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Synthesis and Characterization of Polypyrrole-Coated Sulfur-Rich Latex Particles: New Synthetic Mimics for Sulfur-Based Micrometeorites

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Polypyrrole (PPy) has been deposited from aqueous solution onto submicrometer-sized sulfur-rich poly[bis(4-vinylthiophenyl)sulfide] (PMPV) latex particles. The PMPV seed particles and resulting composite particles were extensively characterized using scanning electron microscopy, X-ray photoelectron spectroscopy, FT-IR spectroscopy, helium pycnometry, Raman spectroscopy, and electrical conductivity measurements. Four-point probe measurements on pressed pellets indicate conductivities of around 6×10^{-5} S cm^{-1} for a polypyrrole loading of approximately 11.5%. This suggests a somewhat patchy, nonuniform polypyrrole overlayer, which is consistent with our Raman spectroscopy studies. Despite their relatively low conductivities, these polypyrrole-coated PMPV latexes can be accelerated up to hypervelocities ($>$20 km s^{-1}) using a high voltage (2 MV) van de Graaf instrument. In view of their high sulfur contents (ca. 28%), these new electrically conductive latexes are expected to be interesting synthetic mimics for understanding the behavior of sulfur-based micrometeorites, whose existence has been postulated by planetary scientists investigating signs of volcanic activity on one of Jupiter's moons (Io).

Introduction

Over the last 2 decades there have numerous reports of the deposition of air-stable organic conducting polymers such as polypyrrole (PPy), polyaniline (PANi), or poly(3,4-ethylenedioxythiophene) (PEDOT) onto colloidal substrates. One of the first reports in this area was by Jasne and Chiklis, who described the preparation of conducting polymer/latex composite films at an electrode surface by the in situ electrochemical synthesis of PPy in the presence of an aqueous dispersion of film-forming latex particles.[1] Other early examples include the synthesis of PPy-sulfonated polystyrene latex composites[2] and the deposition of PPy onto relatively large (noncolloidal) polyolefin-based particles of 10−35 μm diameter, where these coated particles were mixed with uncoated polyolefin-based particles to produce electrically conductive composites that exhibited relatively low conductivity percolation thresholds after melt-processing.[3] More recent work has involved the controlled deposition of conducting polymers onto colloidal sols such as silica[4] or haematite[5] or various polymer latexes.[6−9] Polystyrene (PS) latex has often been employed as a model colloidal substrate because this high T_g polymer is easily prepared as near-monodisperse spheres over a wide particle size range using either emulsion or dispersion polymerization techniques.[10−13] Poly(alkyl methacrylate) latexes can also be used but partial dewetting of the polypyrrole coating can occur on these less hydrophobic particles; beam damage is also much more likely

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during electron microscopy studies.[14] In a series of papers we described the synthesis of PPy-, PANI-, and PEDOT-coated polymer latexes.[10−14] In most cases sterically stabilized latex particles were employed as colloidal substrates, and care was taken to ensure that the thickness of the deposited conducting polymer overlayer did not exceed the steric stabilizer layer thickness, so as to ensure maximum colloidal stability. These core−shell particles were extensively characterized in terms of their conducting polymer loadings, colloidal stabilities, surface compositions, and solid-state electrical conductivities. In particular, X-ray photoelectron spectroscopy (XPS) was found to be extremely useful in assessing the relative uniformity (or otherwise) of the conducting polymer overlayers.[10c,11b,12b,13b]

