Morphological study of poly(phenylacetylene) films, prepared with Rh(I) catalysts, from scanning microscopy investigations

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The morphological evolution of as-grown poly(phenylacetylene) (PPA) free standing films has been studied. Investigations performed by scanning electron microscopy show that the freshly prepared PPA films exhibit a glass-like morphology which subsequently evolves into a microsphere structure. After ageing for 3 months at room temperature, PPA films reach a stable enamel-like phase. The chemical structure of the Rh(I) catalysts does not appear to influence the morphology of PPA. However, different catalysts yield different rates of morphological evolution.

(Keywords: morphology; poly(phenylacetylene); films; scanning electron microscopy)

INTRODUCTION

Morphological information on polymeric materials is important for the understanding of mechanical properties[1], crystallization, phase separation, chemico-physical processes involving thermodynamic parameters[2,3] and electrical conductivity[4]. In the field of organic π-conjugated polymers, morphological studies give an insight into the ordering or degree of crystallinity of the polymeric fibres which are believed to be responsible, upon stretch alignment, for improvement in electrical conductivity[4–7].

Many elegant studies have been reported concerning the morphology of the final state of the synthesized materials[4–9]. Little emphasis has been placed, as far as we know, on the investigation of the intermediate states of the processes which subsequently develop into the stable final phase.

In this paper, results concerning morphological variations at the surface and in the bulk for poly(phenylacetylene) (PPA) samples prepared from different Rh(I) catalysts, will be presented. An attempt to explain the process which leads to the stable phase of PPA films will also be reported.

EXPERIMENTAL

Synthesis

PPA was prepared by the catalytic reaction of phenylacetylene in the presence of the following Rh(I) catalysts: $[Rh_2(cod)_2(im)_2(imH)]PF_6$, $[Rh(cod)(imH)Cl]$, $[Rh(cod)(mid)_2]PF_6$, $[Rh(cod)(imH)_2]BF_4$ and $[Rh(cod)(im)]_3$ (hereafter referred to as A, B, C, D and E, respectively), where cod = *cis,cis*-cyclo-octadiene, im = imidazolate = $C_3H_3N_2$, imH = imidazole = $C_3H_4N_2$ and mid = *N*-methylimidazole.

The polymerization reactions were performed in bulk or in the presence of CH_2Cl_2 as solvent at room temperature following a procedure previously reported[10].

The elemental analysis was in good agreement with calculated values. For C_8H_6(%): calc., C = 94.08, H = 5.92; found, C = 94.20, H = 6.09. Average molecular

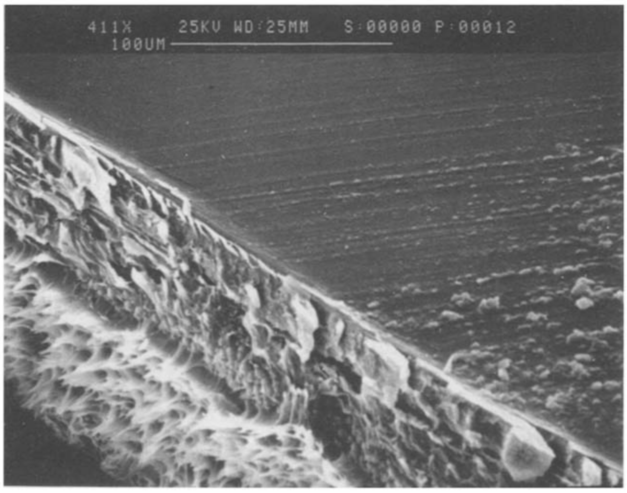

Figure 1 Glass-like phase of freshly prepared PPA-A

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weights, as determined using a Knauer model 11 osmometer in $CHCl_3$ at 300 K, ranged from 10000 to 20000 a.m.u.

Morphological investigations

A scanning electron microscope (Cambridge) was used to observe the PPA films. Before analysis the samples were coated by gold sputtering because they were not conductive. Observations were carried out under the same operating conditions at 20 keV accelerating potential of the tungsten filament. For each compound, investigations either of the air-exposed surface or of the bulk film fracture edges were performed.

First we considered areas at similar magnifications (~ × 1000) for comparison. Likewise, the bulk was also observed at the same order of magnification. In several cases only micrographs of particular magnifications are reported to display particular structures.

