Raman Vibrational Evidence for the Presence of Conjugated Regions in Individual Micron Diameter Polystyrene Particles Irradiated with Visible Radiation

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Micron diameter particles containing or composed solely of polystyrene have been reported to become highly fluorescent shortly after immobilization in a visible optical trap (488.0 nm). It has been proposed that extensive regions of conjugation in the polymer backbone are responsible for this emission. Raman spectroscopic evidence is described in this report that confirms the presence of polymer backbone conjugation. In some experiments Raman signals were enhanced by incorporating silver nanoparticles into the micron-diameter polystyrene particles by photoreduction of silver ion. By monitoring the intensity changes of the C−H and C=C stretching regions while an individual particle is immobilized in the optical trap, the generation of extensive conjugation regions can be observed over time. In addition, the presence of the silver nanoclusters increased the rate and magnitude of the reactions that lead to polystyrene conjugation.

Introduction

Micron diameter polystyrene particles are finding increased application in many advanced materials and optical devices. Recent reports have included the use of polystyrene particle arrays dispersed in thermosensitive polymers for producing a temperature tunable grating for optical applications[1] and the incorporation of core−shell polymer particles in epoxies and resins.[2]

We have recently demonstrated that polystyrene particles become highly luminescent upon exposure to high-intensity visible radiation while immobilized in a optical radiation trap.[3] Parameters that control emission intensity and duration have been described previously.[3] Luminescence also occurs in micron diameter particles of mixed polymer composition that incorporate polystyrene as one of the components. This observation has led to the development of a rapid particle characterization method that is capable of detecting the presence of polystyrene in micron diameter particles. In some cases quantitation of the weight percentage of polystyrene in a single particle is possible. Currently, only time-consuming electron microscopy procedures can provide this information on an individual particle basis. Increased understanding of the mechanism of luminescence generation in these particles is required for further development of this optical technique. Additionally, understanding how the physical characteristics (molecular weight, porosity, and color) of these particles are modified upon exposure to visible radiation is of considerable interest in device development.

A typical emission spectrum of a pure polystyrene particle immobilized in an optical trap generated with 488.0 nm radiation is provided in Figure 1. The emission is very broad, covering most of the visible region. Shoulders in the spectrum are presumed to be polymer regions of differing conjugation lengths.

The optical trap is a convenient method of not only immobilizing individual particles but also providing the capability of simultaneously monitoring Raman and emission spectra. Raman spectroscopy has been used previously in conjunction with an optical trap to monitor the progress of a polymerization
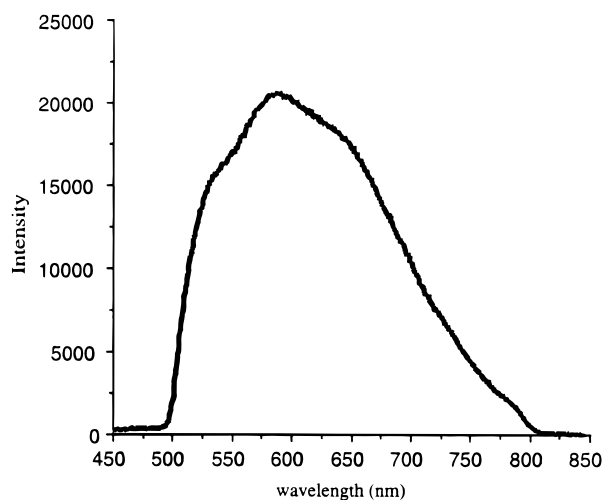
Figure 1. Typical emission spectrum of a 5.872 μm polystyrene particle suspended in 2-propanol and trapped by 8.2 mW of 488 nm laser radiation.

reaction both in a micelle[4] and in a single aerosol droplet.[5] The signal from the C−H stretch due to alkene and alkane hydrogens werewas monitored, and the ratio of the two peaks was compared at various times during the reaction.

