Effect of polymer architecture on metal nanoclusters

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Abstract

Synthesis of metal nanoclusters in polymeric media has been shown to yield small clusters with a narrow size distribution. Embedding such clusters in the three-dimensional structures formed by diblock copolymers will allow the development of ordered structures with high optical and magnetic contrast between the different regions. In this paper we investigate the effect of homopolymer and diblock copolymer properties on the cluster size. We find that in homopolymer solutions, the cluster size reaches a minimum at a specific chain molecular weight (MW). In the case of diblock copolymers, the cluster size is set by the MW of the block with the stronger affinity to the metal surface.
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1. Introduction

One of the most unique features of nanostructured materials is the sensitivity of their properties such as chemical activity, mechanical moduli or optical response to the (nano) domain size and its spatial distribution [1–7]. This feature may be utilized to 'tune' the material performance through manipulation of the nanodomain size and spatial distribution. However, due to the strong correlations between domain size and material properties, even a small degree of polydispersity in domain size may affect the material performance.

Recent studies have shown that conducting the synthesis of inorganic nanoclusters in polymeric media (either bulk/melt or solution) yields narrow size and morphology distributions and suppresses cluster flocculation [8–20]. The most important parameter controlling the nanocluster size has been found to

be the polymer chemistry [8–20]. The size of nanoclusters formed in polymeric melts where no solvent is present was shown to be independent of the polymer molecular weight and the inorganic component volume fraction [11]. Clusters formed in polymeric solutions were shown to vary in size as a function of the chain molecular weight or concentration [12]. It has been suggested that the polymer controls the nanocluster size through equilibrium 'capping' [9–12], although recently we have shown that the narrow size distribution may be due to the kinetics of nucleation and growth in polymeric suspensions [21].

Selective doping of diblock copolymer domains with inorganic nanoclusters may be used to obtain spatially ordered nanocomposites with high refractive index contrast between the domains for optoelectronic applications [10,22–29]. We have recently shown that metal nanoclusters synthesized in situ in diblock copolymer matrices selectively partition into the polymeric phase that has a higher affinity for the particles [30]. As a result, in situ synthesis of inorganic nanoparticles in diblock copolymers is a promising method for obtaining spatially ordered, selectively doped nanocomposites.

The goal of this paper is to determine the effect of polymer structure and microdomain formation on the size of metal

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nanoclusters synthesized in situ by comparing clusters formed in homopolymer solutions to those obtained in diblock copolymer suspensions [8−20,31−34]. We focus on the effect of polymer molecular weight, composition and solvent properties on the size and size distribution of the nanoclusters. The metal particles examined are Co nanoclusters, obtained from the decomposition of $Co_2(CO)_8$. The polymeric species include polystyrene (PS) and poly-methyl methacrylate (PMMA) homopolymers, and PS-PMMA diblock copolymers.

2. Experimental

2.1. Materials

Cyclohexanone, chlorobenzene (spectral grade), 2-ethoxy ethanol (spectral grade) and toluene (spectral grade) were purchased from Fisher Scientific and were used without further purification. Block copolymers of PS-*b*-PMMA of varying molecular weights and varying compositions were purchased from Polymer Source Inc.: $PS_{25,300}$-*b*-$PMMA_{25,900}$, $PS_{71,300}$-*b*-$PMMA_{11,200}$, $PS_{101,100}$-*b*-$PMMA_{165,800}$ and $PS_{47,000}$-*b*-$PMMA_{280,000}$, with PDI ranging from 1.04 to 1.06. Homopolymers of PS and PMMA of various molecular weights were purchased from Alfa Aesar, with PDI values ranging from 1.04 to 1.12.

2.2. Synthesis

Forty-five milliliters of 1 wt% PS-*b*-PMMA in cyclohexanone, which is a common good solvent for both the PS and the PMMA blocks, were added to a three-neck reaction flask that had been evacuated and flushed with N_2 prior to solution introduction. Forty-five milliliters of a 1×10^{-2} M solution of $Co_2(CO)_8$ in cyclohexanone was prepared and added to the

same flask under a counter-current N_2 stream. A 1 mL sample of this solution was removed for FTIR analysis. The combined solution had a final concentration of 5×10^{-3} M $Co_2(CO)_8$. The solution was then heated under nitrogen for about 10 h at 90 °C.

This same procedure was followed for the decomposition of $Co_2(CO)_8$ in a solution of PS-*b*-PMMA in toluene, which is a preferential solvent for the PS block, or in 2-ethoxy ethanol, which is a preferential solvent for PMMA. The PS-*b*-PMMA block copolymers used varied in composition as listed in Table 1.

