

INORGANIC NANOCLUSTERS IN ORGANIC GLASSES

- NOVEL MATERIALS FOR ELECTRO-OPTICAL APPLICATIONS

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ABSTRACT

Polymer glasses which contain regularly arranged ultrasmall inorganic crystallites or clusters of CdS, CoS, NiS, ZnS have been prepared from functionalized diblock copolymers. Size and surface structure dependent variation of the ionization or redox potential respectively the band gap energy of the semiconductor particles in the polymeric glasses can be exploited to control photochemical processes and optical properties. The combination of anorganic and organic compounds provides a simple route to highly ordered, stable and processable materials with a wide range of properties. Regular arrangement of the clusters in a defined supermolecular lattice might be used for tailoring electromagnetic interactions and might provide new materials for infrared and microwave applications.

INTRODUCTION

The properties of solids can be totally different from those of constituent atoms or molecules. Physical and chemical characteristics of molecular aggregates can change significantly at the transition from molecular to bulk state properties when they approach sizes of a few nm [1]. This work is directed towards the preparation of polymer glasses containing regularly arranged inorganic crystallites which are too small to have bulk like electronic wave functions even they exhibit bulk like crystal structure. To discriminate this nanoparticles from normal crystallites of larger size, they will be denoted as nanoclusters. Thus, the inorganic clusters described here, must not be confused with molecular clusters which have been synthesized so successfully by inorganic chemists during the last decades.

Organic polymers which contain small inorganic clusters have been prepared first by milling poly(ethylen-co-methylmethacrylic acid) with various metal acetates at 160°C. The resulting transition metal ionomer was treated with H₂S in order to precipitate the corresponding sulfides, e.g. PbS, as small clusters in the glassy polymer [2-4]. In this way, PbS crystallites or clusters with an average diameter of 2.5 nm could be prepared. The band gap energy changed from 0,37 eV of bulk PbS to 2.1 eV [2]. The materials show promising third order non-linear optical properties. Preparation of inorganic/organic composites with diblock copolymers should be equally simple, however, allows also a control of domain size and distances as well as the salt content in the domains.

EXPERIMENTAL METHODS

Diblock copolymers of polystyrene (PS) and poly-2-vinylpyridine (P2VP) were prepared with narrow molecular weight distribution by sequential anionic polymerization. Films were prepared by solvent evaporation with the corresponding metal salt. Complex formation with vinylpyridine units allowed to concentrate the transition metal salt as CuAc_2 , CuCl_2 , CdAc_2 , CdCl_2 , CoCl_2 , NiCl_2 , ZnCl_2 , AgNO_3 and AgBF_4 in the P2VP domains. The subsequent treatment of the materials with gaseous H_2S was used to precipitate the corresponding metal sulfides. The morphology was observed by transmission electron microscopy (TEM) using a Zeiss CEM 902. Element specific images (ESI) and electron energy loss spectra (EELS) have been recorded with an integrated electron energy loss spectrometer [5]. The quantum size effect of semiconductor clusters was measured by UV-VIS spectroscopy of films.