To confirm the presence of conjugated regions in micron diameter particles and correlate their presence with the onset of particle luminescence, we have employed Raman spectroscopy. Both the C−H and C=C stretches in the backbone of polystyrene were investigated while an individual particle was irradiated. The C−H stretching region for the phenyl substituents, the C−H stretching region in the polymer backbone, and the fluorescence emission from the particle were monitored simultaneously. Unfortunately, intensity from the C=C stretching region was not observable in these same experiments. In an attempt to observe the C=C stretching region, silver ion was used to generate nanometer sized clusters of silver metal on the polymer particle surface and in the particle pores and thus enhance the Raman vibrational intensities through both surface
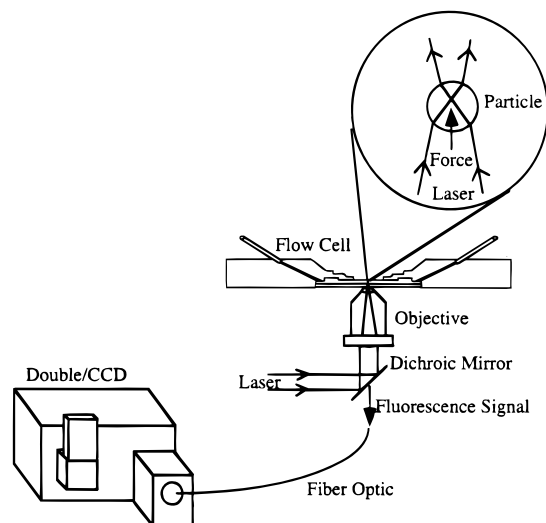
Figure 2. Simplified diagram of the experimental apparatus including the flow cell, objective, and double monochromator/CC. detector. The inset contains a simple diagram showing the origin of the trapping forces.

and resonance enhancement. Silver ion is believed to interact with the phenyl substituents of polystyrene and is localized at the surface of the particle and pore structures.

Results from the Raman experiments demonstrate that the backbone C=C stretch is increased and the backbone C−H stretch is decreased during irradiation. The C−H stretch and C−H deformation originating from the phenyl substituents do not change in intensity during the experiment. The photoreduction of silver ion also serves to increase the rate and extent of the reactions that generate conjugation in these polystyrene particles.

Experimental Section

Nonfunctionalized polystyrene particles were obtained as aqueous suspensions of 10.568 ± 1.034 μm diameter (Polysciences). Silver nitrate (Aldrich) was used as received. Nanopure water (Barnstead) was used for all dilutions. One drop of a dilute solution of the polystyrene particles was added to approximately 25 mL of a 39 μM solution of the silver nitrate. After several hours of incubation the particles were pumped into the flow cell for analysis.

The optical trap, flow cell, and microscope have been described recently in the literature.[3] Briefly, either an Olympus 60x SPlan oil objective (NA = 1.40) or an Olympus 100x SPlan oil objective (NA = 1.40) was used for trapping and Raman analysis of the particles. A suspension of particles was pumped into a flow cell, and individual particles were trapped with an argon ion laser (Coherent Inc.). The Raman signal was collected from the side port of the microscope and focused into a fiber optic which was directed into a double monochromator (Spex, model 1451N) fitted with a liquid nitrogen-cooled charge-coupled device (CCD) detector (Princeton Instruments, EEV 1152×298 chip). Typical experimental parameters included integration times of 5−10 s and excitation powers of 6−7 mW. The signal integrated by the detector was transferred to a Macintosh IIci computer running software written in-house with LabView (National Instruments). A simplified diagram of the instrumental setup is presented in Figure 2.

Results and Discussion

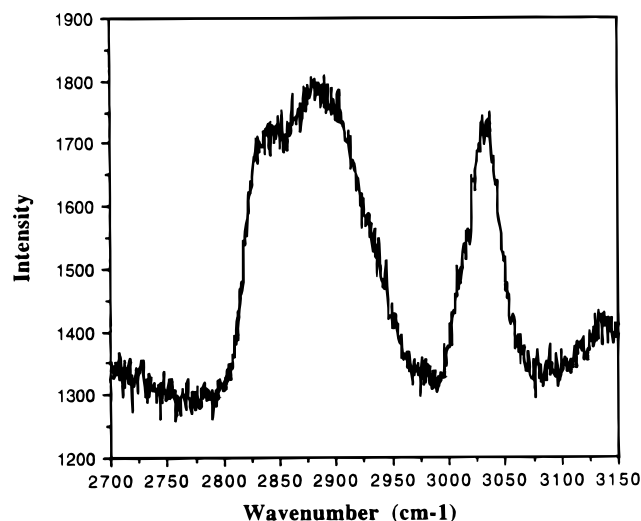A portion of the Raman spectrum (2700−3150 cm^{-1}) obtained from a 10 μm polystyrene particle immobilized in a