Separately, control experiments were performed with both a solution of PS homopolymer alone ($\overline{M}_w = 13,000-330,000$ g/mol) in toluene, and a solution of PMMA homopolymer alone ($\overline{M}_w = 30,000-350,000$ g/mol) in chlorobenzene. Another control experiment was performed with solutions of PMMA homopolymer alone ($\overline{M}_w = 120,000-330,000$ g/mol) in 2-ethoxy ethanol.

2.3. Sample preparation and characterization

Upon completion of the decomposition reactions, transmission electron microscopy (TEM) samples were prepared by placing a drop of the solution onto a formvar-coated TEM grid. The grid was placed on top of a Kimwipe so that when a drop was placed onto the grid, the liquid was pulled through the grid leaving a thin film on top of the grid. The resulting samples were analyzed with a JEOL 100C TEM microscope having a resolution of 100 kV. The particles that were formed were mostly amorphous and consisted mainly of Co clusters with some traces of Co_2O_3 and CoO. The presence of cobalt particles in a particular location was determined by electron diffraction analysis of different spots within each sample. TEM micrographs of several of the systems described in this study are shown in Fig. 1.

Table 1
Summary of the various experiments performed with both PS-PMMA diblock copolymers and PS and PMMA homopolymers with various molecular weights in different selective and non-selective solvents

PMMA MW (g/mol)	PS MW (g/mol)	MMA weight %	Solvent	Overall MW (g/mol)	Cluster size (nm)
11,200	71,300	13.6	Cyclohexanone	82,500	58
25,900	25,300	50.6	Toluene	51,200	52
165,800	101,100	62.1	2-Ethoxy ethanol	266,900	32
165,800	101,100	62.1	Toluene	266,900	29
280,000	47,000	85.6	Cyclohexanone	327,000	20
30,000	0	100	Chlorobenzene	30,000	67
60,000	0	100	Chlorobenzene	60,000	50
120,000	0	100	Chlorobenzene[a]	120,000	28
250,000	0	100	Chlorobenzene[a]	250,000	27
330,000	0	100	Chlorobenzene[a]	330,000	31.5
0	13,000	0	Toluene	13,000	21
0	25,000	0	Toluene	25,000	18
0	120,000	0	Toluene	120,000	17
0	250,000	0	Toluene	250,000	22
0	330,000	0	Toluene	330,000	42

Cyclohexanone is a common good solvent for both PS and PMMA, toluene is a good solvent for PS, 2-ethoxy ethanol and chlorobenzene are good solvents for PMMA. (Note that MW means molecular weight.)

[a] Identical experiment performed also in 2-ethoxy ethanol, another good solvent for PMMA, yielding similar average cluster size.
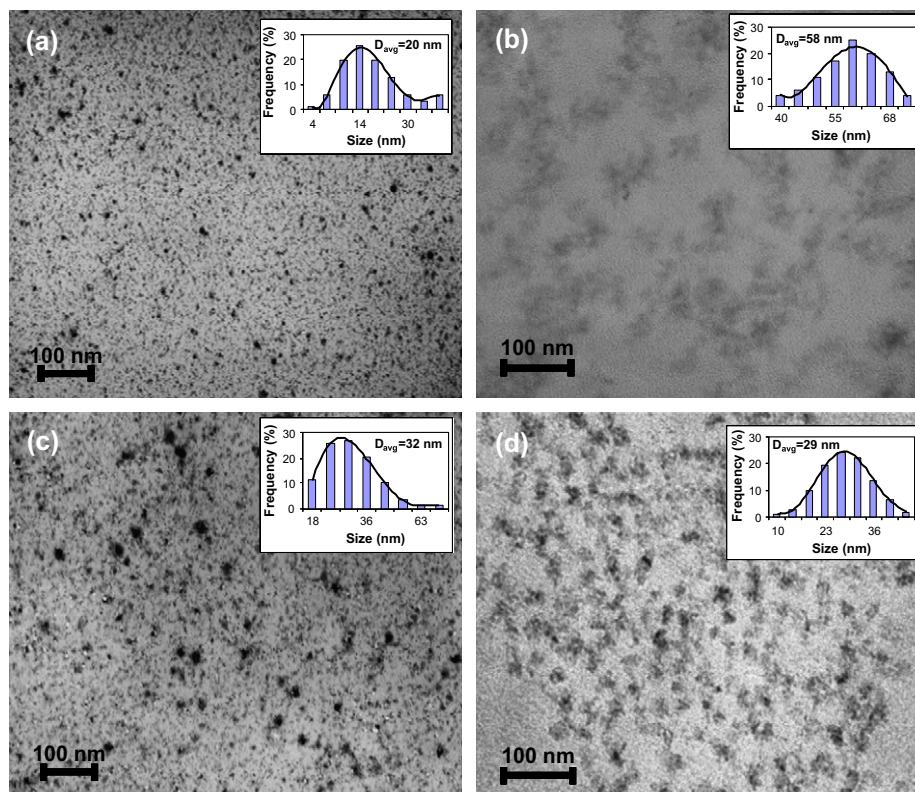
Fig. 1. TEM micrographs of cobalt oxide nanoparticles formed in several polymeric media: (a) in $PS_{47,000}$-b-$PMMA_{280,000}$ block copolymer in cyclohexanone, a common good solvent for both the PS and MMA blocks; (b) in $PS_{71,300}$-b-$PMMA_{11,200}$ block copolymer in cyclohexanone, a common good solvent for both the PS and MMA blocks; (c) in $PS_{101,100}$-b-$PMMA_{165,800}$ block copolymer in 2-ethoxy ethanol, a good solvent for the MMA block; (d) in $PS_{101,100}$-b-$PMMA_{165,800}$ block copolymer in toluene, a good solvent for the PS block.