RESULTS AND DISCUSSION

We have investigated the morphology of samples prepared with different Rh(I) catalysts. The films were prepared in the presence of Rh(I) imidazole complexes with different chemical structures, that is mono-, di- and trinuclear compounds containing imidazole or bridge-bonded

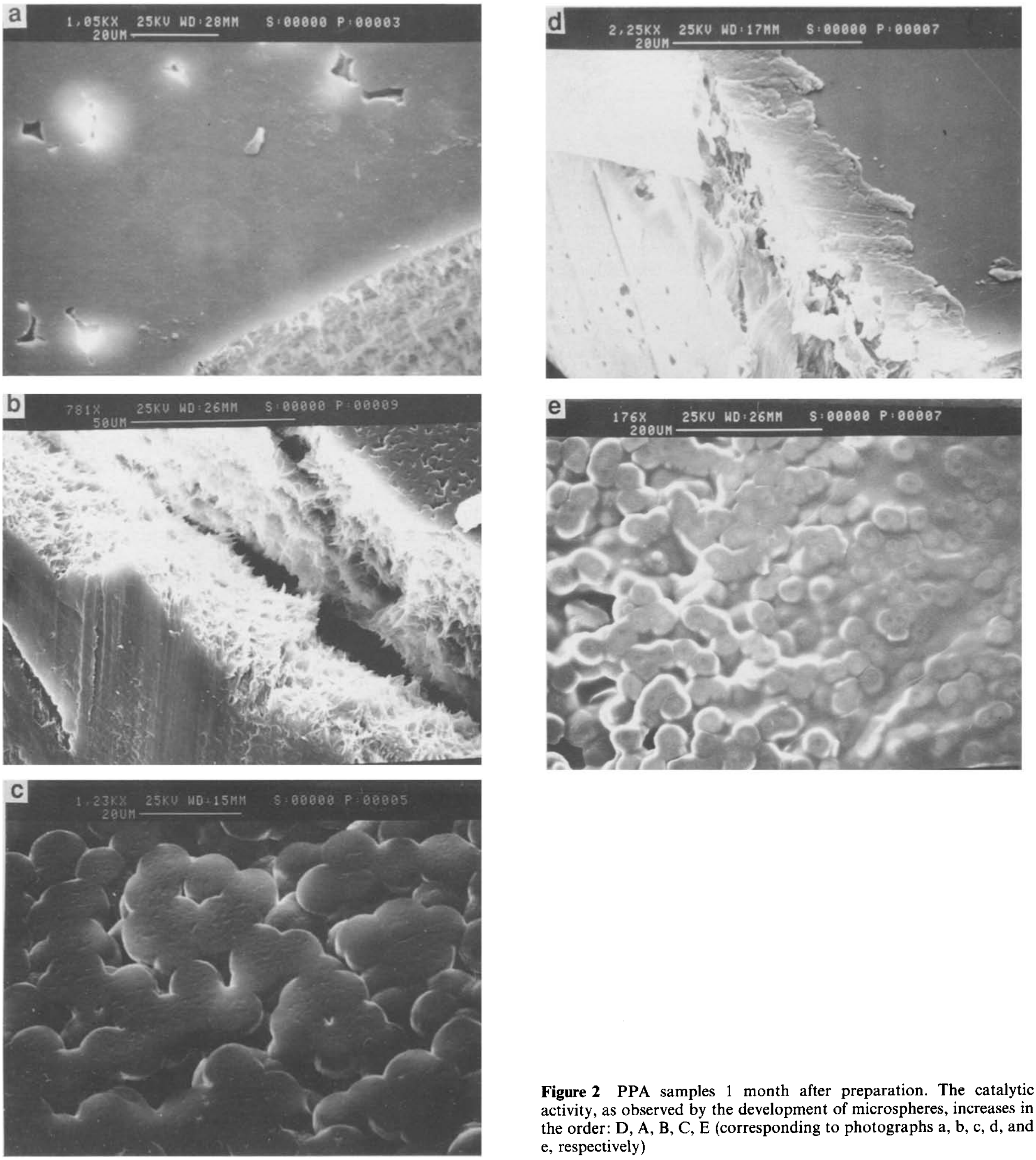

Figure 2 PPA samples 1 month after preparation. The catalytic activity, as observed by the development of microspheres, increases in the order: D, A, B, C, E (corresponding to photographs a, b, c, d, and e, respectively)

imidazolato ligands[10]. The samples will from now on be referred to as PPA-A, PPA-B, PPA-C, PPA-D and PPA-E following the notation used for the catalysts in the Experimental section.

We expected to find a difference in the PPA film morphology as was observed, for example, for polyacetylene prepared in the presence of different Ziegler catalysts[5,6] or polypyrrole electrochemically synthesized in the presence of various solvents[7].

SEM shows no evidence of any influence of the chemical nature of the catalyst on the morphology of PPA. However, a variation in morphology was observed, which depended on the 'ageing' time from the synthesis of the as-grown free standing films. At the beginning of the reaction the polymer shows a glass-like phase where the microfibrils grow randomly oriented around the catalyst grains and develop microspheres (see *Figure 1*).

