

Polymerization in a Reverse Micelle Nanoreactor: Preparation of Processable Poly(*p*-phenylenevinylene) with Controlled Conjugation Length

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Received September 18, 1997. Revised Manuscript Received January 8, 1998

We show that a nanoscale polymerization reaction within the confinement of a reverse micellar cavity yields products with controlled conjugation lengths and, thus, controlled band gaps for applications to electronics and photonics. In addition, control of the physical size (length) of the polymer provides the prospects of monodispersity, improved processability, and preparation of nanocomposites. This novel approach has been successfully applied to produce controlled chain length poly(*p*-phenylenevinylene) (PPV), a polymer that has drawn considerable attention in recent years for its electroluminescence, nonlinear optical, and lasing properties.

Introduction

Multifunctional polymers that simultaneously exhibit more than one property are a new generation of materials that hold considerable promise for numerous applications in the field of electronics and photonics. Polymer light-emitting diodes, polymer lasers, and photorefractive polymers are some significant examples.^{1–11} Nanosize manipulation of molecular architecture and their morphology provides a powerful approach to control electronic and optical properties of a material as well as its processability. This is why the design and processing of nanostructured materials has emerged as a frontier area of materials research.

Most interest in the past focused on inorganic semiconductors in the design and preparation of quantum-confined structures such as quantum dots, quantum wires, and quantum wells.^{12–14} By judicious choice of

the physical size, electron–hole pairs can be quantum confined to control the band gap (excitonic resonances) of materials. The electronic and photonic properties, which are strongly dependent on their band gaps, have been well documented in the case of inorganic materials (semiconductors and metal clusters). By proper design of these nanostructured materials, their electronic, luminescence, and nonlinear optical properties can be controlled.^{15–19} In contrast, nanoscale processing of polymers in a restricted geometry to produce quantum-confined structures and composites is practically unexplored.

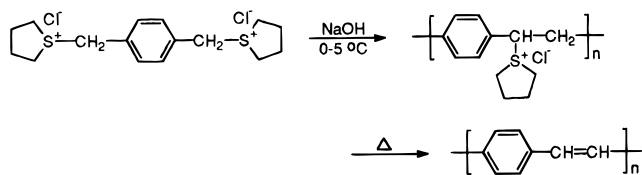
To illustrate nanoscale polymerization, we have chosen the poly(*p*-phenylenevinylene) (PPV) polymer. It has received considerable attention because of its electrical, nonlinear optical, electroluminescence, and more recently lasing properties.^{20,21} Processable PPV derivatives and PPV itself have been used to form an active layer in thin-film light-emitting diodes (LEDs) with promising efficiencies. By tuning the morphologies band gaps, and charge-transport properties of these polymers, device stabilities have been increased, and emitters at a wide variety of wavelengths have been fabricated. Modification of the optical and electrical properties have been noted in devices containing layers

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of different types of PPV in a particular sequence. Also the third-order nonlinear optical properties of PPV are promising.^{22a} Recently, superradiance in the PPV and PPV analogues have been achieved,^{22b} suggesting the prospect of polymer semiconductor lasers. PPV also exhibits a strong two-photon pumped up-conversion emission when excited by near-IR laser pulses of 800 nm. This opens up another prospect, that of up-conversion lasing.²³

The PPV polymer is traditionally made by a base-catalyzed reaction of a water-soluble salt monomer precursor.²⁴ Since the final long-chain polymer is insoluble, one first produces a water-soluble sulfonium salt precursor polymer in which the vinylene double bond is not yet formed. This precursor is then heated to form the final PPV polymer. The reaction scheme is shown below:



Despite the rapidity with which PPV has been developed for electroluminescence applications, many questions and difficulties remain. Due to the difficulty in controlling the base-catalyzed reaction which leads to large polymeric chains, it is extremely difficult to achieve a narrow distribution of molecular weight of PPV. Furthermore, since the final polymer is insoluble, it is difficult to process it in various forms such as a bulk sample or in the form of a blend with other polymers.