3. Results

The results of all experiments are summarized in Table 1, where we list the polymer characteristics (molecular weight, composition), the type of solvent, and the average Co cluster size. As in previous studies [2–13,19,21], the distribution in cluster size is found to be narrow, with a polydispersity of order 10% or less. It should be noted that the distribution of the cluster size is due to the presence of clusters that are either smaller or larger than the average size, thereby suggesting a kinetic control mechanism of the cluster growth process [21]. The cluster sizes were based on the TEM images (as for example those in Fig. 1) of the various samples. The average cluster sizes were calculated from cluster populations greater than 100 clusters for each sample. Dynamic light scattering (DLS) experiments were also performed on the original solutions. While the TEM technique images the metallic core of the clusters, the size of the clusters obtained from the DLS method contained also the stabilizing adsorbed polymer layer together with its associated entangled chains – fact which introduced a large discrepancy between these two types of measurements. For the larger particles, the additional contribution to the particle diameter caused by the thickness of the adsorbed polymer layer, as measured by DLS, does not represent a considerable change compared to the size of the core metallic particle as measured by TEM. Conversely, for smaller nanoparticles ($< \sim 30$ nm), the presence of the adsorbed polymer layer changes the overall size of the particle when measured by DLS and thus creates a discrepancy between the DLS and the TEM measurements. Hence, in order to maintain uniformity and reliability in the cluster size determinations, only the TEM results were taken into consideration.

In Fig. 2 we compare the size of Co clusters formed in the two homopolymers, PS and PMMA, as a function of the chain molecular weight. The solvents used (toluene for PS and chlorobenzene for the PMMA) are known to be good solvents for their respective polymers at the temperature range of the experiment ($\sim 90\,^{\circ}C$).

We see that, in both types of the homopolymer suspensions, the cluster size is minimal at a specific chain molecular weight, at approximately 200,000 g/mol for the PMMA solutions and 100,000 g/mol for the PS solutions. We see that at high chain lengths (above $\sim 300,000$ g/mol) clusters in PS are found to be larger than those in PMMA, in agreement with observations for clusters formed in the respective homopolymer melts [11]. However, in the limit of low chain length, clusters formed in PS solutions are smaller than those formed in solutions of PMMA with the equivalent polymer molecular weight. Determining the effect of polymer molecular weight on cluster size in the diblock copolymer case is somewhat more complex. As shown in Fig. 2, neither the molecular weight of the styrene block, the overall chain molecular weight (namely, sum of both styrene and MMA blocks) or the % MMA affects the cluster size in any consistent manner.
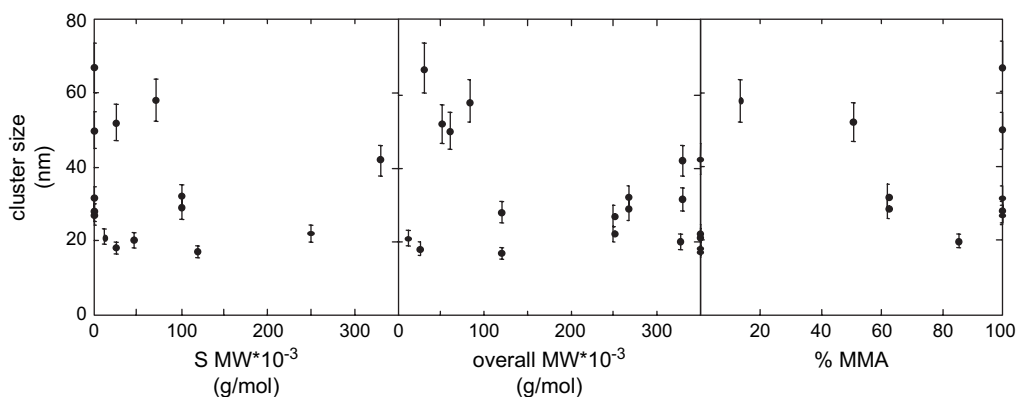
Fig. 2. Effect of some copolymer characteristics on the size of Co clusters. No trends can be distinguished as a function of the styrene block molecular weight (left), the overall chain molecular weight (center) or the % MMA in the copolymer (right).

