. Figure 7 (sample F) shows the sample obtained in the absence of any cocatalyst, whereas Fig. 8 (sample H) shows the sample obtained in the presence

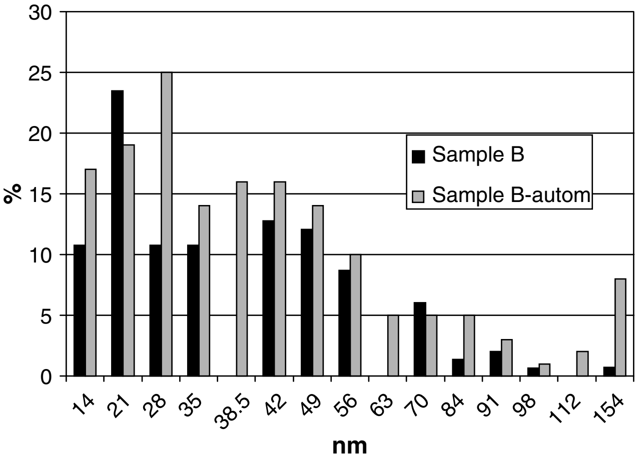

**Figure 4.** Particle size distribution of sample B; image elaboration from Fig. 2.

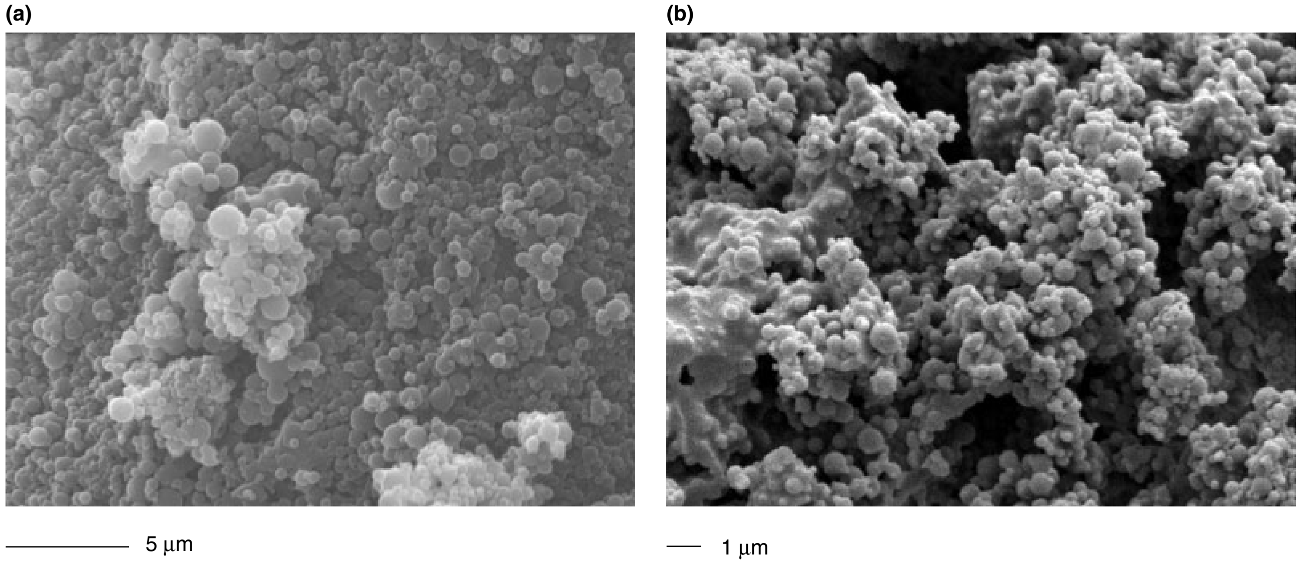

**Figure 5.** SEM micrographs of samples D and E: (pictures a and b show two independent syntheses).

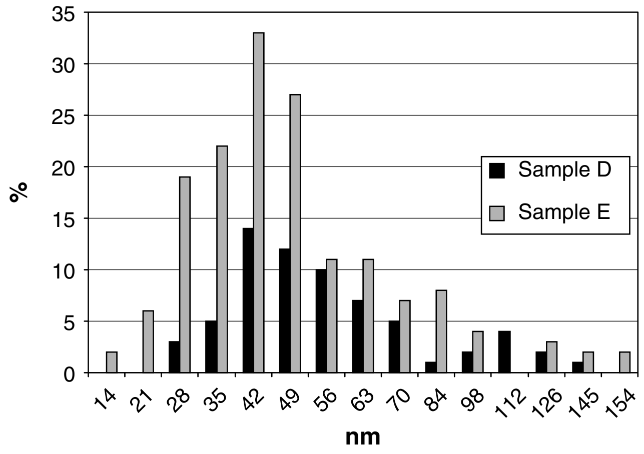

**Figure 6.** Particle size distribution of samples D and E; image elaboration from Fig. 5 (autom.).

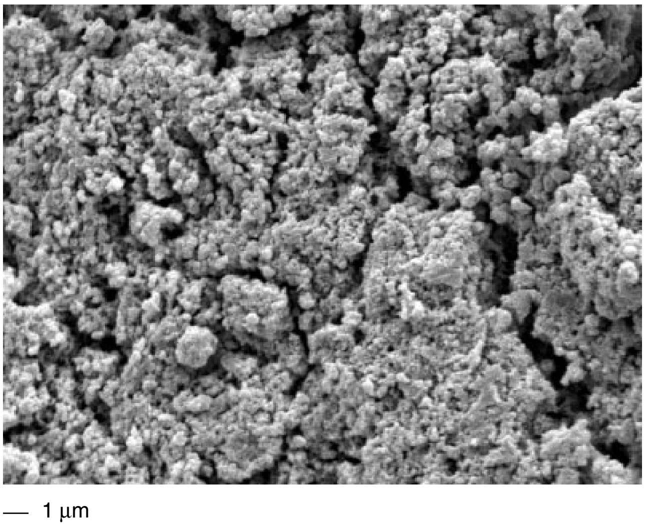

**Figure 7.** SEM micrograph of sample F.

of triethylamine as cocatalyst. Apart from a slight difference in sintering degree, it is apparent that no strong effect of the cocatalyst is visible in the microstructure.

As to the effect of the dilution, an increase of the solvent volume from 5 ml (Fig. 9, sample I) to 13 ml (Fig. 7, sample F) induces the incipient sintering of the nanopowder.

## Effect of the catalyst

When PPA is obtained under homogeneous conditions, no major difference in the morphology is observed in passing from (cod)Rh(AAEMA) to (nbd)Rh(acac) (compare Fig. 2 with Fig. 9). Isolated nanospheres are present in both samples B and I, the second showing a narrower particle size distribution shifted to slightly higher diameters (Fig. 10).

## Optimization of nanosphere particle size distribution

It is known that the matrix may affect the final polymer morphology.[24,25] In order to investigate such an effect in the PPA synthesis we have studied the morphology of PPA obtained using Rh-pol as heterogeneous catalyst. The resulting polymer (sample L) shows the morphology depicted in Fig. 11 and exhibits a narrower nanosphere size distribution with respect to either sample B or I, with the average diameter being intermediate between these two latter samples, as shown in Fig. 12.

In light of the effect of the latest reaction conditions on the particle size distribution, we decided to investigate the