Conducting polymer-coated latexes have been evaluated as antistatic and/or anticorrosion coatings.[15,16] A second, albeit somewhat esoteric, application for these core−shell microparticles was recently established in collaboration with Burchell and co-workers.[17] Due to their electrically conductive overlayer, these coated latex particles easily acquire a high surface charge, and hence can be electrostatically accelerated up to hypervelocities (>1 km s^{-1}) using a 1.5 MV Van de Graaf accelerator. Given their high carbon contents, low densities, and narrow particle size distributions, these conducting polymer-coated latexes are proving to be excellent mimics for carbonaceous micrometeorites.[17] This ongoing work is expected to aid the interpretation of data currently being collected by the cosmic dust analyzer (CDA),[18] which is 1 of 12 detectors on board the CASSINI space probe. The CDA includes a time-of-flight mass spectrometer, which has periodically analyzed the chemical compositions of micrometeorites (also known as "cosmic dust") over the last 7 years as CASSINI traveled through our Solar System toward Saturn, where it is now in orbit. During its voyage CASSINI flew close to Jupiter and detected dust streams originating from that planet and its satellites. In 1979 the Voyager spacecraft discovered that one of Jupiter's moons, Io, has substantial volcanic activity.[19] Spectroscopic analyses of Io suggest that plumes of sulfur particles are regularly ejected into space from its volcanoes, which is expected to produce relatively high concentrations of sulfur-rich micrometeorites in the immediate vicinity of this satellite's orbit.[20]

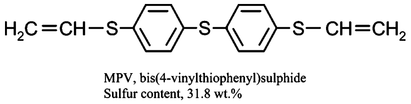

Figure 1. Chemical structure of the commercially available sulfur-rich monomer investigated in this work.

Moreover, Kissel and co-workers recently reported time-of-flight mass spectroscopy analysis of hypervelocity impacts on the STARDUST spacecraft during its flyby of Comet 81P/Wild 2 and suggested that sulfur species may be important in cometary organics.[21] These space science observations inspired us to design new conducting polymer-coated sulfur-rich latex particles to be employed as new synthetic mimics so as to understand the fundamental impact ionization behavior of sulfur-based micrometeorites in laboratory-based studies.

Experimental Section

Materials. Poly(*N*-vinyl pyrrolidone) [PNVP; manufacturer's nominal molecular weight = 360000] and 2,2′-azobisisobutyronitrile (AIBN) were obtained from BDH Chemical Ltd. (Poole, U.K.) and were used without further purification. Analytical reagent grade ethanol was purchased from Fisher Scientific (Loughborough, U.K.) and was used as received. The sulfur-based vinyl monomer used in this work was bis(4-vinylthiophenyl)sulfide (MPV), which was kindly donated by Sumitomo Seika Chemicals Co. Ltd. (Osaka, Japan). The sulfur content of this monomer is 31.8%; its chemical structure is shown in Figure 1. Pyrrole was kindly donated by BASF (Ludwigshafen, Germany) and purified by passing through a column of activated basic alumina, prior to storage at −15 °C before use. Hydrated ferric chloride ($FeCl_3 \cdot 6H_2O$) was purchased from Aldrich and was used as received. Doubly distilled, deionized water was used for latex purification.

Sulfur-Based Latex Synthesis. The following example of the synthesis of a sulfur-rich latex is representative, although a number of exploratory syntheses were conducted on a smaller scale. Ethanol (390 mL) was added to a 1 L round-bottomed flask fitted with a condenser and a magnetic stirrer. The PNVP steric stabilizer (4.0 g) and MPV (40 g) were dissolved in this solvent at 60 °C. The reaction vessel was purged with a stream of nitrogen for 40 min at 60 °C. A solution of AIBN initiator (0.48 g) predissolved in ethanol (10 mL) was then added to the reaction vessel. The magnetic stirrer was set at a constant speed of 250 rpm. The polymerization

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Table 1. Summary of the Microanalytical Data, Mean Particle Diameters, PPy Loading, PPy Overlayer Thickness, Densities, and Conductivity of the Sulfur-Based Seed Particles and PPy-Coated Sulfur-Based Particles

	particle diameter[a] (nm)	microanalyis (wt %)				PPy loading[b] (wt %)	calculated overlayer thickness[c] (nm)	density[d] ($g\ cm^{-3}$)	conductivity of pellet[e] ($S\ cm^{-1}$)
		C	H	N	S				
PMPV	480	63.1	4.70	0.35	31.2			1.29	
PMPV/PPy	496[f]	62.4	4.63	2.14	28.1	11.5	8	1.32	6.0×10^{-5}

