Macromolecules

Volume 22, Number 4 April 1989

Synthesis and Characterization of Polystyrene Latex Particles

Michael R. Ferrick, James Murtagh, and J. K. Thomas*

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556.

Received April 1, 1988

ABSTRACT: Styrene has been polymerized in a CTAB micellar system. A variety of small micelles containing polystyrene are obtained that are stable to dilution. This paper describes the experimental conditions for preparing polymerized systems of precise dimensions. Photoprobing studies with pyrene comment on the nature of the hydrophobic polymerized core of the particles and on the local rigidity of this region.

Introduction

In earlier work, polystyrene and divinylbenzene were polymerized in microemulsion[2] and in vesicle[3] systems, where the polymer formed either the core of the microemulsion or was interlaced with the surfactant molecules of the vesicle. The kinetic properties of these systems were markedly affected by the presence of the polymer, mainly due to the restriction of motion caused by the polymer network. In recent work,[4] a polymerized micelle has been reported which is polymerized close to the head groups. This system also shows increased rigidity compared to a nonpolymerized micelle, but mainly for photoreactions that occur in the vicinity of the surfactant head groups. At this stage, it is desirable to produce small polymerized micellar systems that are anchored or constrained close to the core of the micelle, i.e., very small polystyrene latex particles.

Polystyrene and other latex particles are produced commercially for a wide variety of uses.[6-9] The kinetics of the process are well established, and the sizes of the latex particles can be tailored for particular end uses. The smallest commercially available latex particles are on the order of 300 Å in diameter. Lattices are usually produced from emulsion systems, and earlier work from this laboratory reported lattices produced from a microemulsion system.

Production of latex particles from a micellar system, as described in this paper, is a convenient and efficient way to produce a range of uniform particle sizes and molecular weights, especially of small latex particles. Preparation of the styrene–surfactant micellar system is facile, the yield of the polystyrene latex particles is satisfactory, and the size of the latex particle and polystyrene molecular weight can be controlled by the initiator concentration. The latex particle size can approach that of a swollen micelle.

Experimental Section

Styrene from Aldrich Chemical Co. was vacuum distilled prior to use; cetyltrimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC) were from BDH and used as received; 2,2′-azobis(2-methylpropionitrile) (AIBN) from Kodak was recrystallized from methanol; pyrene was obtained from Aldrich and recrystallized from ethanol prior to use. Other chemicals were reagent grade and used as received.

Absorption spectra were measured on a Perkin-Elmer 552 spectrophotometer, and fluorescence spectra were measured on a Perkin-Elmer MPF 44B spectrofluorimeter. Excited state lifetimes were measured by using laser flash photolysis equipment, which has been described previously.

The Rayonet photoreactor from Rayonet Corporation consists of a cylinder containing fluorescent UV light tubes, of either 254 or 350 nm. The sample is placed in the center of the tubes; a cover is placed on the cylinder for photolysis. A ventilation fan maintains the reaction at approximately room temperature. For the reactions described in the paper, the fan was turned off, resulting in a temperature in the photoreactor around 35 °C. The starting styrene–CTAB–AIBN solutions were thoroughly mixed by using a stir bar and magnetic stirring before initiation of the reaction in the photoreactor. While in the photoreactor, however, no stirring was used.

Synthesis of Particles. The polystyrene latex particles were synthesized from a micellar system using cetyltrimethylammonium bromide (CTAB) as a surfactant. The concentrations of styrene and CTAB were both 0.1 M. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was used as a free-radical initiator. CTAB alone forms spherical micelles, which results in a solution with a viscosity like that of water, but the solution of styrene and CTAB was more viscous, suggesting the presence of rodlike micelles. Similar effects have been reported previously, in particular with added electrolyte.[10] The initiator concentration can be varied in order to produce different particle sizes and polystyrene molecular weights. The solution was deoxygenated by using nitrogen gas bubbling before being subjected to 350-nm light in a Rayonet photoreactor. The UV light produced the free-radical form of AIBN, which initiated the polymerization. The reaction was complete within 45 min as determined by monitoring the reaction mixture absorbance on a specrophotometer. In a typical preparation, the absorbance at 250 nm went from 2.6 to 1.9. The product solution had a viscosity of water that suggested the presence of spherical particles. Yields were good on all systems ranging around 50%.