In this article, we present controlled, nanoscale polymerization of the PPV monomer conducted within the size-controlled cavity of reverse micelles, which yields processable PPV. Reverse micelles are thermodynamically stable aggregates in organic solvents where the polar heads of the amphiphiles cluster to form a micellar core enclosing the polar fluid; the hydrophobic tails extend into the bulk/continuous organic phase.^{26,27} The solute material is dissolved in the polar fluid which is immiscible with the continuous phase. The reverse micelles have a polar fluid-to-surfactant molar ratio, W_0 , which can vary over a range having a maximum ratio that determines the maximum size of reverse micelles.²⁸

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The double-chain surfactant Aerosol OT (sodium bis(2-ethylhexyl)sulfosuccinate) used here has been extensively investigated for its ability to form reverse micellar aggregates in nonpolar solvents and to encapsulate relatively large amounts of water. As the molar ratio, W_0 , increases, the hydrodynamic radius of the spherical polar core increases monotonically with W_0 .

We find that by polymerization in reverse micelles of different W_0 , formation of PPV polymers (oligomers in this case) of controlled band gap can be easily achieved. These PPV analogues (oligomers) can be readily processed through dispersion to prepare polymer blends. For polymerization reactions that are highly exothermic leading to uncontrolled growth, polymerization within a reverse micelle cavity can provide a method to control the extent of polymerization.

Experimental Section

Monomer p -xylylenebis(tetrahydrothiophenium chloride), sodium bis(2-ethylhexyl)sulfosuccinate (AOT), 2,2,4-trimethylpentane (isooctane), and sodium hydroxide were all obtained from Aldrich and used without further purification. Ethyl alcohol (dehydrated) was obtained from Pharmaco.

Reverse micellar solutions were prepared by dissolving appropriate amounts of AOT in isooctane (2,2,4-trimethylpentane) and adding specific volumes of aqueous solution of the base to achieve the desired W_0 value. Volume additivity was assumed in calculating the AOT concentration and the water/AOT molar ratios. The synthesis of the PPV polymer involved a base-catalyzed polymerization of the monomer, xylylene bis(tetrahydrothiophenium chloride), which in the form of an ethanolic solution was mixed with the continuous phase, i.e., isooctane. Because of the interdroplet interaction that arises due to the Brownian motion of the reverse micellar droplets, the monomer slowly diffuses inside the base-catalyzed core and polymerization occurs within the cavity. The size of the reverse micellar cavity as mentioned earlier is governed by the amount of the aqueous solution of the base.

In situ size measurements of the reverse micellar systems with 0.5 M [AOT] and W_0 varying from 5 to 20 in a nonaqueous medium were done using a Brookhaven USA (Model Bi 9000) laser light-scattering (LLS) instrument fitted with a BI 200SM goniometer. An argon ion air-cooled laser was operated at 488 nm as a light source. The reverse micellar solutions were also examined for UV absorption using a UV-3101PC Shimadzu spectrophotometer and for fluorescence using a RF 5000U spectrofluorophotometer. The PPV polymer was extracted from the reverse micellar system by the addition of a 1:1 ratio of water and ethanol. The polymer was washed several times with water and isooctane using sonication to remove any adhering surfactant. The polymer was then characterized using energy-dispersive X-ray spectroscopy (EDXS) for the presence of Na(surfactant).

The morphology of the solution-cast films was determined by scanning electron microscopy using a JEOL 6400 microscope. The accelerator voltage was 25–30 keV with a working distance of 8–12 mm.

Results and Discussion

Figure 1 shows the UV-vis spectra obtained from the in situ synthesis of the PPV polymer formed in reverse micelles of various droplet (W_0) sizes. As observed at lower droplet size, the UV-vis spectrum shows a structured absorption band around 380 nm with the absorption edge at 440 nm indicating that at low droplet size, the polymer has very few repeating units. With increase in the droplet size, the intensity of these bands increased and became more broadened at $W_0 = 20$ with

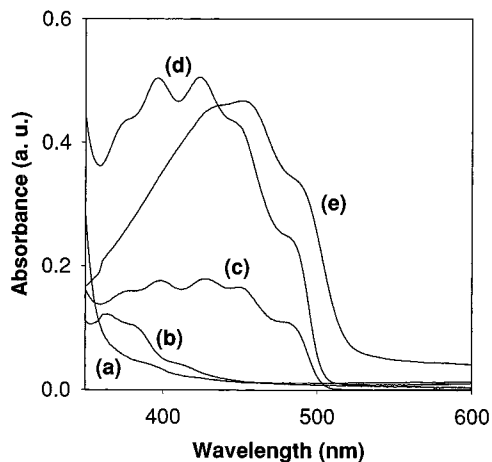


Figure 1. UV-vis spectra of poly(*p*-phenylenevinylene) synthesized within the reverse micellar cavities of varying droplet sizes: (a) $W_0 = 5$, (b) $W_0 = 10$, (c) $W_0 = 15$, (d) $W_0 = 20$, and (e) PPV extracted from the micellar system ($W_0 = 20$).

