Interconversion of ZnF_2 and ZnS Nanoclusters within Spherical Microdomains in Block Copolymer Films

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We recently demonstrated the synthesis of well-defined organometallic block copolymers[1-7] and their self-assembly into films exhibiting specific morphologies. The morphology and the size of metal-containing microdomains depend on the copolymer composition and block molecular weights.[4] Control over size of synthesized clusters in the polymer matrix should be optimal for the case of spherical[7] microdomains, which may be viewed as nanoscale reactors into which chemical reagents can be loaded and subsequent chemistry carried out.

In this report, we make use of block copolymers to produce stable clusters and subsequently to interconvert reversibly between one type of cluster and another. This methodology provides a new approach to synthesis of clusters. We will use interconversion of ZnF_2 and ZnS to illustrate the concept. The clusters were synthesized in poly[bTAN] domains[2] within poly[MTD] matrix, where bTAN = 2,3-*trans*-bis(*tert*-butylamidomethyl)norborn-5-ene[2] and MTD = methyltetracyclododecene. The polymers were synthesized by sequential addition of the monomers to $W(CH^tBu)(NAr)(O^tBU)_2$ initiator[8] in benzene with MTD added first and $[bTAN(ZnPh)_2]$ second.[2] As a typical example, the procedure to prepare a $[bTAN(ZnPh)_2]_{40}/[MTD]_{600}$ diblock copolymer is described here (see Scheme I). A solution of 3.2 mg (5.5×10^{-6} mol) of catalyst in 0.32 mL of benzene was added to a stirring solution of 582 mg (3.3×10^{-3} mol) of MTD in 10 ml of benzene. After ~15 min, 1.9 mL of reaction mixture was withdrawn, and the reaction in the aliquot was terminated with excess of benzaldehyde. The homopolymer product was characterized by GPC. A solution of 100 mg (1.85×10^{-4} mol) of $bTAN(ZnPh)_2$ in 3.5 mL of benzene was added to the remaining reaction solution. After about 40 min, 1.82 μL (1.9×10^{-5} mol) of pentadiene was added to terminate the reaction. The solution was then stirred for another 1 h to ensure the completion of the termination step. The benzene solution of the copolymer (~3 wt %) was dried slowly in a nitrogen glovebox over 7 days, resulting in *ca.* 0.5-mm thick films.

Zinc fluoride clusters were produced by exposing the films to hydrogen fluoride–pyridine (HF–Py) complex (Aldrich) containing 70% HF; the film was suspended above ~2 mL of HF–Py complex for 6 h, removed from the glovebox, thoroughly washed with acetone and distilled water, and dried under vacuum for 24 h. Transmission electron microscopy (TEM) indicated the formation of ZnF_2 clusters within the spherical microdomains.