[a] Number-average diameter determined by scanning electron microscopy (70 particles counted). [b] Percentage mass of conducting polymer loading on the latex particles, as determined by nitrogen microanalyses (comparing to a nitrogen content of 15.5% for chloride-doped polypyrrole bulk powder). [c] This overlayer thickness was calculated using the equation described in ref 10a from the known densities of the two polymers (1.29 g cm^{-3} for PMPV; 1.46 g cm^{-3} for PPy) and the chemical compositions of the coated latexes, assuming a smooth, uniform conducting polymer coating. [d] As determined by helium pycnometry (Micromeritics Accupyc 1330 instrument). [e] Pressed pellet conductivity at 20 °C determined using the conventional four-point probe technique. [f] This has been estimated by adding twice the calculated overlayer thickness to the original particle diameter.

was allowed to proceed for 72 h before cooling to room temperature. The resulting latex particles were then purified by repeated centrifugation−redispersion cycles, replacing successive supernatants first with hot ethanol (since this is a good solvent for any remaining MPV monomer) and then with doubly distilled, deionized water. The resulting PNVP-stabilized PMPV latex was subsequently used as a seed latex for the deposition of PPy (see below).

Deposition of PPy onto Latex. $FeCl_3{\cdot}6H_2O$ oxidant (25.37 g) was dissolved in 270 mL of a 10.0% aqueous dispersion of PMPV latex within a 500 mL flask with the aid of magnetic stirring. Pyrrole (2.7 g) was added by syringe and the polymerization was allowed to proceed for 24 h. The Fe^{3+}/pyrrole molar ratio was 2.33 in order to ensure the production of highly conductive PPy in high yield.[22] The PPy-coated PMPV latex particles were subsequently purified by repeated centrifugation−redispersion cycles (successive supernatants being replaced by deionized water) in order to remove the unwanted inorganic byproducts ($FeCl_2$ and HCl) that were produced during the pyrrole polymerization.

Characterization of Sulfur-Based PMPV Latex and PPy-Coated PMPV Latexes. The solid-state densities of the dried latex particles were determined by helium pycnometry using a Micromeritics Accu Pyc 1330 instrument. Elemental microanalyses were carried out at an independent laboratory (Medac Ltd. at Brunel University, U.K.). Electrical conductivity measurements were conducted on compressed pellets of dry powders using a homemade four-point probe apparatus. FT-IR spectra were recorded for the dried latexes dispersed in KBr disks using a Nicolet Magna Series II spectrometer (64 scans, 4 cm^{-1} resolution). Raman spectra were recorded using a Renishaw RM 1000 series Raman microscope equipped with a 2400 groove/mm holographic grating and a peltier-cooled CCD array detector. The excitation wavelength selected was 514.5 nm, originating from a 3.75 mW Ar ion laser; reduced laser power was used to minimize photodecomposition. The system was calibrated using the 520.0 cm^{-1} resonance of a single-crystal silicon wafer prior to the experiments. The morphologies of the PMPV seed latex and PPy-coated PMPV latexes were examined by scanning electron microscopy (SEM). Each sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample-charging problems.

X-ray Photoelectron Spectroscopy (XPS) Study. For XPS analysis, powder samples were pressed into pellets (13 mm diameter, 7.5 tonnes for 8 min) and mounted onto sample stubs using conducting tape. XPS measurements were carried out using a VG CLAM2 spectrometer, using a nonmonochromated Mg Kα X-ray gun operating at 10 W. The base pressure was below 1×10^{-8} mbar. Pass energies of 100 and 20 eV were employed for the survey spectra and elemental core-line spectra, respectively. Quantification of the atomic % composition was obtained from the high-resolution spectra using the sensitivity factors listed by Briggs and Seah[23] (after prior verification of these sensitivity factors for our instrument using standard samples). Spectra were aligned to the hydrocarbon component of the C(1s) peak set at 284.6 eV.

Hypervelocity Experiments. The charging and electrostatic acceleration of conducting polymer-coated latex particles has been previously demonstrated.[17] The PPy-coated PMPV particles in the current study were accelerated using a van de Graaf accelerator facility at the Max-Planck Institute in Heidelberg, Germany. Charging was achieved by contact with a needle maintained at a high voltage (a few kV). The charged particles were then accelerated in a vacuum chamber through an electric field of dc voltage (V). In preliminary experiments an accelerating voltage of 20 kV was used. Particle charge was measured in flight by passing the particles through a hollow conducting cylinder (length 8 cm). The magnitude of the induced charge (q) was measured, and the duration of the charge signal gave the time-of-flight for a given particle through the cylinder (and hence its velocity, v). The particle mass (m) was determined using the energy balance relationship $qV = {}^1\!/_2 mv^2$ and solving for m. Particle diameters were calculated by assuming that the PPy-coated latex particles were spheres with the particle density given in Table 1. A second series of experiments was then performed with the same PPy-coated PMPV latex particles using a high-voltage (2 MV) accelerator. Again, six events were recorded.

