Sonochemical Production of Fluorescent and Phosphorescent Latex Particles

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Abstract: A novel method for producing nanosized polymer latex particles doped with fluorescent and phosphorescent solutes is described. Methyl methacrylate monomer (10 wt %) containing either pyrene, 4-dicyanomethylene-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (DMDP), or 1-bromonaphthalene was ultrasonically dispersed in water and simultaneously polymerized to produce ~60 nm diameter latex particles. A fluorescence spectroscopic examination of the latex dispersion containing either pyrene or DMDP showed that the solutes were not covalently bound to the polymer and that they were embedded in a highly viscous environment possessing a low polarity (dielectric constant on the order of 2). The fluorescence lifetime of the pyrene in the core of the poly(MMA) latex was found to be 520 ns, irrespective of the oxygen concentration in the dispersion. Room-temperature phosphorescence was observed from 1-bromonaph-thalene, with a lifetime of 2.0 ms in an argon atmosphere. In the presence of air, phosphorescence was still observable although with a partially reduced emission intensity.

Introduction

The production of composite polymer particles by the incorporation of organic molecules and the encapsulation of inorganic powders into polymer particles has led to several advances of both academic and commercial interest.[1,2] For example, the incorporation of fluorescent molecules into small particles accelerated the development of molecular probes that have applications in living cell biology, flow tracing, and fluid mechanics.[3]

There are a number of reports in the scientific[4−9] and in the patent literature[10−12] on methods for producing light-emitting polymer particles. The incorporation of fluorescent chromophores into polymer particles is usually conducted using a functionalized and polymerizable organic molecule that becomes an intrinsic part of the polymer backbone.[4−7] Alternatively, hydrophobic fluorescent chromophores can be incorporated into the polymer phase during emulsion or solution polymerization,[8] or adsorbed into the latex particles once they are formed.[9]

Polymer coated pigments are often produced by a conventional emulsion polymerization process using a semicontinuous feed to maintain monomer-starved conditions.[13] Recent methods for the encapsulation of inorganic pigments have employed the dispersing property of ultrasound in the mixing phase to deagglomerate the suspended pigment, thereby increasing the probability of monomer coating onto individual particles prior to polymerization in an otherwise conventional miniemulsion polymerization process.[14−18] The technique of phase separation of polymer solutions by varying the solvency to encapsulate inorganic powders also uses ultrasound to break up agglomerates.[19]

It is known that ultrasound can be used as the initiating source to produce latex particles in a free-radical emulsion polymerization process.[20−22] The free radicals are produced during acoustic cavitation that involves the formation, growth, and implosive collapse of microbubbles. At an ultrasound frequency

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of 20 kHz, the mean temperature realized upon microbubble collapse is 4300 ± 200 K.[23] In aqueous medium, these high localized temperatures lead to the thermal decomposition of water within the cavities into hydrogen atoms and hydroxyl radicals, which initiate the polymerization process.

In recent publications by Wang et al.,[24,25] it was reported that polymer/inorganic composites were prepared through ultrasonically initiated emulsion polymerization. The encapsulation of hydrophilic nanoparticles of SiO_2, Al_2O_3, and TiO_2 into poly-(butyl acrylate) was shown directly by transmission electron microscopy and indirectly by Fourier transform infrared spectroscopy.

In this paper, we show that ultrasound induced radical production can be used to synthesize latex particles with the simultaneous incorporation of unmodified fluorescent and phosphorescent molecules. There are several distinct advantages of this synthetic technique over other methods of preparing fluorescent latex. Nanosized latex particles (~60 nm) are readily produced. The particle size of the sonochemically produced latex is similar to that produced during chemically initiated microemulsion polymerization,[26] however, at a relatively lower surfactant concentration. Also, ultrasound initiated polymerization can be conducted at room temperature, whereas chemical or thermal initiation is often carried out at elevated temperatures.

Experimental Section

Reagents. All solutions were prepared using methyl methacrylate (MMA) monomer (supplied by Dulux, Australia), sodium dodecylsulfate (SDS) (BDH chemicals), and Milli-Q water. The monomer was filtered through basic aluminum oxide (Aldrich) twice to remove the inhibitor. Research grade samples of pyrene and 1-bromonaphthalene (Aldrich) and 4-dicyanomethylene-2-methyl-6-(*p*-diemthylaminostyryl)-4*H*-pyran (DMDP) (Exciton Chemical Co. Inc.) were used as received.