Isolation of Polystyrene from the Latex Particles. After polymerization, the polystyrene produced was recovered by diluting the reaction mixture 1:10 in methanol. The CTAB and

Table I
Summary of Synthesis of Polystyrenes[a]

[AIBN], M	MW	particle radius, Å	$\bar{N}$[b]	% yield
1×10^{-5}	2.4×10^{6}	273	22	62
1×10^{-5}	1.9×10^{6}	286	32	50
2×10^{-5}	1.6×10^{6}	222	17	58
1×10^{-4}	8.3×10^{5}	183	19	50
1×10^{-3}	1.0×10^{5}	130	57	56
1×10^{-2}	9.0×10^{3}	54[c]	46	36

[a] CTAB = 1×10^{-1} M; styrene = 1×10^{-1} M; AIBN initiator; 30 min of 350-nm UV light. [b] $\bar{N}$ is the number of polymer molecules per particle. [c] Estimated from measurements made on an electron micrograph.

Table II
Summary of Pyrene Fluorescence Experiments

	ratio of peak III to peak I (III/I)			
[CTAB], M	CTAB only	286-Å PS	273-Å PS	54-Å PS
2×10^{-2}	0.84	0.90	0.89	0.86
1×10^{-2}	0.82	0.88	0.89	0.85
5×10^{-3}	0.81	0.89	0.90	0.85
2×10^{-3}	0.80	0.89	0.91	0.84
1×10^{-3}	0.79	0.89	0.90	0.81
5×10^{-4}	0.60	0.89	0.93	0.78
2×10^{-4}	0.60	0.90	0.93	0.74
1×10^{-4}	0.63	0.89	0.92	0.71

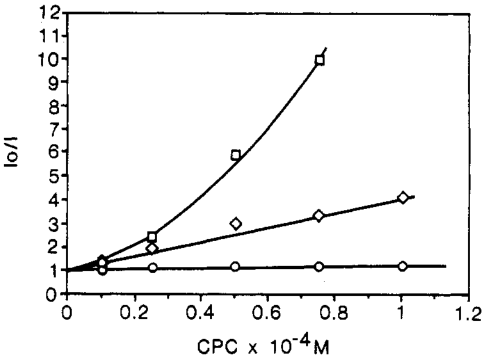

Figure 1. Quenching of excited pyrene by cetylpyridinium chloride, CPC, in polystyrene in micelle aggregates. (□) 2×10^{-3} M CTAB, 1×10^{-5} M pyrene. (◇) 54-Å-radius particle, 2×10^{-3} M CTAB, 1×10^{-5} M pyrene. (○) 273-Å-radius particle, 5×10^{-4} M CTAB, 2.5×10^{-6} M pyrene.

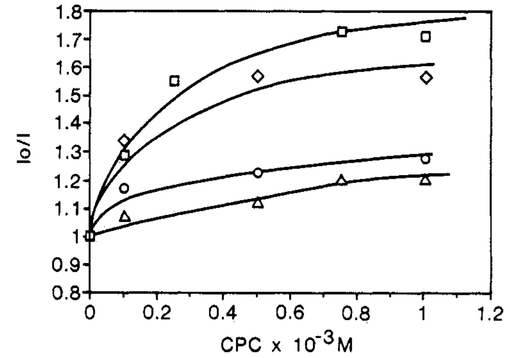

Figure 2. Extension of Figure 1 to higher [CPC]. All are solutions of the 273-Å-radius particle. (□) 1×10^{-2} M CTAB, 5×10^{-6} M pyrene. (◇) 5×10^{-3} M CTAB, 2.5×10^{-5} M pyrene. (○) 2×10^{-3} M CTAB, 1×10^{-5} M pyrene. (△) 5×10^{-4} M CTAB, 2.5×10^{-6} M pyrene.

low molecular weight styrene are soluble in 90% methanol, while polystyrene is not. The precipitated polystyrene was recovered by centrifugation, washed several times with methanol, and allowed to dry. The weight of this recovered polystyrene was used for calculation of the yield. Solutions of this polystyrene in tetrahydrofuran were then prepared for characterization by gel permeation chromatography.

Characterization of Polystyrene Latex Particles. Determination of Polystyrene Molecular Weights and Particle Sizes. Molecular weights were determined by gel permeation chromatography using Waters linear Ultrastyragel columns with a tetrahydrofuran mobile phase (Aldrich, HPLC grade). The columns were calibrated using polystyrene standards, MW from 800 to 1 860 000 (Supelco). Refer to Table I for results. Latex particle sizes were determined by laser light scattering (Nicomp) and verified by transmission electron microscopy. The 273-Å-radius particle gave a typical set of data with a standard deviation of ±0.36 Å and $x^2 = 0.84$. The distribution of particle sizes and polystyrene molecular weights were very narrow in all systems. The lowest [AIBN] produced the largest particles containing the highest molecular weight polystyrene, and the highest [AIBN] produced the smallest particles with the lowest molecular weight polystyrene. This result is due to the greater degree of termination taking place with the higher [AIBN]. Intermediate particle sizes and polystyrene molecular weights can be produced using [AIBN] in between these extremes.