Figure 3. Raman spectrum from an optically trapped 10 μm polystyrene particle (7 mW, 488 nm, 100× objective and integration time of 10 s). The peak at 2900 cm^{-1} originates from the C−H stretch from the polystyrene backbone and microscope objective refractive index matching oil. The peak at 3050 cm^{-1} originates from the polystyrene phenyl C−H stretch.
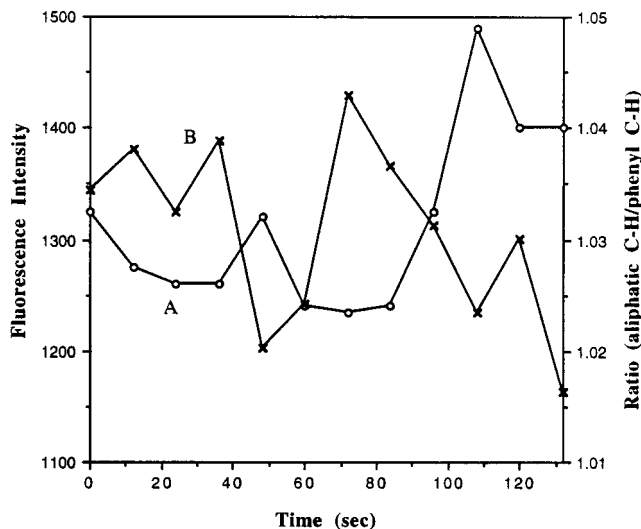

Figure 4. (A) Plot of the ratio of the C−H stretch intensity from the polystyrene backbone to the polystyrene phenyl C−H stretch intensity for an optically trapped 15 μm particle, over time (7 mW, 488.0 nm). (B) Change in fluorescence intensity observed with vibrational bands over the same time period.

488 nm optical trap is provided in Figure 3. The peak at 2900 cm^{-1} originates from the C−H stretch of the polystyrene backbone and from the C−H stretch from the backbone of the aliphatic compounds that comprise the microscope objective refractive index matching oil. This oil provides a large background signal which must be subtracted from the particle signal and unfortunately is required for efficient use of the objective lens system. The peak at 3050 cm^{-1} originates from the polystyrene phenyl C−H stretch.

A plot of the ratio of these two vibrational peaks over time is presented in Figure 4. The phenyl C−H intensity remains constant over the time period that the particle is immobilized in the trap and indicates that very little loss of the phenyl substituent of polystyrene occurs upon particle irradiation. The intensity of the 2900 cm^{-1} band however does vary with time while the particle is irradiated. Also plotted in Figure 4 is the intensity of fluorescence emission monitored near the two

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Raman bands. Although these data are from an individual particle, there is a clear trend present. The ratio of the C−H backbone stretch to the C−H phenyl stretch is high when the fluorescence intensity is low, and the ratio of the C−H backbone stretch to the C−H phenyl stretch is low when the fluorescence intensity is high. The variation of the signals over time is a result of melting and diffusional processes in the center of the polymer particle as well as movement of the particle (Brownian motion) in the optical trap. It is not possible to average the data from several particles due to the randomness of these events. Data from each particle investigated does provide the same trends.

These results demonstrate qualitatively that during irradiation of polystyrene particles immobilized in the optical trap there is a loss of hydrogen from the polystyrene backbone and an increase in the fluorescence intensity resulting from the formation of carbon double bonds. Direct measurement of the C=C stretch with these particles was unsuccessful most likely due to the fluorescence background and the limited number density of conjugated regions. Previous work[3] has demonstrated the reduced level of conjugation generated in particles suspended in aqueous solution, a result of both limited photochemical reaction in the polymer backbone and reaction participation by the solvent.