Latex Synthesis. A conventional 19 mm diameter 20 kHz horn sonifier (Branson 450) was inserted into a custom-built reaction vessel. The experimental apparatus is described in detail elsewhere.[20] The power generated at the tip of the horn and absorbed by the solution was measured by calorimetry to be 8 W cm^{-2}. The concentration of MMA monomer was 10 wt % and of SDS was 0.7 wt % in water for all of the batch polymerization reactions performed. The incorporation of the fluorescent/phosphorescent molecules was achieved by dissolving these molecules in the monomer phase prior to preparing the o/w emulsion. The maximum amount of approximately 0.4 wt % in the monomer phase of the luminescent solute was used for convenience. However, higher amounts should be able to be used provided the solutes do not interfere with the polymerization of the monomer.

In a typical preparation, 5 g of monomer containing the soluble chromophore, 0.35 g of SDS, and 45 g of water was thoroughly deaerated by gently purging with high purity argon for 45 min in the reaction vessel at room temperature. Thereafter, the argon gas stream was removed from the emulsion and was allowed to pass over the surface of the liquid mixture. The polymerization reaction was then initiated by subjecting this mixture to continuous sonication. The use of an ice water bath helped maintain the solution temperature at 25 ± 5 °C.

Monomer Conversion. Small samples of the reaction mixture were periodically removed with a syringe, via a sampling inlet, throughout the reaction. The samples were left to air-dry overnight and were then
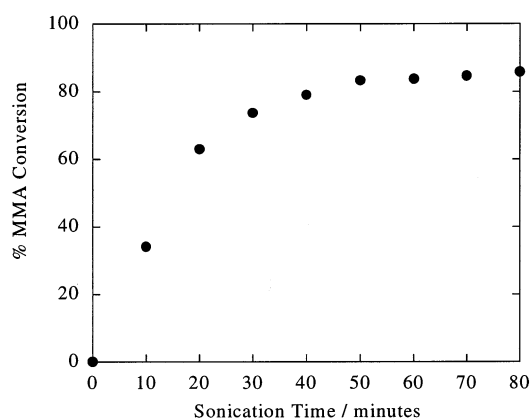

Figure 1. MMA monomer conversion (±4%) as a function of sonication time in the presence of 25 mM SDS.

oven-dried at a moderate temperature (<80 °C) for 3 h. The dried samples were used to monitor the progress of the reaction by gravimetric analysis at room temperature. The error associated with this measuring protocol was approximately 4%.

Particle Sizing. Particle size averages (volume average diameters (d_V)) were determined using a Malvern (Autosizer) dynamic light-scattering instrument (4800 spectrometer). The samples were diluted in Milli-Q water, and measurements were taken at a scattering angle of 90 °C and at a solution temperature of 25 °C.

Molecular Weight Determination. Polymer samples dissolved in HPLC grade tetrahydrofuran (THF) were analyzed for molecular weight using gel permeation chromatography (GPC) using a Waters HMW7 Styragel column attached to a Waters 410 differential refractometer. Data were collected and processed on a Waters Millenium 32 work station calibrated against polystyrene standards.

Latex Surface Potential. The surface potentials on the latex particles were derived from microelectrophoresis measurements of the particles in solution using a Coulter DELSA-440 (Doppler electrophoretic light-scattering analyzer). The measured mobilities were converted to zeta potential using the Helmholtz−Smoluchowski equation.[27]

Spectroscopy. Absorption spectra were recorded on a Carey Bio50 (Varian) UV−vis spectrophotometer. The fluorescence and phosphorescence spectra were recorded on a CareyEclipse (Varian) fluorescence spectrophotometer. Fluorescence lifetimes were measured using a 337 nm nitrogen laser source (Laser Photonics LN300C; pulse width 5 ns) to excite the fluorescent solutes. The repetition rate of the instrumentation was 30 Hz. The emission intensity was detected by a photomultiplier, recorded on an oscilloscope, and transferred onto a computer for analysis. The phosphorescence lifetime measurements were performed on a Hitachi F-4500 fluorescence spectrophotometer.