Results and Discussion

The MPV monomer (see Figure 1) was originally developed by its manufacturer for the synthesis of polymers with high refractive indexes. In contrast, in the present study we simply wished to synthesize colloidal particles comprising sulfur-rich vinyl polymers that would fragment relatively easily during hypervelocity impacts to afford cationic organosulfur species. For this reason, we had already discounted the possibility of coating inorganic sols such as $BaSO_4$ since the sulfur species generated within the impact plasma are likely to remain anionic (e.g., SO^-, SO_2^-, SO_3^-, SO_4^{2-}) and hence remain undetected. Unlike other micrometeorite detectors,[24] the CDA detector can analyze only cations due to its fixed voltage bias. To achieve efficient acceleration up to the hypervelocities that are characteristic of micrometeorites (typically 1−100 km s^{-1}), it is necessary to coat electrically insulating latexes with a thin overlayer of a conducting polymer in order to allow the efficient accumulation of sufficient surface charge.[17] Thus, in this paper we report the synthesis and characterization of submicrometer-sized

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(24) For example, the STARDUST CIDA instrument can operate using either positive or negative accelerating voltages, hence allowing acquisition of both positive and negative ion time-of-flight spectra.

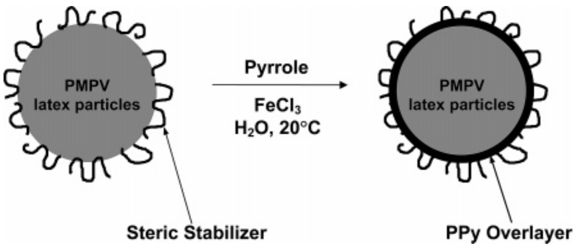

Figure 2. Schematic representation of the coating of PMPV-based latex particles with a thin overlayer of polypyrrole (PPy).

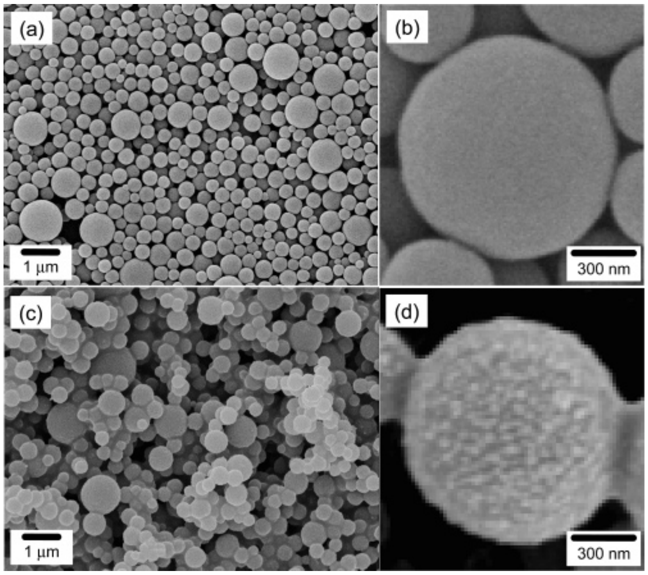

Figure 3. Typical SEM images obtained for (a) uncoated PMPV latex and (c) PPy-coated PMPV latex (11.5 wt % PPy). Figures (b) and (d) are magnified images of parts (a) and (c), respectively.