Examining the diblock copolymers reveals that as the PMMA block MW increases, the cluster size decreases — regardless of the PS block MW or the solvent type. Moreover, the cluster sizes seem to correspond to those expected for the comparable homopolymer MW. As shown in Fig. 3, the effect of the MMA block MW on cluster size for those clusters formed in the diblock copolymeric media indeed follows the same trend as for clusters formed in PMMA homopolymer. Note that this trend holds *regardless* of the solvent type (common good, selective for PS *or* selective for PMMA).

4. Discussion

In this paper we examine the effect of homopolymer and diblock copolymer molecular weight and composition on the synthesis of Co nanoclusters. In all cases we find that the

clusters are relatively small (on the order of 70 nm or less), and their size distribution is relatively narrow.

We find that in solutions of homopolymers in good solvent, the cluster size is minimal at a specific chain molecular weight, as shown in Fig. 4: approximately 200,000 g/mol for PMMA and 100,000 g/mol for PS. Clusters formed in low molecular weight PS are smaller than those formed in low molecular weight PMMA, but this trend reverses at higher chain molecular weight.

Two mechanisms have been suggested to explain the effect of polymeric media on cluster size and size distribution. The
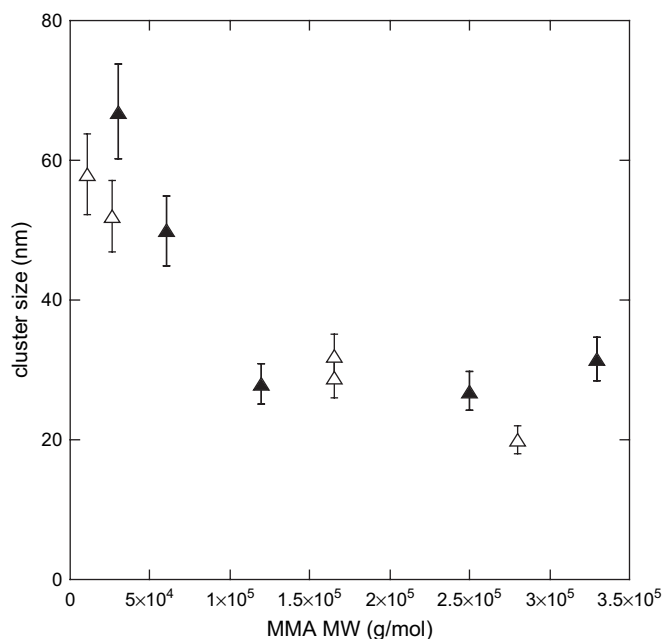