Results and Discussion

Sonochemical emulsion polymerization has been shown to be a convenient method for producing high molecular weight, nanosized latex particles.[28] The mechanism for polymerization has been concluded to be via a miniemulsion polymerization process that involves the direct polymerization of small monomer droplets that are produced by the shearing forces generated in the emulsion by acoustic cavitation.[28] Ultrasonically initiated emulsion polymerization of MMA was readily achieved at room temperature, and a typical percentage conversion as a function of sonication time is shown in Figure 1. On complete conversion of the MMA monomer, a colloidal dispersion of poly(MMA)

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Table 1. Physical Properties of the Poly(MMA) Latex Produced by Ultrasound Initiated Emulsion Polymerization

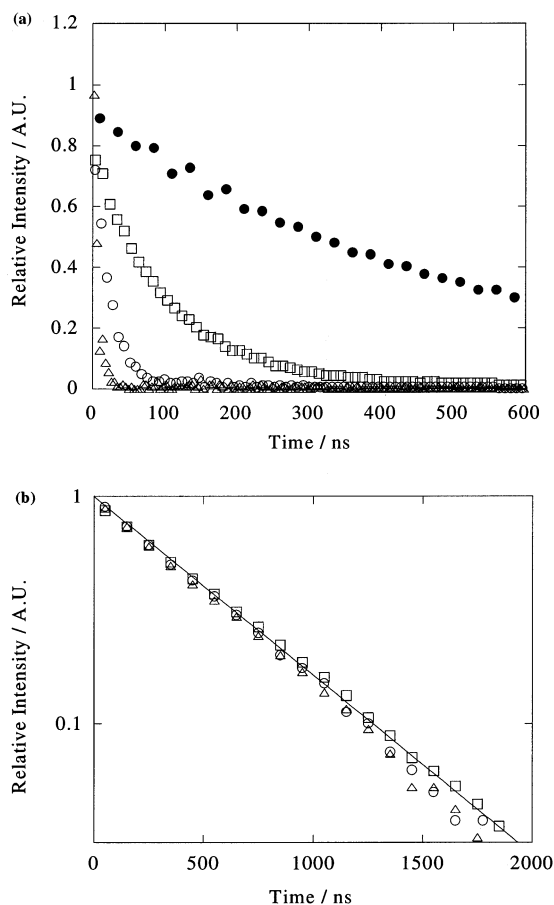| [SDS]/ M	M_W/ ($\times 10^6$) g mol^{-1}	d_V/nm (± 10 nm)	zeta potential/mV (± 10 mV)	
			prepared	dialyzed
0.025	3.6	64	-38	-12
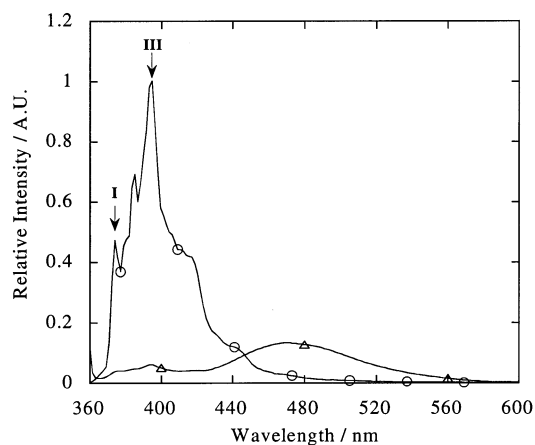
Figure 2. Fluorescence emission spectra of pyrene in the MMA emulsion ($\triangle$) and in the poly(MMA) latex particles ($\bigcirc$). The 10 wt % monomer phase contained 2×10^{-2} M pyrene and was emulsified in a 25 mM aqueous SDS solution. Excitation was at 350 nm. The peaks labeled I and III are referred to in the text.

latex was formed. The main characteristics of the poly(MMA) latex produced are reported in Table 1.

To explore the potential applications of this sonochemical latex formation technique, we have investigated the incorporation of fluorescent/phosphorescent molecules by dissolving these molecules in the monomer phase prior to preparing the o/w emulsion. The physical properties of the ultrasonically produced latex particles, such as particle size, molecular weight, etc., were not affected by the incorporation of either the fluorescent or the phosphorescent solutes in the monomer at the concentration of the solutes used ($<2 \times 10^{-2}$ M).