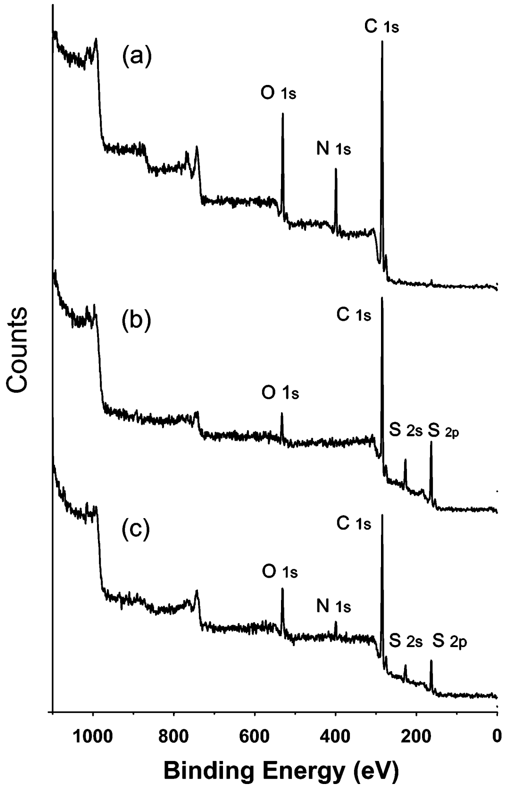

Figure 4. XPS survey spectra obtained for (a) PNVP homopolymer, (b) PMPV homopolymer, and (c) PNVP-stabilized PMPV latex particles.

sulfur-rich latexes coated with an ultrathin PPy overlayer (see Figure 2).

Synthesis of Sulfur-Rich Latexes. Dispersion polymerization of the MPV monomer yielded colloidally stable PMPV latex particles. Unfortunately, the bifunctional nature of the MPV meant that these latex particles were highly cross-linked, which precluded both molecular weight analysis and also solvent extraction experiments to assess the core–shell morphology.[10c] The MPV conversion was less than 75% after 24 h as judged by gravimetry (after washing with hot ethanol to remove any unreacted MPV monomer); thus subsequent polymerizations were conducted for 72 h to obtain MPV conversions of more than 90%. Figure 3a shows a scanning electron micrograph of PNVP-stabilized PMPV particles synthesized by dispersion polymerization for 72 h in ethanol at 60 °C. Unfortunately, these particles were relatively polydisperse, with particle diameters ranging from 120 to 1200 nm being observed; a high-magnification image shown in Figure 3b indicated a relatively smooth surface morphology. The number-average diameter was estimated to be around 480 nm (at least 70 particles were counted), whereas the hydrodynamic diameter and polydispersity index determined from dynamic light scattering studies (Brookhaven Instruments Corp. BI-200SM) in dilute aqueous solution were 690 nm and 0.197, respectively. The weight-average diameter measured by disk centrifuge photosedimentometry (DCP; Brookhaven Instruments) was 600 ± 330 nm and the particle size distribution curve had a long tail to lower diameters. There is some literature evidence to suggest that polydisperse latex particles are often obtained by dispersion polymerization in the presence of cross-linking comonomers.[25] Our PMPV latex syntheses involve the *homopolymerization* of a bifunctional monomer and appear to be similarly problematic. The microanalytical nitrogen content of the PMPV latex was consistent with a PNVP stabilizer content of approximately 2.8% by mass; this calculation ignores any nitrogen contribution arising from the AIBN initiator fragment. Assuming that this PNVP stabilizer is solely located at the surface of the PMPV latex particles, the adsorbed amount of stabilizer, Γ, is estimated to be approximately 2.9 mg m^{-2}. The sulfur content of the PMPV latex particles was 31.2%, which is in good agreement with that calculated from its chemical structure (31.8%), if due allowance is made for the PNVP stabilizer. As far as we are aware, this is the first example of the synthesis of polymer latex particles with a sulfur content of more than 30 wt %. Given their relatively high refractive index, these highly cross-linked PNVP-stabilized PMPV seed particles may also have potential applications as light diffusion agents,[26,27] although this is not the focus of the present work.

Figure 4 shows the XPS survey spectra recorded for (a) the PNVP homopolymer, (b) PMPV homopolymer (prepared

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(27) Sumitomo Seika Chemicals Co. Ltd., Japanese Patent, H9-281339, 1997.

