

Communications to the Editor

Preparation of Narrowly Distributed Stable and Soluble Polyacetylene Block Copolymer Nanoparticles

Chi Wu,^{*,†,‡} Aizhen Niu,[†] Louis M. Leung,[§] and T. S. Lam[§]

Department of Chemistry
The Chinese University of Hong Kong
Shatin, N.T., Hong Kong
The Open Laboratory for Bond-Selective Chemistry
Department of Chemical Physics
University of Science and Technology of China
Hefei, Anhui, China
Department of Chemistry
Hong Kong Baptist University
Kowloon, Hong Kong

Received October 13, 1998

Forty years ago, polyacetylene (PA) as a black powder was first discovered by Natta et al.¹ Twenty years later, Chiang et al.² found that the doped PA film had a conductivity close to metal. As a potential conducting and nonlinear optical material, polyacetylene has been extensively studied in the last two decades.³ 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 that block and graft copolymers could form polymeric micelles in solution if one could make one of the blocks insoluble.^{4–9} 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 nonsolvent 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 hydrophobic at higher temperatures.¹⁰ Note 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.

[†] The Chinese University of Hong Kong.

[‡] University of Science and Technology of China.

[§] Hong Kong Baptist University.

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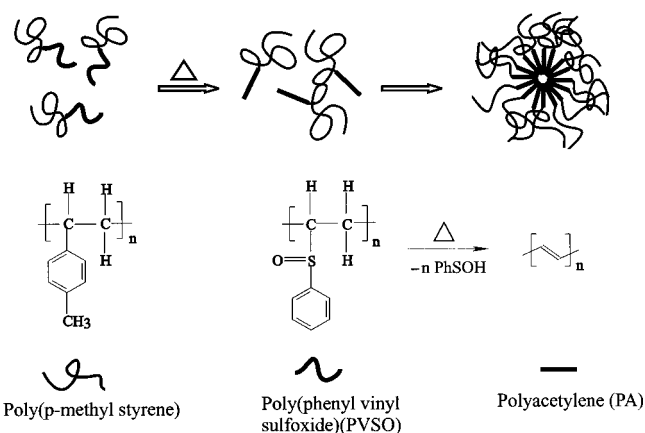


Figure 1. Schematic of chemical reaction-induced self-assembly of poly((MS)-b-PVSO) diblock copolymer chains in solution upon heating.

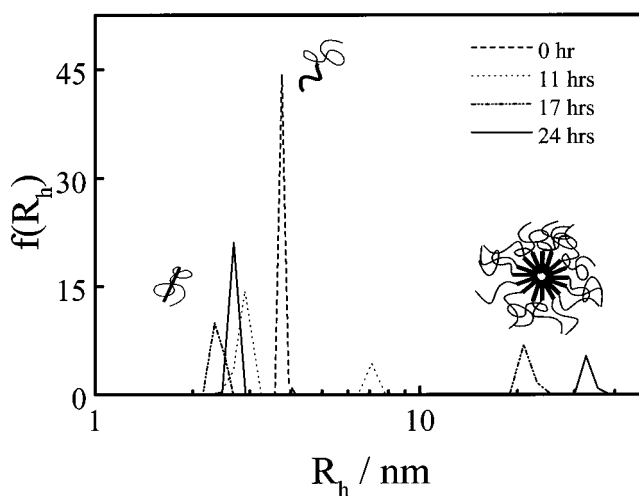


Figure 2. Time dependence of the hydrodynamic radius distribution $f(R_h)$ of poly((MS)-b-PVSO) in tetrahydrofuran at 55 °C during the reaction, where the initial copolymer concentration was 4.02×10^{-3} g/mL.

Recently, Leung et al.¹¹ reported that poly(phenyl vinyl sulfoxide) (PVSO) 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.^{11–13} It is expected that, if PVSO as one polymer block is connected to another 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 resultant 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.

The 4-methyl styrene (MS)-b-PVSO copolymer ($M_w = 17\,060$, $M_w/M_n = 1.12$, and $n_{MS}:n_{VSO} = 117:60$) was prepared by a similar anionic polymerization method detailed before.¹¹ The purification of monomers (MS and PVSO) and solvents was standard.¹² The

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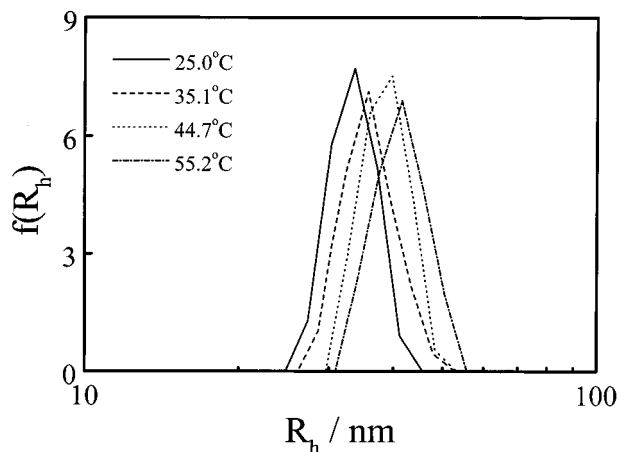


Figure 3. Temperature dependence of the hydrodynamic radius distribution $f(R_h)$ of the resultant polyacetylene core-shell nanoparticles in tetrahydrofuran.

reaction was initiated by end-capped *sec*-BuLi. The molar mass and composition of the MS and PVSO blocks and of the resultant copolymer were determined by GPC and ^1H 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.^{14,15} The Laplace inversion of the measured intensity-intensity time correlation function in dynamic LLS led to the hydrodynamic radius distribution $f(R_h)$.

Figure 2 shows the intensity-weighted hydrodynamic size distributions at different reaction stages. It clearly shows that before the chemical reaction ($t = 0$), the copolymer chains are narrowly distributed with an average hydrodynamic radius $\langle R_h \rangle$ located at 3.76 nm. As the reaction proceeded, the solution gradually changed from colorless to yellow and finally 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 particles (block copolymer micelles) is in the range 30–60 nm which is expected on the basis of the molar mass and composition of the copolymer chain. The peak around 2 nm reflects individual copolymer chains (unimers). Initially, we were puzzled by the question as to why individual MS-*b*-PA chains have a smaller $\langle R_h \rangle$ than original MS-*b*-PVSO chains. Later, we found that one of the possible explanations could be a self-wrapping; namely, the insoluble PA block was wrapped by the soluble MS block so that the interaction between the insoluble PA block and solvent was minimized, which is schematically shown in Figure 2. It should be noted that in a laser light scattering measurement, the large “particles” with a higher molar mass are more visible so that it is not very accurate to determine the size of small species (individual chains in this study) in the presence of large ones. This is why the position of the peak around 2 nm varies.

We also observed that the micelles were very stable at 55 °C and that there was 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 micelles only slightly increases as the solution temperature increases, which is due to the swelling of the soluble MS shell at higher temperatures and further indicates that in the temperature range 25–55 °C, the micelles were very stable in the solution, which is important in the application of these novel polyacetylene micelles. Our studies also showed that the dispersion could be cast into a thin film or a thin tube or any other desired shapes. One of the envisioned applications is to make an optically transparent polymer material with a higher refractive index so that it can be used to manufacture ultrathin vision-correction glasses (lenses).

Acknowledgment. The financial support of this study by the Research Grants Council (RGC) of Hong Kong Government Earmarked Grants 1997/98, (CUHK4181/97P, 2160082, RGC/96-97/03) and The National Distinguished Young Investigator Fund (1996, 29625410) are gratefully acknowledged.

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