Pyrene was chosen as a representative fluorescent solute as its fluorescence characteristics have been well studied.[29–31] The emission spectra, observed from an o/w MMA emulsion and from an aqueous dispersion of ultrasonically produced poly-(MMA) latex particles, both containing pyrene, are shown in Figure 2. In the emission spectrum observed from the o/w emulsion, the characteristic structured band from vibronically excited molecular pyrene (P*) is observed at shorter wavelengths (<440 nm). It is accompanied by a broad, structureless emission band at longer wavelengths (>440 nm) due to emission from pyrene excimer (P$_2$*). In the emission spectrum observed from the latex particles, there is a relative enhancement in the P* emission intensity and no emission from P$_2$*.

To gain some information about the local environment within monomer droplets and latex particles, the fluorescence lifetimes of P* were measured in the o/w emulsion, and in the latex particles in their as-prepared state, when exposed to atmospheres of oxygen, air, and nitrogen (i.e., under varying oxygen concentrations). The results are shown in Figure 3.

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Figure 3. (a) Pyrene (2×10^{-4} M) fluorescence decay in the monomer emulsion (10 wt %): air ($\bigcirc$), oxygen ($\triangle$), and nitrogen ($\square$) atmospheres. The fluorescence decay in air is shown for the latex ($\bullet$) and is representative of the decay in all atmospheres. Excitation was at 337 nm, and fluorescence emission was monitored at 400 nm. (b) Constant first-order decay kinetics observed in latex particles exposed to the atmospheres listed in (a).

Table 2. Fluorescence Data for 2×10^{-4} M Pyrene in a 10 wt % MMA Emulsion and Aqueous Latex Dispersion

component	atmosphere	fluorescence $\tau_f/(\pm 5)$ ns	
		emulsion	latex
2×10^{-4} M pyrene in MMA monomer phase	air	20	524
	oxygen	7	524
	nitrogen	118	524

The fluorescence decay rate of excited pyrene within the monomer droplets was strongly affected by the oxygen content of the emulsions. The fluorescence lifetimes in the emulsions are given in Table 2. If it is assumed that the oxygen content within a monomer droplet is typical of the solubility of oxygen in an organic solvent ($8-10$ mM[32]), a second-order quenching constant of about 1×10^{10} M^{-1} s^{-1} can be calculated using the data in Table 2. This second-order rate constant is comparable to those obtained for the oxygen quenching of P* in bulk solvents and indicates that there is no restriction to the diffusion of oxygen in the monomer droplets of the o/w emulsion.[33]

In contrast to the emulsion case, when pyrene is within the polymer latex particles, the fluorescence decay of P* is

(32) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.
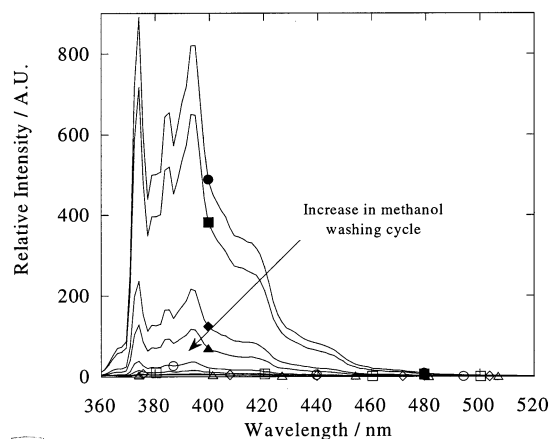(33) Thomas, J. K. *Acc. Chem. Res.* **1977**, *10*, 133.

Figure 4. Pyrene emission in the poly(MMA) latex following consecutive methanol washings. The initial concentration of pyrene in the poly(MMA) was 2×10^{-2} M.

independent of the oxygen content of the dispersion. Also, the lifetime of the emission is considerably longer than it was under any of the conditions examined in the emulsion and is comparable to that obtained for P* when it is in an inert environment.[30]

To investigate whether pyrene was present in the core of the latex particles or adsorbed to the surface of the particles, the water-soluble fluorescence quencher Tl$_2$SO$_4$ (up to 8 mM) was added to the latex dispersion. The lifetime of the pyrene fluorescence and the emission intensity was the same in the presence and absence of this quencher,[34] which indicates that pyrene resides in the core of the latex particles.