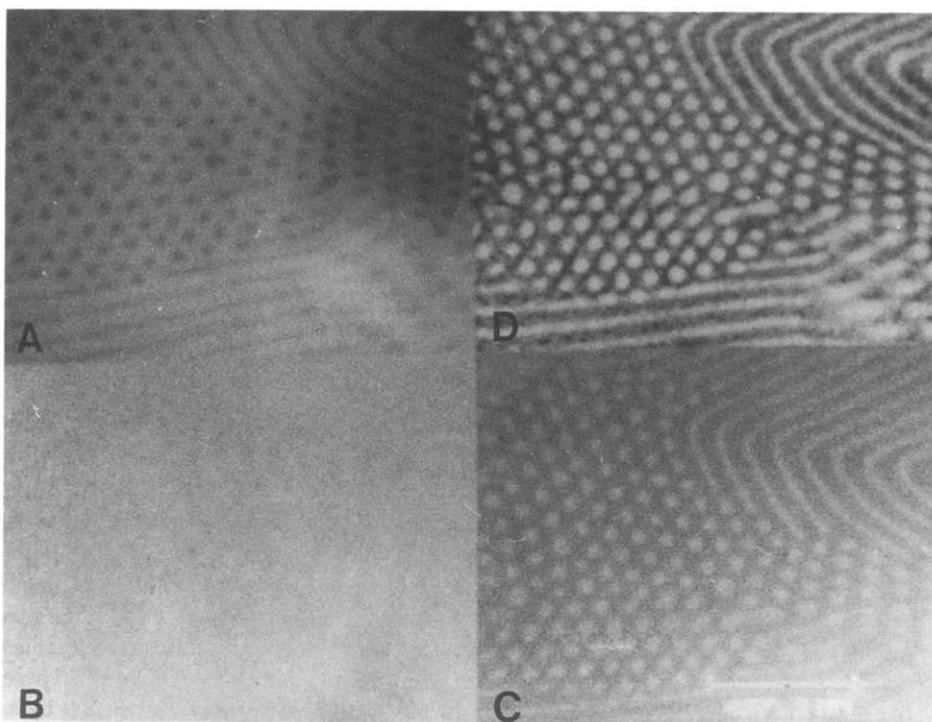


Fig. 1. TEM images using a Zeiss CEM 902
 PS(307)-b-P2VP(76) cast together with CoCl_2 from DMF at 100°C
 ($0,55\text{mol CoCl}_2/\text{mol VP}$); treated with H_2S at 25°C
 A) $\Delta E = 0\text{ eV}$ (elastic brightfield image)
 B) $\Delta E = 780\text{ eV}$ ($< \text{Co-L}_{2,3}$ ionization edge)
 C) $\Delta E = 820\text{ eV}$ ($> \text{Co-L}_{2,3}$ ionization edge)
 D) Cobalt image

(the numbers in brackets give the numbers of monomer units)

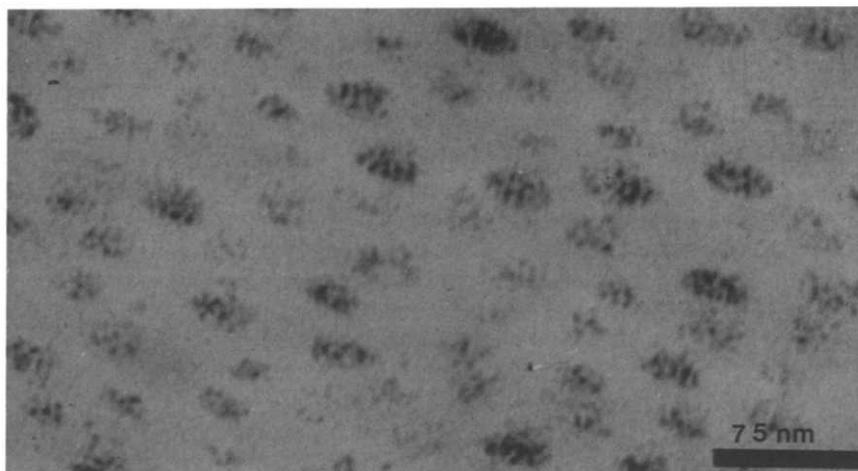


Fig. 2. TEM elastic bright-field image using a Zeiss CEM 902 PS(307)-b-P2VP(76) cast from DMF with CdAc_2 (0.55 mol/mol VP); treated with H_2S at 25°C