Results and Discussion

Latex Particle Photochemistry. Pyrene was used as a fluorescent probe in order to further characterize the polystyrene latex particles. When pyrene is excited with light energy, it produces a steady-state emission spectrum which is very structured. The ratio of peak III to peak I of pyrene's fluorescence spectrum is a sensitive indicator of the polarity of pyrene's environment.[5] Thus, the spectrum gives information about pyrene's environment and its mobility in that environment. A more polar environment produces a lower III/I ratio. Table II summarizes pyrene fluorescence data for CTAB micelles and selected latex particles in CTAB solution. The particles are identified by their radius in angstroms. Each system started with 2×10^{-2} M CTAB and 1×10^{-4} M pyrene, and spectra were obtained for a water dilution series of each system to 1×10^{-4} M CTAB. Dilution of the CTAB only solution resulted in a change in the pyrene III/I ratio due to the transition from surfactant micelles to free molecules. Once the solution was diluted below the critical micelle concentration (CMC) of CTAB (0.9×10^{-3}) mol/dm^3,[11] there were only free molecules, and pyrene's III/I ratio in this system was similar to the III/I ratio of pyrene in pure water.[5] Dilution of the large (273-Å radius) particles did not display this drop in the III/I ratio; the pyrene remained in a less polar environment such as the interior of a latex particle. This demonstrated that the particles do stay intact upon dilution, as has been shown for microlatex particles generated from microemulsion systems.[2] The III/I ratios which were obtained for the dilution series of the small (54-Å radius) particles were in between those of the CTAB only case and the large particles. This result can be interpreted in one of two ways. Either the smaller latex particles are less stable upon dilution than the large ones or more of the pyrene is closer to the more polar surface of the particles because of their small size.

Cetylpyridinium chloride (CPC) can be used as a quencher of pyrene's fluorescence. The steady-state spectrum of pyrene's fluorescence was obtained for various particle systems with increasing concentration of the quencher CPC. Figures 1 and 2 summarize these data. I_0/I is the ratio of pyrene fluorescence intensity of the solution without quencher to the fluorescence intensity of the solution with a concentration of quencher which is given on the x axis. The y axis is therefore a measure of quenching.

The CTAB only system showed an increasing effect of quenching with increasing quencher concentration as can be seen by the upward curve of the plot. This behavior is typical of micelle systems. The two latex particle systems, on the other hand, displayed a leveling off of the effect of the quencher. In order for the pyrene to be quenched, it and/or the quencher must move in the particle or micelle. Reactant movement is not hindered in the CTAB only system, but movement is restricted in the latex particle systems. In the particle systems, only pyrene in the CTAB surface layer of the particles is quenched initially, the pyrene in the interior of the particles exhibiting no quenching by the CPC. More pyrene fluorescene quenching was observed in the smaller particle system than the larger, and this points to the fact that the smaller particles are less rigid. Similar effects have been observed previously with polymerized microemulsions.[2]

Conclusions

This work points to a relatively easy and convenient method of producing stable polystyrene latex particles which have a variety of useful properties. The 54-Å-radius particle is one of the smallest of these kinds of particles ever reported. The different size particles can be reproduced with accuracy and with narrow size distributions. It is noteworthy that the particles do not dissociate on dilution. This indicates a strong hydrophobic interaction between the polystyrene and the CTAB surfactant tails. These systems are convenient hosts for introducing hydrophobic photosystems into a hydrophilic environment.

Registry No. CTAB, 57-09-0; CPC, 123-03-5; AIBN, 78-67-1; polystyrene, 9003-53-6.