The characteristics of the emission spectrum of the pyrene within the latex particles suggest that pyrene is physically incorporated in the polymer and not covalently bound. This conclusion was supported by the following experiment. An aliquot of pyrene-doped poly(MMA) latex was flocculated out in methanol (the latex is insoluble in methanol). The clear methanol supernatant was removed, the latex was redispersed in water, and the fluorescence spectrum was recorded. This process was repeated for several methanol "washings" of the latex, and successive spectra are shown in Figure 4. It can be seen in these spectra that after each consecutive methanol wash of the latex, the relative fluorescence yield of the pyrene decreases. The result that pyrene elutes into the methanol phase clearly indicates that the pyrene is physically incorporated in the latex particles.

As the pyrene is physically bound in the latex particles and no excimer emission is observed at relatively high local concentrations of pyrene (2×10^{-2} M), it can be concluded that the core environment of the latex particles must be highly viscous. A lower limit to the viscosity can be calculated using the diffusion relationship

$$k_{diff}(M^{-1} s^{-1}) = \frac{8000RT}{3\eta} \qquad (1)$$

where the viscosity (η) is in units of kg m^{-1} s^{-1} (1 P = 10^{-1} kg m^{-1} s^{-1}). If it is assumed that at a pyrene concentration of

(34) The quenching rate constant of Tl$^+$ with p* in water is 5×10^9 M^{-1} s^{-1} taken from ref 33. At 8 mM of Tl$^+$, the lifetime of P* would be reduced to about 25 ns. It should be noted that as the latex particles are negatively charged, the concentration of Tl$^+$ should be even greater at the surface of the particles as compared with that of the bulk solution.
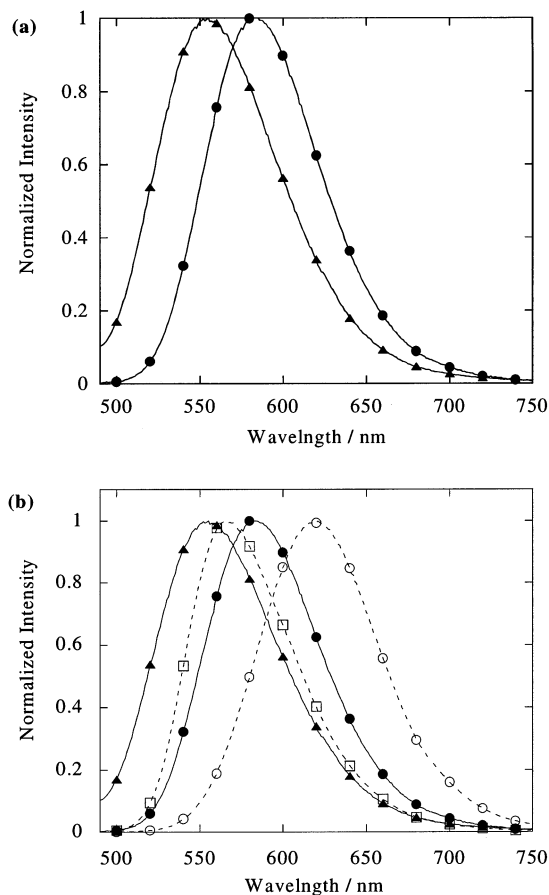
Figure 5. (a) Fluorescence emission of DMDP in the MMA monomer (●) and the corresponding poly(MMA) latex particles (▲). Excitation was at 470 nm. (b) Fluorescence emission spectra of DMDP in a series of solvents: poly(MMA) latex (▲); chloroform (□); MMA monomer (●); and methanol (○). Excitation was at 470 nm.

2×10^{-2} M, the collision rate of P* with pyrene is less than 1% of the observed fluorescence decay rate (with a rate constant of $1/(520 \times 10^{-9})$ s^{-1}), a lower limit for the viscosity of 6500 cP can be calculated.

It is well known that the III/I ratio of the pyrene bands shown in Figure 2 changes depending on the nature of the solvent, and therefore the value of the ratio provides information on the local environment experienced by the pyrene.[29] The III/I peak ratio decreases with increasing dipole moment of the solvent, and for solvents with the same dipole moment, the one with the higher dielectric constant (ϵ) has the smaller ratio. The III/I ratio of the pyrene fluorescence in the aqueous latex dispersion shown in Figure 2 is ~2, which is similar to that observed in hydrocarbon solvents.[29] Therefore, there is minimal interaction of pyrene with water (the III/I ratio in water is 0.55[31]), which is in agreement with the invariance in the lifetime of pyrene in the presence of the water-soluble quencher Tl$^+$.