In an attempt to directly observe the C=C stretch nanometer sized silver clusters were generated on the surface of the particles and in the particle pores. This was accomplished by exposing polystyrene particles to a solution of silver nitrate for several hours and then irradiating with laser radiation. Immediately upon irradiation of the particles silver metal is formed. The presence of the silver metal negated our ability to optically trap these particles. Particles were therefore investigated after they had settled and become electrostatically immobilized on the glass coverslip surface. The glass coverslip served as the bottom window of the flow cell. It was anticipated that the presence of the silver clusters would provide surface enhancement for the C=C stretch. The extent of polymer conjugation would also be increased, a result of the silver ion reduction.

Photoreduction of silver ion in solution and at interfaces has been reported previously. Illumination of silver ion in aqueous solution with ultraviolet light (253.7 nm) leads to the photoreduction of the silver ion and production of hydrogen ion and hydroxyl radicals from water molecules.[6] The hydroxyl radical is very reactive and can abstract hydrogen from other compounds, such as alcohols resident in solution. Stable silver nanoparticles have also been produced by photoreduction in the presence of poly(N-vinyl pyrrolidone)[8] and in alcohol solutions.[6] One reported method for the production of silver nanoparticles as substrates for surface-enhanced Raman spectroscopy (SERS) has been the photoreduction of silver ions in an ionic sol.[7] When carbonyl-containing species are present, the reaction rate may be increased due to additional absorption of the UV light.[8,9] Another study has demonstrated that solutions of AgCl colloids with excess silver ion irradiated in the visible leads to the production of oxygen from water even in the absence of catalysts.[10] In addition, Barnickel and Wokaun coated polystyrene and poly(methyl methacrylate) particles with silver metal via chemical reduction schemes.[11] Micrographs provided in this reference as well as our own electron microscopy data (data not shown) clearly indicate silver "plating" at the particle surface. It is believed that the silver ion interacts with the phenyl substituents in polystyrene,[12] thus localizing the silver ion at the polystyrene particle interface. Since aqueous silver ions cannot penetrate deeply into the hydrophobic core of the
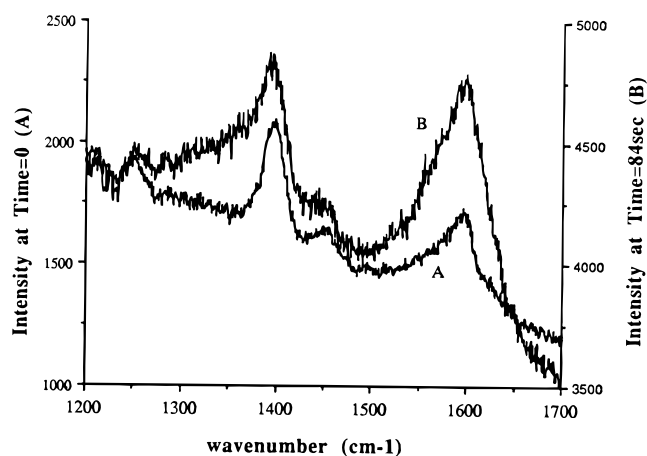

Figure 5. Raman spectrum from a 10 μm polystyrene particle containing silver nanoclusters. The peaks at 1400 cm^{-1} and 1600 cm^{-1} are the polystyrene phenyl C−H deformation and C=C stretch, respectively. Experimental parameters were the following: 6 mW 488 nm, and a 5 s integration.

polystyrene particle, it is reasonable to assume that the silver clusters generated are isolated at the particle surface and in the particle pore structure.