The growth rate of the microspheres is dependent on catalyst activity. In fact, samples of freshly prepared films show essentially a continuous glass-like matrix structure with a more or less enhanced texture of spheres. This behaviour may be due to the polymerization procedure[10] which leads to films inside containing catalyst (catalyst/monomer molar ratio = 1/1000) that retains its activity, leading to variations in PPA morphology. Evidence of this effect is shown in photographs of PPA prepared with different catalysts and taken after the same time period (~1 month from preparation). An evolution of morphology (*Figure 2*) can be seen. *Figure 2* shows that every PPA sample can evolve at a different rate from a glass-like morphology to a texture of microspheres. We suggest a catalytic activity trend increasing in the order: D, A, B, C, E. This can be seen by observing the development of microspheres (see *Figure 2*).

The evolution goes on with time until the morphology is complete when every prepared sample achieves a stable enamel-like appearance in the surface and in the bulk. This has been tested by analysing the samples during a storage period of 3 months at room temperature. *Figure 3* is an example of the stable enamel phase for PPA-E; the other compounds are not shown because they have very similar morphology.

In order to investigate the evolution of the morphology until the stable phase (enamel) was reached we sped up the catalytic process by increasing the temperature. All the samples were thermally treated up to 393 K, which was the upper limit because no chemico-physical variations occur as shown by t.g.a. In particular, no fusion effect is involved in this process because the heating temperature is far below the melting point of all the samples (m.p. range 493–503 K). Only the results for PPA-A and PPA-C are reported here; these are representative of the phase where microsphere morphology is present. Photographs of the two selected PPAs were obtained after annealing at temperatures of 333, 363 and 393 K for different times varying from 2 to 20 h. In the samples annealed for 2 h at 333 K it is possible to observe the development of microspheres from the glass-like phase (*Figure 4*). In the following step (2 h at 363 K), entanglement of the microspheres which contain randomly oriented microfibrils is readily observed (*Figure 5*). In one area of the micrograph (lower left-hand corner) contact between microspheres occurring through the microfibrils is seen.

This kind of morphology resembles the gel models proposed by Callister *et al.*[2], who discussed the phase separation and vitrification of non-crystalline polymers and in particular polystyrene. It is interesting to note that the authors associated the morphology of polymer at low molecular weight, as in our case, with a structure consisting of distinct spheres in loosely packed contact. As far as we know, the morphology of organic polymers with π-conjugated C=C bonds in the backbone has never

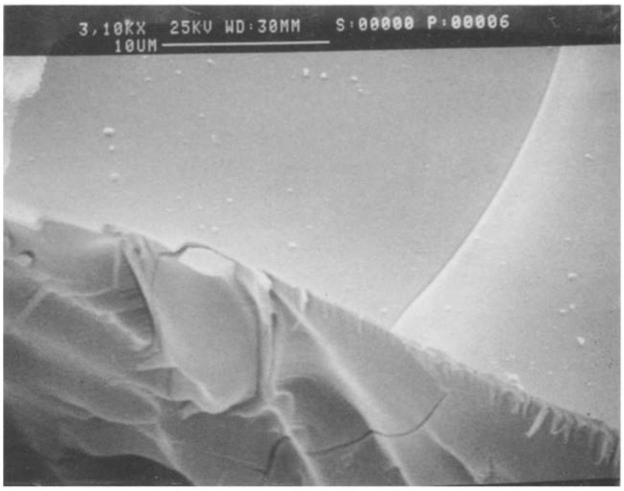

Figure 3 Stable enamel phase of PPA-E after storage for 3 months at room temperature