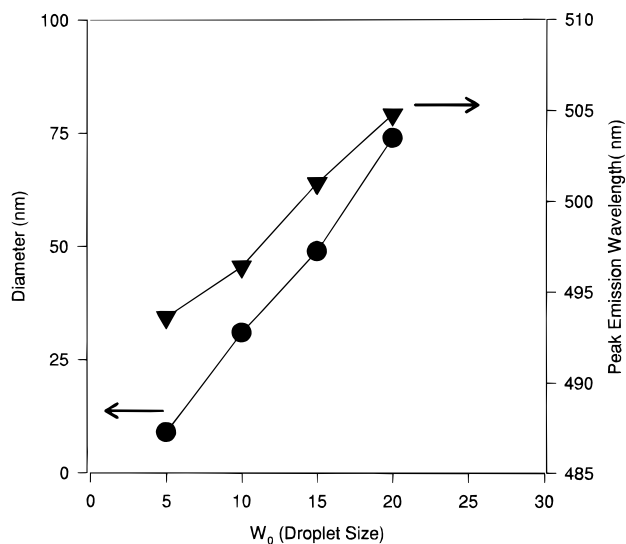
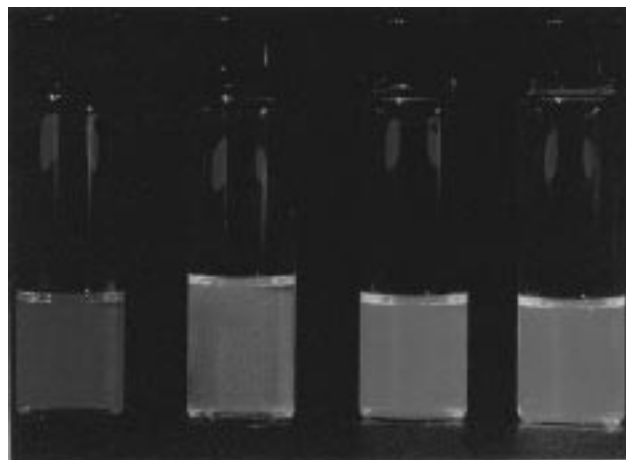
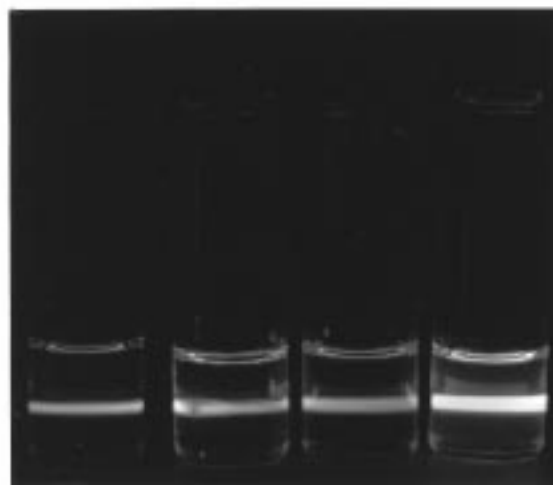


Figure 2. Size measurement of polymeric nanoparticles within reverse micellar system having various droplet sizes: $W_0 = 5, 10, 15, 20$ using laser light scattering and their corresponding peak emission wavelengths.

the absorption edge at 500 nm, indicative of a more conjugated system. In all the cases, the retention of the structure in the absorption spectra is due to the conjugated sequences resulting from the chains which are essentially oligomeric.²⁴ Also with the increasing cavity size (W_0), a shift in the absorption edge toward longer wavelengths was observed. This is in exact correlation with the data obtained by laser light-scattering (LLS) measurements of different droplet sizes as shown in Figure 2. Since, in the reverse micelles the size of the aqueous droplet is directly related to the amount of electrolyte dissolved into the polar core,²⁹ the LLS data reveal that the particle size increases from 9 to 74 nm as W_0 is increased from 5 to 20. Thus the degree of unsaturation (chain length) can be controlled by varying the droplet size of the reverse micellar system.