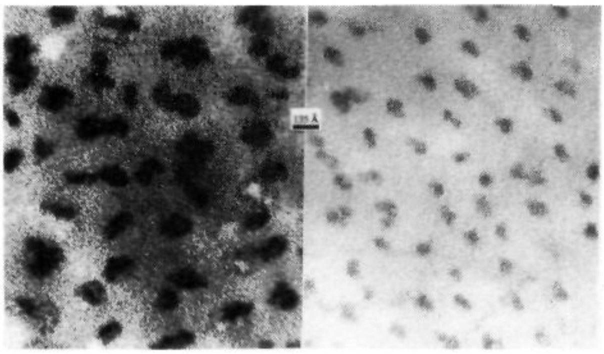
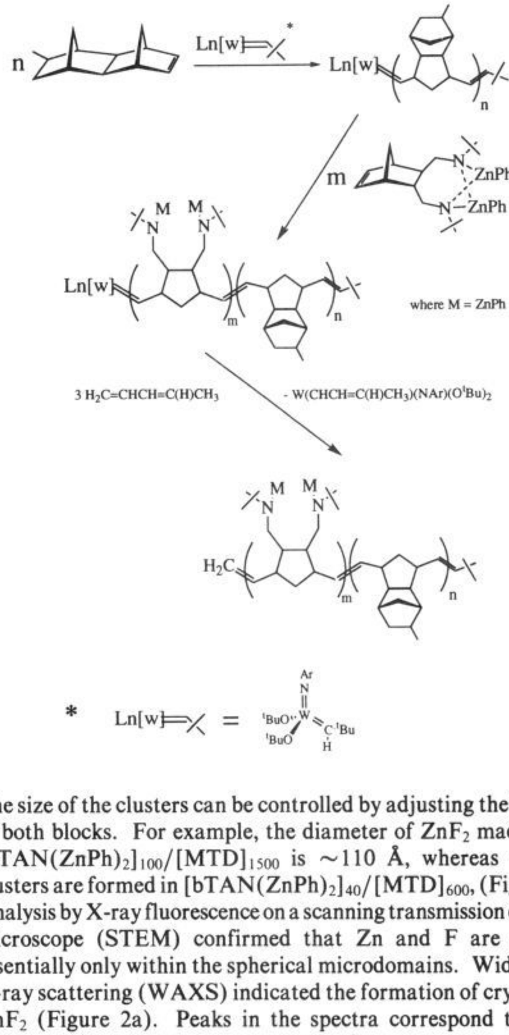


Figure 1. Electron micrographs of ZnF_2 made from $[bTAN(ZnPh)_2]_{100}/[MTD]_{1500}$ (left) and $[bTAN(ZnPh)_2]_{40}/[MTD]_{600}$ (right).

Scheme I



The size of the clusters can be controlled by adjusting the lengths of both blocks. For example, the diameter of ZnF_2 made from $[bTAN(ZnPh)_2]_{100}/[MTD]_{1500}$ is ~110 Å, whereas ~60-Å clusters are formed in $[bTAN(ZnPh)_2]_{40}/[MTD]_{600}$, (Figure 1). Analysis by X-ray fluorescence on a scanning transmission electron microscope (STEM) confirmed that Zn and F are present essentially only within the spherical microdomains. Wide-angle X-ray scattering (WAXS) indicated the formation of crystalline ZnF_2 (Figure 2a). Peaks in the spectra correspond to those expected for bulk ZnF_2 in the rutile form[9] ($2\theta \sim 16°$ is amorphous scattering from the poly[MTD]).

Consider the reaction for the conversion of ZnS to ZnF_2:

$$ZnS + 2HF \rightleftharpoons ZnF_2 + H_2S$$

Values[10] of enthalpy and entropy of formation for the forward reaction indicate that the free energy change is negative (about –2.8 kcal/mol) and formation of ZnF_2 is favored at room

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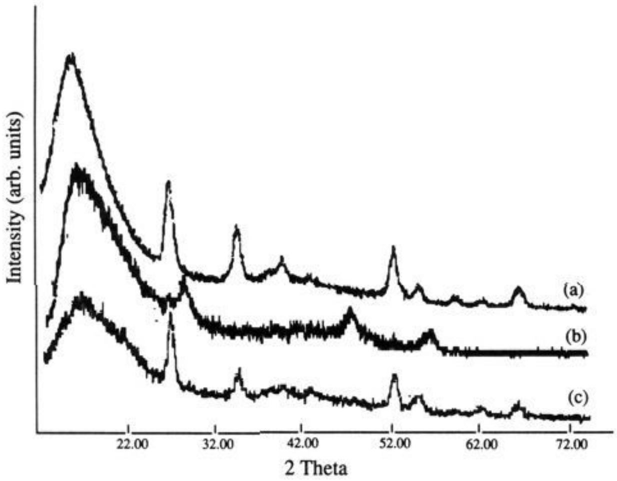