Fig. 3. The effect of MMA block molecular weight on the size of metal clusters formed in PMMA homopolymer (full symbols) and copolymer (open symbols) suspensions, as listed in Table 1.
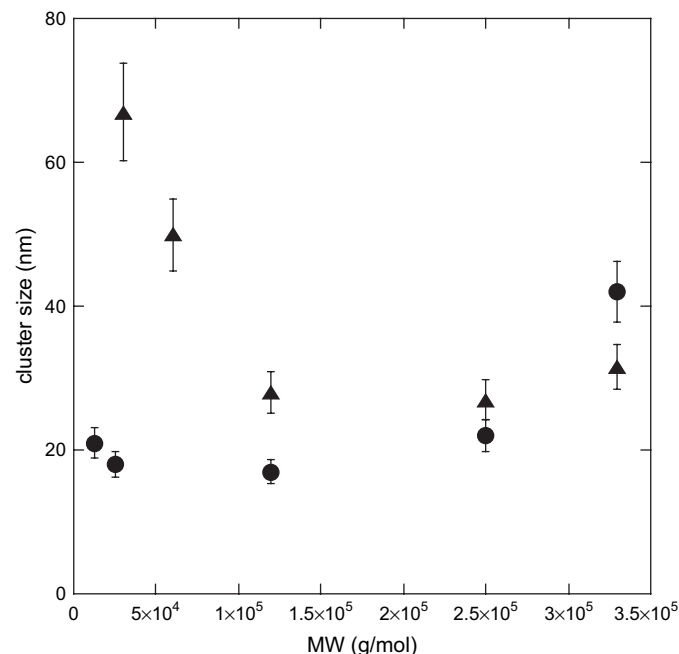

Fig. 4. The effect of homopolymer MW on the Co cluster size. Triangles denote PMMA in chlorobenzene and circles denote PS in toluene; the solvents are good solvents for their respective polymers under the synthesis conditions. We see that in both types of polymeric media the cluster size is minimal at a finite chain length: approximately 200,000 g/mol for PMMA and 100,000 g/mol for PS. Clusters formed in suspensions of low molecular weight PS are smaller than those formed in low molecular weight PMMA; However, at higher molecular weight (>300,000) clusters formed in PMMA are smaller than those formed in PS suspensions.

'polymer capping' model [11,12] is based on the fact that polymer chains — whether in bulk or in solution — tend to adsorb onto the growing clusters, thus creating a layer that can inhibit growth. The capping model has been shown to successfully explain several system characteristics, such as the effect of chain molecular weight on cluster size in solution [12] and in bulk [11]. However, while the 'polymer capping' model successfully addresses the lack of clusters that are larger than the average size set by the capping mechanism, it cannot explain why *smaller* clusters are not found.

Recently, we conducted a study on the kinetics of cluster formation in bulk polymeric media [11]. We showed that the narrow cluster size distribution can be attributed to a combination of cluster formation kinetics and the capping mechanism. The analysis shows that the average size of the clusters, R^*, should scale as [21]:

$$R^* \sim \gamma/\varepsilon \tag{1}$$

where γ is the surface tension (energy per unit area) between the media and the cluster and ε is the energy of cluster formation per unit volume. ε defines the energy gain associated with metal atoms aggregating into a metal cluster when compared to their distribution in solution, and is thus relatively insensitive to the specific system. However, the surface tension is sensitive to the media properties: for clusters synthesized in a homogeneous solvent solution, γ is set by the chemical interactions between the cluster and the solvent. For clusters formed in a polymer-containing solution, γ accounts not only for the chemistry of the system, but also for the effect of chain molecular weight.

In the case of cluster formation in a polymeric solution, the layer in contact with the cluster is composed of both solvent and polymer. Thus, the surface tension depends on the density of the polymer in the adsorbed layer, ϕ:

$$\gamma \sim (1 - \phi)\gamma_s + \phi\gamma_p \tag{2a}$$

We have previously shown [12] that

$$\phi \sim \sqrt{\frac{\ln N}{N\left(1 - \sqrt{1 - \ln N/N\delta^2}\right)}} \tag{2b}$$

Here, γ_s is the interfacial tension between the solvent and the cluster. γ_p is the surface tension between the polymer and the cluster, N is the degree of polymerization and δ is the adsorption energy gained by monomer adsorption onto the cluster surface, associated with the energy gain due to monomer–cluster interactions when compared to monomer–solvent interactions. The resulting scaling for the optimal cluster size is then:

$$R^* \sim \frac{\gamma_s}{\varepsilon} + \frac{(\gamma_p - \gamma_s)}{\varepsilon}\sqrt{\frac{\ln N}{N\left(1 - \sqrt{1 - \ln N/N\delta^2}\right)}} \tag{3}$$

In Fig. 5 we plot the cluster size as a function of chain molecular weight. We see that the cluster size is minimal at a specific chain length, as observed for both PS and PMMA suspensions.