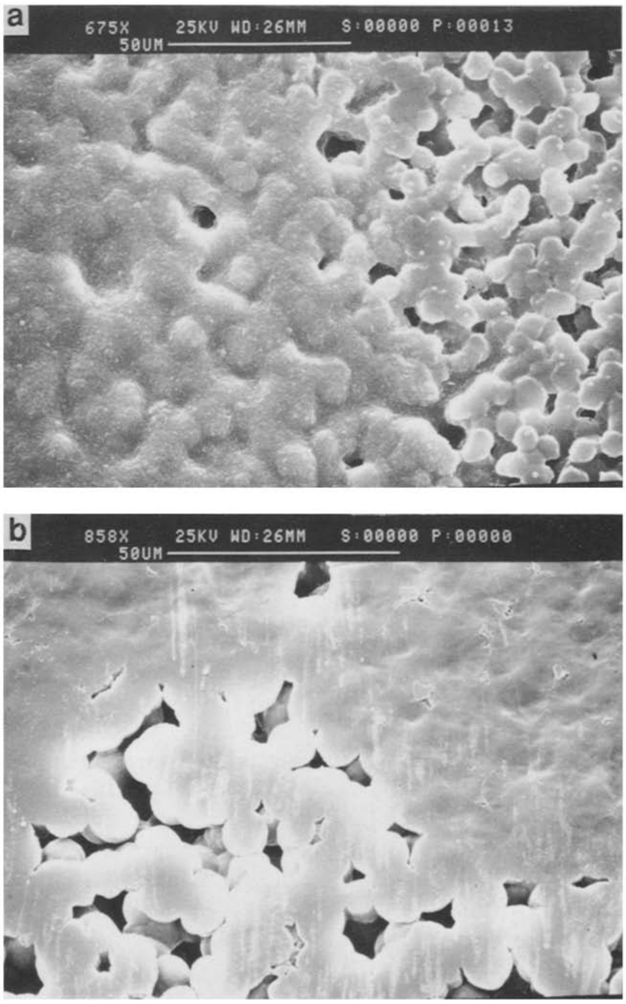

Figure 4 Development of microspheres from the glass-like phase in samples annealed for 2 h at 333 K: (a) PPA-A; (b) PPA-C

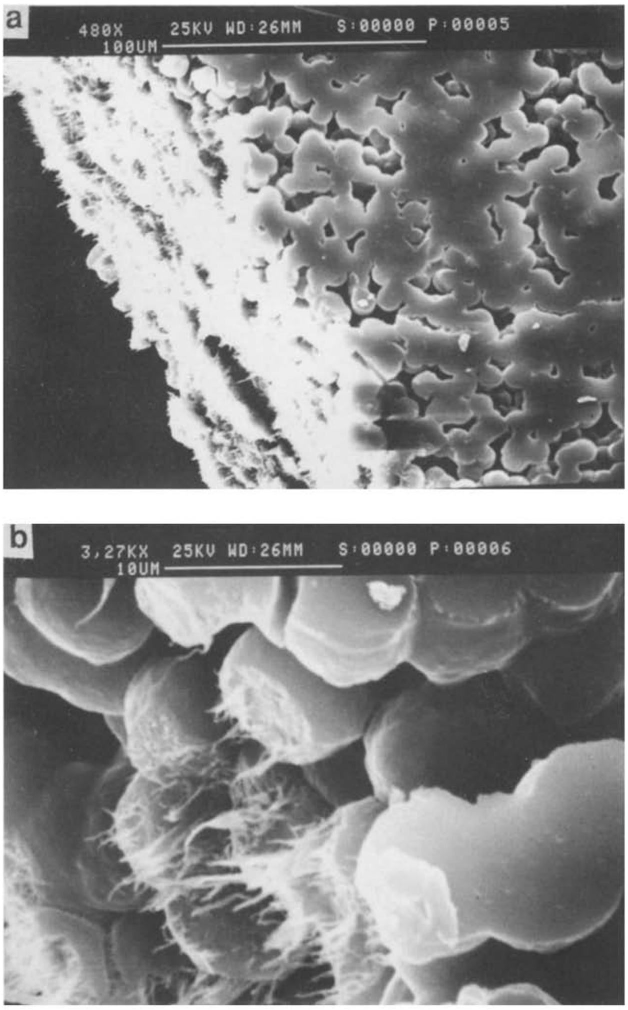

Figure 5 Morphology achieved after annealing for 2 h at 363 K. The entanglement of microspheres containing fibrils is shown: (a) PPA-A; (b) PPA-C

Figure 6 Enamel-like morphology of PPA-A after annealing for 20 h at 393 K

Figure 7 Enamel-like morphology of PPA-C showing evidence of the 'unwinding' of the microspheres

been associated with a gel-type matrix. Perhaps this is because these polymers have not been observed in the course of the catalyst working in the solid state.

Upon further annealing for 20 h at 393 K, the final enamel-like morphology, which comes from enchainment of the microfibrils, is shown (*Figure 6*). This phenomenon is evident in the fracture in the middle of the micrograph where the elongated fibrils appear. This can be the effect of the 'unwinding' of the microspheres as the features on the surface observed in *Figure 7* reveal.

CONCLUSIONS

The morphological modifications of PPA free standing films have been studied considering that Rh complexes could influence the kinetics of formation of the stable phase which is achieved after a storage period of ~3 months at room temperature. A microsphere structure was observed during the time which leads to a stable final state of polymerization. The existence of microfibrils is demonstrated and also their arrangement into microspheres. From these results, the rate of change of morphology has been suggested to depend on the catalysts used in the polymerization reaction.

These results may be considered an important preliminary step in the investigation of PPA films because they show the existence of microfibrils in the polymer. The study reported here suggests that stretching should be performed before the microsphere gel-like morphology is reached. Therefore an extension of our project will be to apply this kind of investigation to stretched PPA samples which should exhibit alignment of the fibrils, the presence of which is expected to improve the electrical properties of PPA.

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