RESULTS

The contrast between the phases of a block copolymer of PS and P2VP is too weak to image the phase separation without staining. But an excellent contrast was observed when the transition metal salts were added. Dark P2VP domains in the bright-field images present a first proof for the successful incorporation of the salts into the P2VP domains. Conventional ultramicrotoming preparation of ultrathin sections by floating off from the knife edge was not possible because water dissolved the salts. In comparison to samples without transition metal salts a change of the morphology can be observed, which might be explained by a different coordination behaviour. Partial reduction to $\text{Ag}(0)$ and formation of relatively large $\text{Ag}(0)$ particles were observed. In the case of copper, a reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ caused degradation of P2VP. Upon preparation of Cu-samples at lower temperature, the reduction was less and a morphology similar to other salt polymer systems was observed. Smaller quantities of metal salts yielded smaller VP domains. Therefore the morphology of block copolymers can be manipulated also by the amount of the salt used. Limits are given by the morphology of block copolymer without salt and that of samples when maximal complexation was achieved. As in ideal models, the morphology of these block-copolymer salt systems is a function of the domains after complexation.

The formation of transition metal sulfides was indicated by changes in the colour of the polymer films. In this case the ultrathin sections for TEM could be prepared in contact with water due to the reduced solubility. No dramatical changes in morphology could be observed after the treatment with H_2S . Sulfide formation was proved by element specific images (ESI) and by element energy loss spectroscopy (EELS). In Fig. 1. Picture A shows an elastic brightfield image, B and C are images from inelastically scattered electrons beyond and on the $\text{Co-L}_{2,3}$ ionization edge. The element specific image D (B subtracted from C), in which brightness is proportional to the element concentration, shows that the VP domains contain cobalt with high selectivity. Nanometer size transition metal sulfides in the P2VP domains can be shown by darkfield images and by brightfield images (Fig. 2) and 3nm diameter CdS particles can be recognized in the P2VP domains.

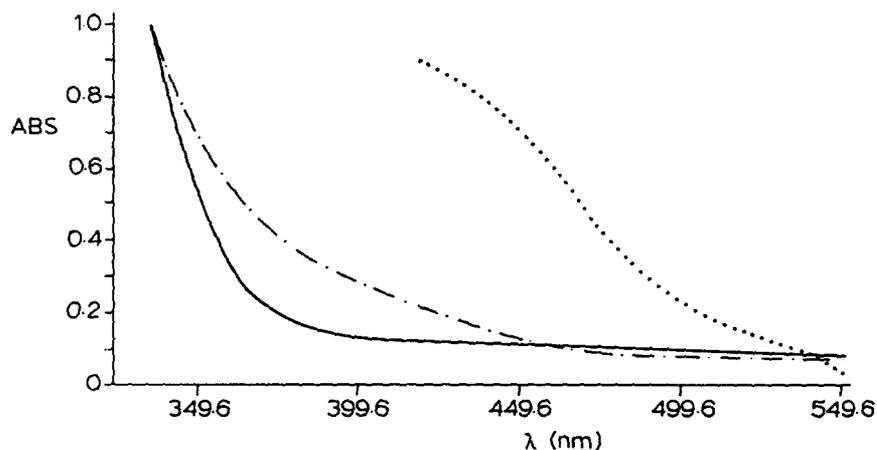


Fig. 3. UV-VIS absorptions spectras
 --- PS(307)-b-P2VP(76) cast from DMF with CdCl_2
 (0,55 mol/mol VP); treated with H_2S
 - - - PS(384)-b-P2VP(11) cast from DMF with CdCl_2
 (0,55 mol/mol VP); treated with H_2S
 ... Bulk film of CdCl_2 cast from DMF
 and treated with H_2S

Table 1

UV/VIS absorption edge and corresponding particle diameter for CdS [6]

diameter	λ threshold
bulk	490 nm
5,7 nm	461 nm
3,9 nm	416 nm
3,0 nm	367 nm
2,1 nm	286 nm

UV/VIS absorption spectroscopy confirm the particle size (Fig. 3). The band gap energy and the correlated particle size can be calculated from the absorption edge. Similar results could be found for ZnS particles. The existence of the smallest crystallites in the polymer with greatest VP domains can be explained by an increasing segment mobility with decreasing chain length. It has been expected that crystal growth is controlled by the hindered diffusion of small crystallites through the polymer matrix. This was verified by annealing experiments. A considerable increase in crystallite size was observed.

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