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Preparation of Narrowly Distributed Novel Stable and Soluble Polyacetylene Nanoparticles

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INTRODUCTION

In this report, we demonstrated that upon heating a diblock copolymer of *p*-methyl styrene and phenyl vinylsulfoxide (MS-*b*-PVSO) in tetrahydrofuran, the soluble and flexible PVSO block could be converted into an insoluble and rigid PA block via a chemical reaction, resulting a self-assembly of the copolymer chains into a core-shell nanostructure with the PA blocks as the core and the MS blocks as the shell. The reaction and self-assembly rates could be simply controlled by the reaction temperature. This is an important step towards the processing of intractable polyacetylene as a useful and potential material.

Forty years ago, polyacetylene (PA) as a black powder was first discovered by Natta *et al.* (1984) Twenty years later, Chiang *et al.* (1978) found that the doped PA film had a conductivity close to metal. As a potential conducting and non-linear optical material, polyacetylene has been extensively studied (Nalwa, 1997) in the last two decades. However, polyacetylene is so intractable that its many potential applications have been hindered. It has been a long dream in the field to modify polyacetylene so that it could be processed into different real components for real applications.

On the other hand, extensive studies showed (Vannice, 1984; Dai, 1993; Zhang *et al.,* 1995) that block and graft copolymers could form polymeric micelles in solution if one could make one of the blocks insoluble. It is generally accepted that diblock copolymeric micelles have a core-shell nanostructure with the insoluble block as the core and the soluble block as the swollen shell, resembling small molecule surfactant micelles. Normally, the solvent quality was varied by slowly adding a copolymer solution into a non-solvent for one of the polymer blocks. For water soluble block copolymers, one could also vary the solution temperature to induce the micelle formation if one of the blocks could change from hydrophilic to hydrophobia at higher temperatures (Wu and Qiu, 1998). Noted that the micelle formation is thermodynamically driven and the process is usually so fast in dilute solution that its observation is difficult, if not impossible. To our knowledge, the formation kinetics has not yet been reported.

Recently, Leung *et al.* (1994) reported that poly(phenyl vinyl sulfoxide) could be slowly converted into polyacetylene upon heating. The morphology and the electrical properties of PVSO before and after thermolysis in bulk and its thermolysis kinetics and optical properties in solution have been studied(Leung et al., 1993; Leung et al., 1997). It is expected that if PVSO as one polymer block is connected to another

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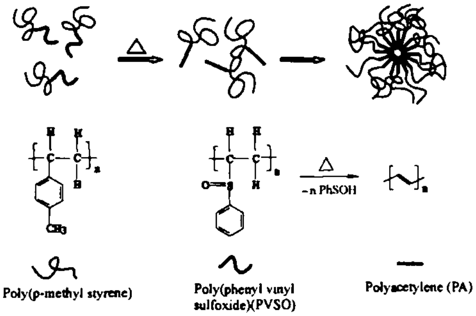

Figure 1. Schematic of chemical reaction-induced self-assembly of poly(4-methyl styrene-*b*-phenylvinylsulfoxide) diblock copolymer chains in solution upon heating.

polymer block to form a diblock copolymer, we will be able to observe a chemical reaction induced self-assembly of the copolymer chains because the resulting PA block from the PVSO block is insoluble. Figure 1 shows a schematic of our idea. It should be noted that by properly choosing a reaction temperature in the range 30–80°C, we are able to control the self-assembly rate and study the self-assembly kinetics in solution.

EXPERIMENT

The MS-*b*-PVSO copolymer (M_w=17,060g/mol, M_w/M_n=1.12 and n_{MS}:n_{vso}=117:60) was prepared by a similar anionic polymerization method detailed before. The purification of monomers (MS and PVSO) and solvents were standard. The reaction was initiated by endcapped sec-BuLi. The molar mass and composition of the MS and PVSO blocks and the resulting copolymer were determined by GPC and H^1-NMR, respectively. In this study, the self-assembly of the MS-*b*-PVSO chains in tetrahydrofuran (THF) was monitored by using a modified ALV/SP-150 laser light scattering (LLS) spectrometer with an ALV-5000 time correlator and a HeNe laser with a power of 40 mW at 632.8 nm. The details of LLS can be found elsewhere(Pecora, 1976; Chu, 1991). The Laplace inversion of the measured intensity-intensity time correlation function in dynamic LLS led to the hydrodynamic radius distribution f(R_h).

RESULTS AND DISCUSSION

Figure 2 clearly shows that before the chemical reaction (t=0), the copolymer chains are narrowly distributed with an average hydrodynamic radius <R_h> located at 3.76nm. As the reaction proceeded, the solution gradually changed from colorless to dark red and the initial narrow peak in Figure 2 was split into two peaks. The appearance of the peak with a larger and increasing size is due to the self-assembly of the resultant MS-*b*-PA chains and the final size of the nanoparticles is in the range 30–60nm which is expected on the basis of the molar mass and composition of the copolymer chain. The peak around ~2nm reflects individual copolymer chains (unimers). Initially, we were puzzled by the question why individual MS-*b*-PA chains have a smaller <R_h> than original MS-*b*-PVSO chains. Later, we found that it could be explained by the self-wrapping; namely, the insoluble PA block was wrapped by the soluble MS block so that the

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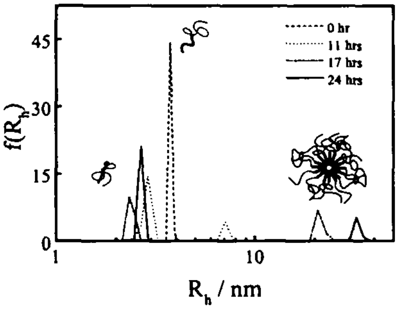

Figure 2. Time dependence of the hydrodynamic radius distribution f(R_h) of poly(4-methyl styrene-*b*-phenyl vinylsulfoxide) in tetrahydrofuran at 55°C during the reaction, where the initial copolymer concentration was 4.02×10^{-3}g/mL.

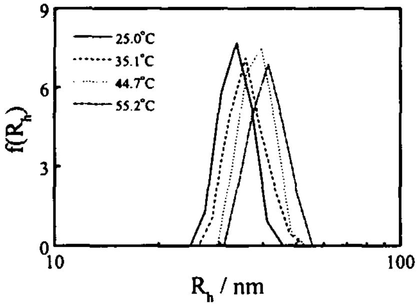

Figure 3. Temperature dependence of the hydrodynamic radius distribution f(R_h) of the resulting polyacetylene core-shell nanoparticles in tetrahydrofuran.

interaction between the insoluble PA block and solvent was minimized, which is schematically shown in Figure 2.

We also observed that the nanoparticles were very stable at 55°C and no color change in the dispersion, indicating that, the PA blocks protected by the MS shell were very stable in the dispersion. Figure 3 shows that the size of the nanoparticles only slightly increases as the solution temperature increases, which is due to the swollen of the soluble MS shell at higher temperatures and further indicates that in the temperature range 25–55°C, the nanoparticles were very stable in the solution. This is very important in the application of these novel polyacetylene nanoparticles. Our studies also showed that the nanoparticle dispersion could be cast into a thin film or a thin tube or any other desired shapes.

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