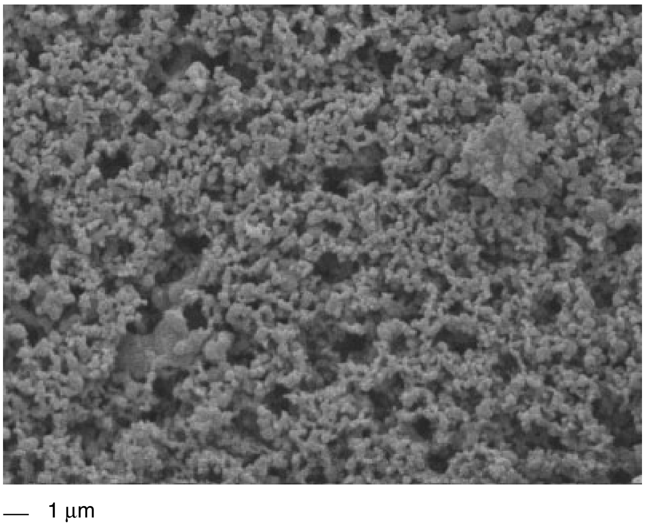

**Figure 8.** SEM micrograph of sample H.

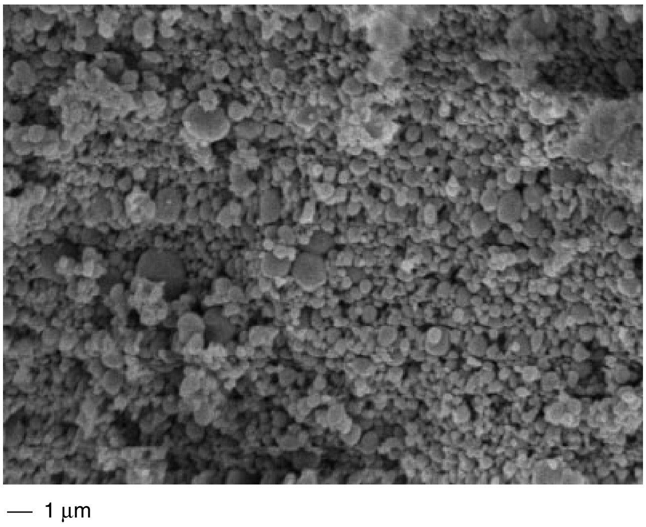

**Figure 9.** SEM micrograph of sample I.

effect of the reaction temperature. An experiment carried out at 0 °C (sample M, Fig. 13) gave the most satisfactory results: an outstandingly narrow particle size distribution, ranging from 30 to 70 nm [average diameter at 47 ± 2 nm (standard deviation)], can be deduced from Fig. 14, which reports data from four independent syntheses. Lowering the reaction temperature seems to accelerate nucleation, as if simultaneously formed nuclei grew with same rate to end in spherical particles with very similar diameter size.

It should be remembered that the isolation procedure of the polymer also plays a role in the final morphology. When PPA was isolated by pouring its chloroform solution into a beaker containing stirred methanol (instead of adding methanol to the chloroform solution), sponge-like samples were obtained instead of nanopowders.