References and Notes

(1) The authors thank the NSF for support of this work.
(2) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981,** *103,* 4279; **1982,** *104,* 5868.
(3) Murtagh, J.; Thomas, J. K. *Faraday Discuss. Chem. Soc.* **1986,** *81,* 127.
(4) Chu, D.-Y; Thomas, J. K. *Macromolecules* **1987,** *20,* 2133.
(5) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977,** *99,* 2039.
(6) Karamata, D. *J. Ultrastruct. Res.* **1971,** *35,* 201.
(7) Snyder, S.; Rhodes, P. H.; Miller, T. Y.; Micale, F. J.; Mann, R. V.; Seanan, G. V. F. *Sep. Sci. Technol.* **1979,** *21,* 151.
(8) Ottewill, R. H.; Shaw, J. N. *J. Electroanal. Chem.* **1972,** *37,* 133.
(9) Cantarero, L. A.; Butler, J. E.; Osborne, J. W. *Anal. Biochem.* **1980,** *105,* 375.
(10) Winsor, P. *Chem. Res.* **1968,** *68,* 1. Kalyanasundaram, K.; Grätzel, M.; Thomas, J. K. *J. Am. Chem. Soc.* **1975,** *97,* 3915. Anacker, E. W. *J. Phys. Chem.* **1958,** *62,* 41.
(11) Ekwall, P. J. *Colloid Interface Sci.* **1971,** *35,* 519. Critical Micelle Concentrations of Aqueous Surfactant Systems. NSRDS-NBS 36, 1971; NBS, Washington, DC.

Synthesis and Characterization of a Novel Conducting Coordination Oligomer

Gregory K. Rickle

Central Research, The Dow Chemical Company, Midland, Michigan 48674.

Received July 6, 1987

ABSTRACT: Copper(I) chloride, 1,4-diaminoanthraquinone, and oxygen react to give a crystalline electrically conducting coordination oligomer. The oligomer is believed to consist of alternating 1,4-diaminoanthraquinone units connected by mainly (μ_2-dioxo)dicopper units and is of low molecular weight, DP = 2–4. The oligomer is oxidatively and thermally stable, insoluble, and infusible but possesses interesting electronic properties. It is an intrinsic p-type semiconductor having a conductivity of 0.10–0.60 S/cm and an activation energy of 0.090 eV. Various analogues of the coordination oligomer were made by replacing both the copper and the 1,4-diaminoanthraquinone in the oligomer synthesis. All of the analogues have lower conductivity and are p-type conductors except the copper(II) analogue which is n-type. The coordination oligomer is effective as a catalyst for the oxidative polymerization of 2,6-dimethylphenol to poly(2,6-dimethylphenylene oxide) of narrow molecular weight distribution (heterogeneity index = 1.1), and as an electrocatalyst in the oxychlorination of ethylene to give 1,2-dichloroethane.

Introduction

Conducting organic materials have received considerable attention several times in the past. In 1960 Acker et al.[1] discovered complexes of tetracyanoquinodimethane (TCNQ) and electron donors that form crystalline charge-transfer conductors. In 1964 Little[2] proposed the possibility of room temperature superconductivity with conjugated polymers. No room temperature superconductors were discovered and interest waned until MacDiarmid, using the Shirakawa method for polymerizing acetylene, oxidized polyacetylene films with arsenic pentafluoride.[3,4] The oxidized polyacetylene films had a conductivity of 200 S/cm, comparable to mercury on a weight basis. Since 1977 several polymers have been found to be highly conducting when oxidized and/or reduced. These include poly(*p*-phenylene),[5] poly(phenylene sulfide),[6] poly(pyrrole),[7] and phthalocyanine-containing polymers.[8-10] The oxidation and/or reduction produces charged species that are responsible for conductivity. At ambient conditions these highly reactive ions can react with moisture and/or oxygen destroying the conductivity.[11,12] Incorporation of oxidant or reductant into the polymer structure also reduces the conductivity-to-mass ratio.

Introduction of less reactive species into the conducting pathway which can exhibit multiple oxidation states was thought to be one method of producing a stable, intrinsically conducting polymer. The multiple oxidation state species could serve as an internal oxidant or reductant so the polymer would require no oxidation or reduction by external reagents to achieve a conducting state. Therefore the conductivity-to-mass ratio would be increased.

In this paper the synthesis and characterization of a novel conducting coordination oligomer, oligo[[(μ_2-dioxo)dicopper 1,4-diaminoanthraquinone]-*co*-[(μ_2-oxo)dichlorodicopper 1,4-diaminoanthraquinone]] (ODOD) having the proposed structure depicted in Figure 1, and some analogues will be discussed. The oligomer is stable at ambient conditions and is an intrinsic semiconductor and catalyst.

Results and Discussion

Synthesis and Characterization of ODOD. Planar coordination polymers consisting of difunctional ligand

0024-9297/89/2222-1517$01.50/0 © 198' American Chemical Society