To demonstrate the versatility and ease of the sonochemical production of fluorescent latex particles, the incorporation of the dye DMDP[35] was also investigated. Figure 5a shows the fluorescence emission spectra of DMDP in MMA monomer and poly(MMA) latex particles. It is clear from the emission spectra that there is a shift to shorter wavelength when DMDP is incorporated into the latex particles produced by sonochemically

(35) Brackmann, U. *Lambdachrome Laser Dyes*; Lambda Physik Lasertechnik: 1986.

Table 3. Fluorescence λ_{max} of DMDP in Different Solvents (ϵ_{water} 80.4)[a]

solvent	dielectric constant (ϵ @ 20 °C)	λ_{max}/nm
PMMA latex[b]	2.8	554
chloroform[a]	4.8	566
methyl methacrylate		583
methanol[a]	33.6	619

[a] Taken from ref 37. [b] Taken from ref 36.

initiated emulsion polymerization. DMDP is a solvatochromic dye, and the observed shift in the fluorescence spectra is indicative of a change in the local environment in which DMDP is solubilized.

To confirm whether a change in solvent polarity is the reason for the observed shift in the fluorescence spectrum of DMDP in the latex particles, DMDP fluorescence spectra were recorded in a series of solvents of varying polarity. The emission spectra are shown in Figure 5b, and in Table 3 are presented the dielectric constant of the solvents and the maximum wavelength of fluorescence. It can be observed that there is a shift to shorter wavelengths in the fluorescence spectra of DMDP with decreasing dielectric constant. The emission maximum of DMDP in poly(MMA) latex particles is consistent with DMDP being in a low dielectric constant environment of at least less than 4.8. This is in good agreement with the literature value for bulk poly(MMA).[36] The result is also self-consistent with the pyrene III/I ratio results above.

These observations led us to consider incorporating a solute into the latex that might have a reasonable phosphorescence yield at room temperature. Figure 6 shows the phosphorescence spectra observed from 1-bromonaphthalene incorporated in latex particles under air and argon atmospheres. (The phosphorescence lifetime in argon was measured at 2.0 ms.) In comparison to these emission intensities, a negligible emission was observed from 1-bromonaphthalene in an argon-saturated MMA o/w emulsion.

Although oxygen does quench the phosphorescence in the latex, the effect was relatively small. This means that either the oxygen solubility within the polymer is very low or the local

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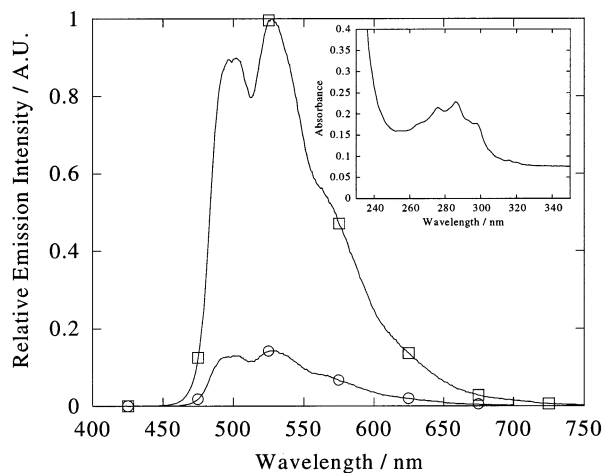
Figure 6. Phosphorescence spectra of 1-bromonaphthalene incorporated into the poly(MMA) latex particles under air (○) and argon (□) atmospheres. Inset: absorbance spectrum of 1-bromonaphthalene in the poly(MMA) latex particles. Excitation was at 250 nm.

viscosity is at such a level that oxygen diffusion within the particle is greatly retarded. It is most likely the latter case on the basis of the pyrene results discussed above.

Conclusion

This study has shown that solutes possessing either fluorescent or phosphorescent properties can be physically incorporated into nanosized latex particles in a one-step ultrasound initiated emulsion polymerization process.

From an examination of the emission spectra and lifetimes of the fluorescent and phosphorescent solutes used, it has been concluded that the core of the MMA latex produced is highly viscous and of low polarity.

The relative ease of preparation of luminescent latex particles by the ultrasound method described suggests that it may be a suitable method for use in incorporating or encapsulating other hydrophobic materials, such as organic or inorganic nanoparticles.