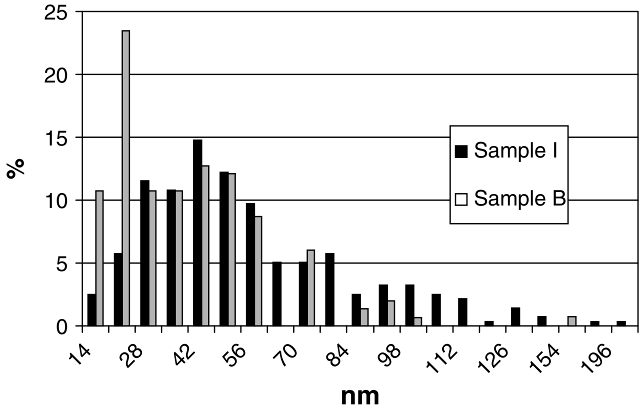

**Figure 10.** Comparison of particle size distribution of samples B and I.

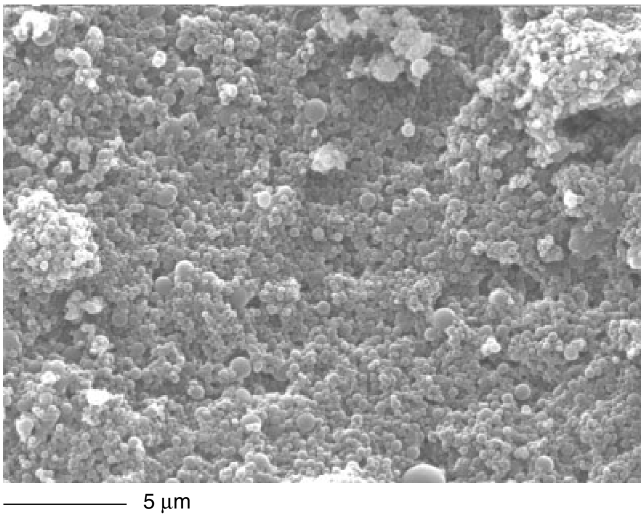

**Figure 11.** SEM micrograph of sample L.

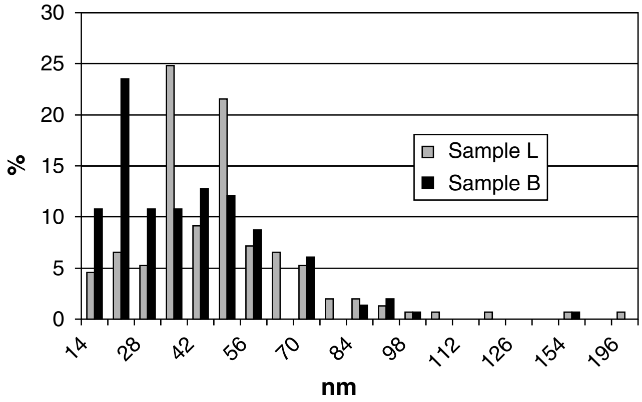

**Figure 12.** Comparison of particle size distribution of samples L and sample B; image elaboration from Figs 2 and 11.

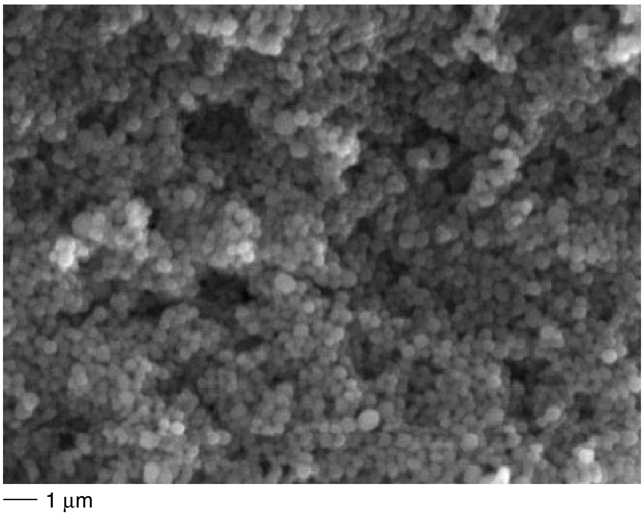

**Figure 13.** SEM micrograph of sample M.

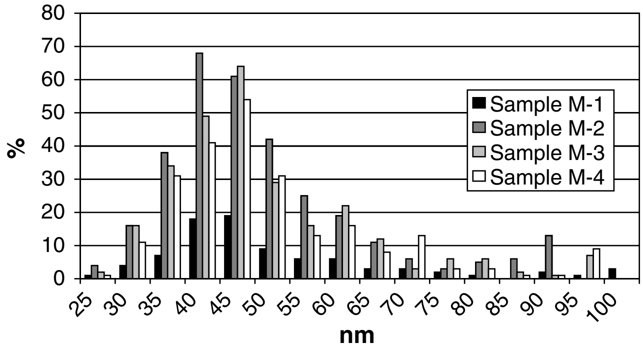

**Figure 14.** Particle size distribution of four different replicates of sample M.

Finally, the ageing study performed on sample M revealed that, after a time lag of 2 years, the particles extracted from the test tube in which they were kept in air at room temperature showed no changes in morphology or agglomeration degree, which is different from what has been reported for free-standing PPA films.[20,21] This difference can be ascribed to: (i) the more stable geometry of the spheres/particles compared with a layer structure; (ii) the lower metal content in the final products ensured by the isolation procedure.

## CONCLUSIONS

SEM was used to carry out a systematic investigation of the morphology of PPA obtained by catalytic rhodium(I) polymerization. The THF-soluble fraction of the polymers exhibited a spherical morphology of submicrometre size. Carrying out the polymerization of phenylacetylene in THF with a $\beta$-ketoesterate rhodium(I) complex led to a bimodal dispersion of nanospherical morphology centred at 20 and 40 nm. The morphology of the final polymer is strictly dependent on the solvent in which the polymerization is carried out: in benzene or DCE the size distribution of the nanospheres is centred at higher values and exhibits incipient sintering. Carrying out the polymerization using a heterogeneous rhodium(I) catalyst and at 0 °C has the effect of lowering the particle size and narrowing its distribution. The nanospherical PPA morphology is reproducible and stable over time.

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