The effect of diblock copolymer characteristics on the size of the Co clusters is more complex. In a common good solvent, where one might expect that the essential parameter setting the cluster size is the overall chain molecular weight, we find (Table 1) that clusters formed in a diblock copolymer with a combined molecular weight of 327,000 g/mol are much smaller (20 nm) than those obtained in the similar molecular weight PMMA homopolymer (31.5 nm), *or* the similar molecular weight PS homopolymer (42 nm) — both of them in their respective good solvents. The copolymer composition does not play a direct role in setting the cluster size either. Comparing copolymers with different overall molecular weights but with similar MMA content ($\sim$50–60%) in similar solvents, yields different values for the average cluster sizes: 52 nm for a total molecular weight of 51,200 g/mol and 29 nm for a total MW of 266,900 g/mol. These may be explained by the different affinities of the two polymers to the cluster: after all, there is a difference in cluster size between those formed in PS of a given molecular weight and those in same molecular weight PMMA (Fig. 4). However, we also find that the cluster size is nearly insensitive to the solvent type: comparing clusters formed in the $PS_{101,100}$-b-$PMMA_{165,800}$ in a solvent selective for the PS block (29 nm) are quite similar in size to those formed in the solvent selective for the PMMA block (32 nm). This observation is somewhat confusing, since in the former the solution of the diblock copolymer consists of micelles with a PMMA core and PS corona, while in the latter the micelles are reversed.

As shown in Fig. 3, plotting the cluster size as a function of the PMMA block molecular weight yields an identical trend to
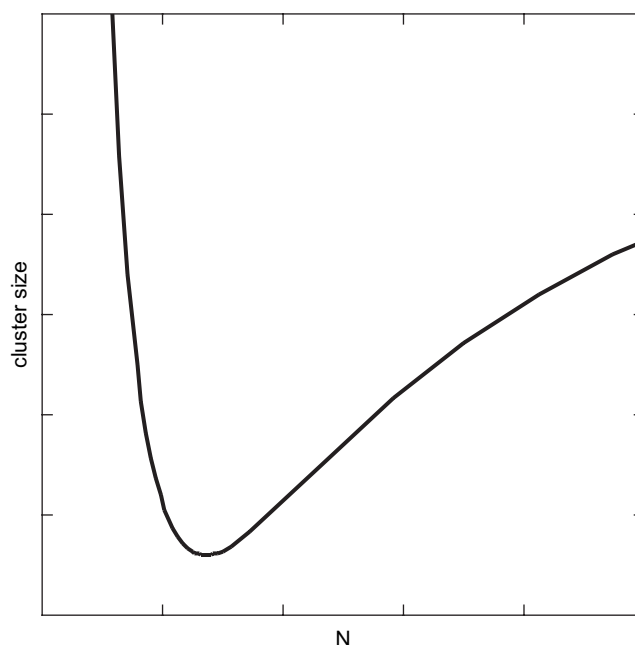

Fig. 5. The effect of homopolymer molecular weight on cluster size, as given by Eq. (3). N and the cluster size are taken to be in arbitrary units.

that obtained for homopolymer PMMA – regardless of the quality and specificity of the solvents used in these experiments. We recognize the fact that in our experiments we only sampled a subset of all possible variations in the important system parameters, i.e., molecular weight of the polymers, molar ratio of the blocks and solvent specificity. However, the almost-identical particle sizes obtained for the metal oxide clusters formed in the $PS_{101,100}$-b-$PMMA_{165,800}$ block copolymer, both in a selective solvent for the PS block (toluene) and in a selective solvent for the PMMA block (2-ethoxy ethanol), indicate that the nature of the solvent had very little influence on their final size distribution. Since in the two extreme cases of solvent specificity the resulting particle size was not affected, it would be very unlikely that a common good solvent for both the PS block and the PMMA block would behave differently. Thus, we must conclude that the only parameter (for a fixed copolymer molar composition) controlling the cluster size in the suspensions of diblock copolymers is the molecular weight of one block, in this case PMMA, and it is indifferent to other parameters including the molecular weight of the other block (PS) or the solvent quality.

Why PMMA and not PS? The interactions between PMMA and metal clusters are much stronger than those between the clusters and PS [11,21]. Thus, the synthesis of Co nanoclusters in the PMMA-PS block copolymer suspension occurs within the MMA region exclusively, and is unaffected by the presence of the PS block. The solvent quality affects the cluster size to some degree (see Table 1), but only through its effect on the local PMMA concentration: in a common good solvent, the local concentration of the PMMA chains is set by the average solution concentration. In a selective solvent for the MMA, the local concentration is higher due to the formation of micelles with MMA coronas, whose concentration is higher than the average value. In a solvent selective for PS, the clusters form in the MMA core, namely, in a bulk MMA environment.

Acknowledgments

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