Raman spectra for 10 μm diameter polystyrene particles suspended in a solution containing silver ion and irradiated with 488 nm radiation are presented in Figure 5. The C=C stretch is observed at 1600 cm^{-1} along with the C−H deformation from the phenyl substituent at 1400 cm^{-1}. During exposure of the particles the phenyl C−H deformation changes little in intensity but does broaden considerably, presumably as a result of the presence of the silver particles. The intensity of the C=C stretch increases in both intensity and width over time, indicating an increase in the presence of carbon double bonds and distribution in conjugation lengths, in the polymer backbone. In previous investigations[13] of benzene and benzene derivatives little shift in the 1600 cm^{-1} is observed with ring substitution. Resonance Raman study of β-carotene and its synthetic homologues[14] reveals a shift in the C=C stretching frequency from above to below 1500 cm^{-1}, as conjugation length increases. In addition, resonance Raman investigations[15,16] of *trans*-polyphenylacetlyenes indicates and absence of the phenyl stretch at 1600 cm^{-1} and the appearance of a broad vibrational band at 1550 cm^{-1}. A decrease in the Raman shift in this case, is presumed to be related to the significant resonance conjugation present between polymer side group (phenyl) and the polymer backbone. Further investigation of both the SERS and resonance Raman spectra of these conjugated polystyrene systems is ongoing.

A time-dependent plot of the ratio of the C=C intensity to the C−H deformation intensity is presented in Figure 6 along with an overlayed plot of fluorescence intensity monitored near these Raman peaks. These plots increase simultaneously with time, indicating that increases in fluorescence intensity occur in conjunction with the generation of conjugation in the backbone of polystyrene.

Signal enhancements of 10^4−10^6 have been observed for SERS-active substrates.[17] The experimentally observed enhancement in this case is difficult to quantify since the vibrational bands were not observed without enhancement. Estimates for this enhancement are between 1000 and 10 000. The photoreduction of the silver ion in the presence of polystyrene is observed to increase the rate of fluorescence intensity generation as well as significantly increase the maximum intensity from individual particles. The increase is in excess of 400-fold,[18] and must be related to the extent of
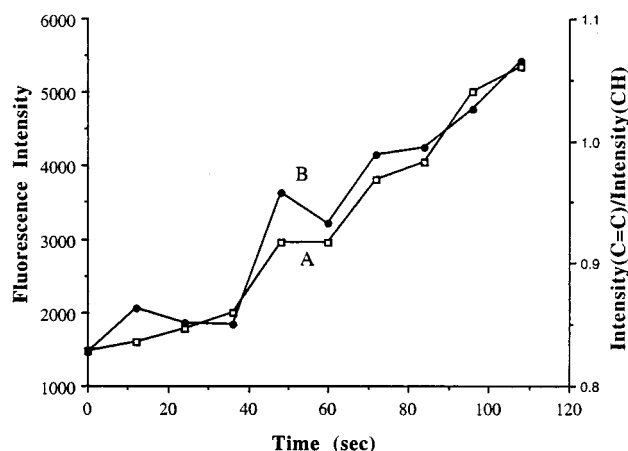
Figure 6. (A) Time-dependent change for the C=C stretching intensity from the 10 μm particle in Figure 5. (B) Time-dependent change for the fluorescence intensity from the 10 μm particle in Figure 5.

polymer conjugation. The mechanism for silver reduction most likely includes increases in the number of radicals in the polymer backbone which would lead to increased amounts of conjugation. As the number of conjugated sites increases throughout the particle, resonance enhancement in addition to surface enhancement can occur. It is unlikely that the full volume of the particle is providing the SERS signal, since we believe only the outer surface has significant contact with the silver metal, while the full volume of the particle is providing fluorescence intensity and resonance Raman intensity.

This work raises several important questions. First, what is the mechanism of silver reduction in the presence of polystyrene when irradiated with visible radiation? Second, to what extent is there electron transfer between polystyrene and silver ions as conjugation proceeds throughout the polymer backbone. Yonezawa[19] et al.[19] have demonstrated photoreduction of silver in the visible with uranine as the photosensitizer and zinc oxide as a solid electron-transfer mediator. Direct uranine silver reduction was not apparent. Understanding and control of polystyrene metal reduction mechanisms could have significant practical importance.

The results presented in this paper demonstrate that as the fluorescence intensity increases in a polystyrene particle, the Raman signal from the aliphatic C—H stretch decreases and the Raman signal from the C=C stretch increases. The combination of the decrease in the C—H stretch from the polystyrene backbone and the increase in the C=C stretch in the Raman spectrum is convincing evidence that the fluorescent emission observed for these particles is a result of hydrogen abstraction from the polystyrene backbone and the subsequent formation of double bonds leading to extended conjugated regions.

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