(a)



(b)

Figure 3. Fluorescence emission from poly(*p*-phenylenevinylene) of different conjugation lengths synthesized within reverse micelles (from left to right: $W_0 = 5, 10, 15, 20$). (a) UV excitation; (b) two-photon excitation at 800 nm.

Figure 1 also shows the UV-vis spectra of the PPV film made by extracting the polymer from the reverse micellar system. The spectrum of the extracted polymer ($W_0 = 20$) shows a bathochromic (red) shift, suggesting that the polymeric chains once removed from the reverse micelle cavity are free to link, perhaps, due to the presence of the reactive end groups. They thus form large aggregates by interacting with other polymer chains. This process is otherwise prevented due to encapsulation within the surfactant headgroups. This feature can also be observed from the light-scattering data, which show that the particle (polymer) size increases from 74 to 135 nm when the polymer is extracted from the reverse micellar system. Also the loss of structured sequence in the absorption spectra of the extracted polymer indicates that the polymeric chains are no longer oligomeric; rather they have grown/interconnected to form longer chain polymers.

Infrared spectroscopy of the extracted PPV polymer (from reverse micelles) revealed a very strong absorbance at 966 cm^{-1} for the *trans*-vinyl CH out-of-plane bending mode,³⁰ suggesting that the polymerization reaction yielded exclusively *trans*-PPV. The peak at 835 cm^{-1} is consistent with a para-substituted ring, indicat-

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ing that the phenylene rings are present only in the para-substituted form. The presence of a small peak in the 2900 cm^{-1} , the $\text{sp}^3\text{C-H}$ stretch region, indicated a small fraction of uneliminated units. These, however, were of fairly low concentration and were not expected to significantly alter the properties of the PPV films.

Figure 3a shows the UV lamp excited fluorescence emission from poly(*p*-phenylenevinylene) of different conjugation lengths synthesized within reverse micelles of different droplet sizes. The colors of emission clearly show that with an increase in the cavity size, fluorescence emission shifts to longer wavelengths. This is also seen from Figure 2, which shows that the peak emission wavelength shifts from 493 to 505 nm with an increase in W_0 (droplet size) from 5 to 20. This is explained to be due to an increase in the length of the conjugated sequence with increasing W_0 (droplet size); as a result the transition energy gap between the filled π and empty π^* orbitals reduces and thus the emission is observed in the longer wavelength region. This is as would be expected from a simple model of a particle in a one-dimensional box.³¹ We have also observed two-photon excited fluorescence from the above micellar solutions when excited with a femtosecond Ti sapphire laser at 800 nm. This emission is shown in Figure 3b, which shows the same trend as observed with the single-photon excitation.

The morphology of a solution-cast film was determined by scanning electron microscopy (SEM), which showed that the films were fully homogeneous and

dense with no void space. The EDXS studies did not indicate the presence of Na (from the surfactant). Using an ethanol dispersion of PPV, produced by the reverse micelle approach, we have been able to cast a film or blend PPV with another polymer (such as PMMA, PVK) through solution phase mixing. These blends could be used for applications in light-emitting devices, solid-state polymeric laser systems, and photorefractive polymeric devices. Therefore, the reverse micelle approach has provided processability to PPV.

In conclusion, we believe that nanoscale polymerization can be a versatile powerful method to produce multifunctional polymers and composites. This approach of producing a multiphase composite can be used to produce n- and p-type inorganic:organic semiconductor junctions such as CdS:PPV with a nanometer control of electron transfer. Since PPV is a p-type (hole transporting) semiconducting polymer and CdS is n-type (electron transporting), this nanocomposite system can exhibit interdomain charge transfer and produce novel p-n junctions. Efforts are underway in our laboratory to produce these novel composites.

Acknowledgment. This research was supported by a University of Southern California MURI program sponsored by the Chemistry and Life Sciences Directorate of the Air Force office of Scientific Research through Contract F49620-96-1-0035. We are also grateful to Dr. A. N. Maitra, Department of Chemistry, Delhi University, India for providing the laser light-scattering facility for particle size measurements.

CM970634D

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