Table 2. Surface Atomic Composition and S/N, C/N and C/S Atomic Ratios as Determined by X-ray Photoelectron Spectroscopy

	atom%					atomic ratios		
	C	N	S	O	Cl	S/N	C/N	C/S
PMPV seed particles	73.9	5.5	8.0	12.6		1.45	13.4	9.2
PPy-coated PMPV particles	72.3	10.7	2.39	12.2	2.42	0.22	6.8	30.3

by precipitation polymerization with AIBN initiator in ethanol in the absence of any PNVP stabilizer), and (c) PNVP-stabilized PMPV particles. The oxygen signal observed from the PMPV homopolymer suggests that this sample is prone to surface oxidation, as expected for organosulfur species.[28] No N(1s) peak was observed for PMPV homopolymer, suggesting that the surface concentration of AIBN initiator end-groups is negligible. Peaks assigned to the S(2s), S(2p), and O(1s) core levels were observed at binding energies of 229, 163.5, and 533 eV, respectively. The survey spectra confirm that the PNVP-stabilized PMPV latex contains both nitrogen and sulfur, as expected. A nitrogen surface concentration of 5.5 atom % and a C/N atomic ratio of 13.4 can be estimated as shown in Table 2 (named before Table 1). These values should be compared to N = 11.3 atom % (theoretical value is 12.5%) and a C/N atomic ratio of 6.8 (theoretical value is 6.0) calculated from the PNVP homopolymer reference spectrum. This suggests that either the XPS sampling depth (typically 2−10 nm) is greater than the PNVP layer thickness (and hence the underlying PMPV latex core is also interrogated) or that the PNVP stabilizer layer is "patchy" and does not provide complete surface coverage of the PMPV latex particles in the solid state. Similar conclusions were reported by Deslandes et al. for micrometer-sized, PNVP-stabilized PS latexes.[29]

PPy-Coated PMPV Latex Particles. A summary of the microanalytical data, latex particle diameter, PPy loading, calculated PPy overlayer thickness, particle densities, and electrical conductivity of the uncoated PMPV latex particles and PPy-coated PMPV particles is shown in Table 1. Figure 3c depicts an SEM image of PPy-coated PMPV particles synthesized by chemical oxidative polymerization of pyrrole in the presence of the PMPV latex. The pyrrole monomer was expected to polymerize exclusively in aqueous solution and/or on the latex surface since their high degree of cross-linking prevents any monomer swelling of these particles. Moreover, hydrated Fe^{3+} cations should not diffuse into the hydrophobic PMPV particles, so pyrrole polymerization within the latex interior is highly unlikely. Thus, PPy-coated PMPV latex particles with core−shell morphologies were expected. SEM studies indicated that the PPy coating was relatively rough; see Figure 3d. A correlation between the morphology of the PPy overlayer and the surface hydrophobicity was observed in our earlier studies of PPy-coated latexes.[14] Smooth, uniform coatings were obtained on hydrophobic polystyrene latexes,[10b,10c] whereas much more inhomogeneous coatings were observed on relatively hydrophilic poly(methyl methacrylate) latex particles,[14] with poly(*n*-butyl methacrylate) latex exhibiting intermediate behavior.[14] In the present study, the non-uniform, granular nature of the PPy overlayer is readily distinguished from the smooth surface morphology of the PMPV latex (see Figure 3b and Figure 3d). Visual inspection of the PPy-coated PMPV latex confirmed some degree of flocculation compared to the original uncoated latex. Similar flocculation was also observed in the case of PPy-coated PS particles for PPy loadings of more than 10% by mass.[10b] This incipient flocculation is caused by the PPy overlayer interfering with the steric stabilization mechanism conferred by the PNVP stabilizer.

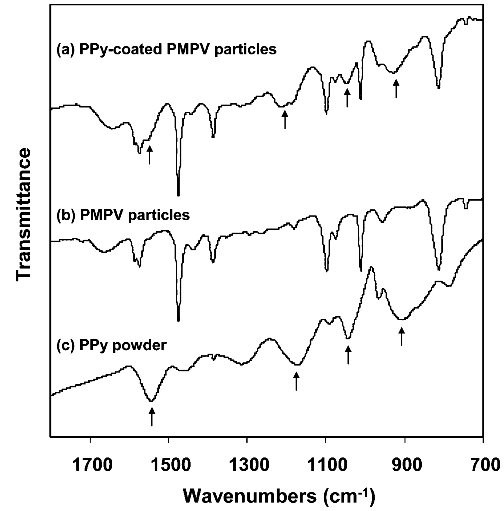

Figure 5. FTIR spectra recorded for (a) PPy-coated PMPV latex particles with 11.5 wt % PPy loading, (b) uncoated PMPV latex particles, and (c) PPy bulk powder.