Figure 2. WAXS spectra of (a) ZnF_2 obtained after $[bTAN(ZnPh)_2]_{40}/[MTD]_{600}$ was treated with HF–Py complex at room temperature; (b) ZnS from the conversion of the ZnF_2 treated with H_2S at 140 °C; and (c) ZnF_2 from the ZnS of spectrum b treated with HF–Py at room temperature.

temperature. However, above ~120 °C the net free energy change becomes positive and ZnS is more stable than ZnF_2. Therefore, it is possible to synthesize ZnS by treating ZnF_2 with H_2S at high temperature or to do the reverse conversion by exposing ZnS to HF at room temperature. Figure 2 shows WAXS spectra for the clusters made by this interconversion process. Our film containing ZnF_2 clusters (Figure 2a) within poly[MTD] matrix was loaded into a glass bomb reactor equipped with a Teflon-brand stopcock. The reactor was then evacuated, refilled with H_2S, and placed in a constant temperature oil bath. These ZnF_2 clusters were completely unreactive to H_2S at room temperature even after 96 h. However, on increasing the temperature to 140 °C for 12 h, the reaction proceeded smoothly and completely to yield ZnS clusters, as confirmed by X-ray diffraction (Figure 2b). Three peaks at $2\theta = 28.33°, 46.89°$, and 55.58° correspond to periodic lattice spacings (d) of 3.15, 1.90, and 1.66 Å. The broad peaks make it difficult to determine whether our ZnS clusters are in the cubic or the hexagonal crystalline form[9] or whether they contain a periodic mixture of crystalline features, i.e., the random polytype structure proposed[11] for CdSe clusters. Further treatment of the same film with HF–Py at room temperature resulted in the conversion of ZnS to ZnF_2 (Figure 2c).

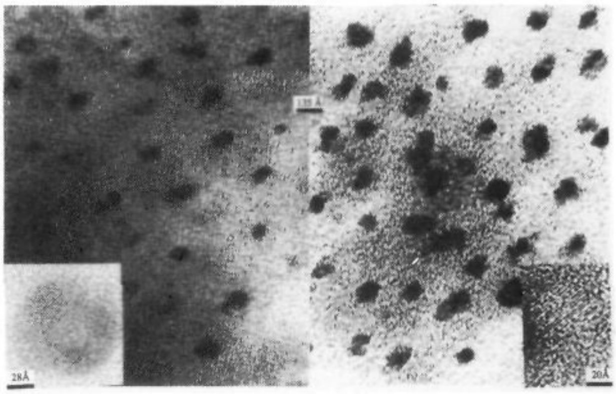

Figure 3. Electron micrographs of ZnF_2 made from $[bTAN(ZnPh)_2]_{80}/[MTD]_{1200}$ (left) and ZnS from the conversion of the ZnF_2 (right). Insets are high-resolution TEM micrographs for ZnF_2 and ZnS, respectively.

In all of these manipulations, the clusters were confined within the domains and there is no evidence of migration of either ZnS or ZnF_2 between neighboring domains. Investigation of the films by small-angle X-ray scattering (SAXS) and by TEM showed that the morphology was preserved. The TEM micrographs for the conversion of ZnF_2 to ZnS are shown in Figure 3. Figure 3a (left) is the micrograph of ZnF_2 made from $[bTAN(ZnPh)_2]_{80}/[MTD]_{1200}$, and Figure 3b is the one for ZnS obtained from the conversion process. Both pictures show dark, roughly spherical clusters confined within the domains. Close examination of both clusters reveals lattice fringes consistent with the results obtained from WAXS.

We conclude that the general approach to carry out a chemical reaction within a nanoscale region of a block copolymer film is feasible. Each domain acts as an isolated reactor. Different kinds of clusters can be synthesized from a given starting material. For example, thermodynamic data[10] indicate that PbS can be synthesized by treating PbF_2 clusters with H_2S at temperatures above 70 °C; for the case of CdF_2/CdS, this interconversion process can be accomplished well below room temperature. This approach has generated ZnS quantum clusters which are superior in quality (WAXS) to other techniques we have employed.[12]

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