FT-IR spectra of (a) PPy-coated PMPV latex, (b) the uncoated PMPV latex, and (c) PPy bulk powder (synthesized by aqueous precipitation polymerization in the absence of the PMPV latex) are depicted in Figure 5. The strongest band in the spectrum of the PMPV latex is at 1474 cm^{-1}, which corresponds to the C═C stretch. The FT-IR spectrum of PPy bulk powder is in good agreement with the literature and confirms that this material is highly doped, as expected.[8a,30] A number of characteristic broad bands are observed, particularly those at 1550 cm^{-1} and 1316, 1186, and 910 cm^{-1} in the 1000−1150 cm^{-1} region. Characteristic bands due to both the PMPV and PPy components were observed in the spectrum of the PPy-coated PMPV latex particles, as expected.

The conducting polymer loading of the PPy-coated latex was determined by comparing its nitrogen content of 2.14% to that of the uncoated PMPV latex (N = 0.35%) and conventional PPy bulk powder (N = 15.5%) synthesized in the absence of PMPV latex; see Table 1. Good agreement (within experimental error) was observed between the theoretical and actual PPy loadings: essentially no macroscopic precipitation of PPy was observed, indicating efficient deposition. The mean PPy overlayer thickness of 8 nm was calculated using a previously published formula,[10a] assuming

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(28) (a) Savige, W. E.; MacLaren, J. A. In *The Chemistry of Organic Sulfur Compounds*; Kharasch, N., Meyers, C. N., Eds.; Pergamon Press: Oxford, 1966; Vol. 2. (b) Field, L. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York and London, 1977; pp 303−382. (c) Allen, P., Jr.; Book, J. W. *J. Org. Chem.* **1962**, *27*, 1019.

(29) Deslandes, Y.; Mitchell, D. F.; Paine, A. J. *Langmuir* **1993**, *9*, 1468.

(30) Armes, S. P.; Aldissi, M.; Hawley, M.; Beery, J. G.; Gottesfeld, S. *Langmuir* **1991**, *7*, 1447.

a uniform core−shell particle morphology and using densities of 1.293 and 1.46 g cm^{-3} for the PMPV latex and PPy homopolymer, respectively. Since the minimum "grain size" of the deposited PPy nuclei is believed to be around 5−10 nm,[12] this PPy coating thickness suggests approximate monolayer coverage of the latex particles by the PPy nuclei. This situation corresponds to the minimum conductivity percolation threshold.

The pressed pellet conductivity of the PPy-coated PMPV latex particles was measured to be 6.0×10^{-5} S cm^{-1}, which is relatively low compared to the conductivities reported for PPy-coated polystyrene particles.[10] The reason(s) for this unexpectedly low electrical conductivity could be either overoxidation of the PPy overlayer or a nonuniform surface morphology for the PPy coating. Using the mild $FeCl_3$ oxidant should minimize overoxidation and indeed there is no evidence for this in the FT-IR spectrum of PPy bulk powder (no carbonyl band is observed in the lower spectrum in Figure 5). However, there is some XPS evidence for PPy over-oxidation (see below). SEM studies indicate that the PPy coating is relatively inhomogeneous, possibly due to partial dewetting of the partially oxidized (and hence relatively hydrophilic) PMPV latex surface by the conducting polymer. Although the relatively low conductivity measured for the PPy-coated PMPV latex is somewhat disappointing, it is worth emphasizing that pressed pellets prepared from the heterogeneous admixture comprising 91 vol % PMPV latex particles and 9 vol % PPy bulk powder had even lower electrical conductivities, which were below the lower limit for our four-point-probe setup ($<10^{-6}$ S cm^{-1}). This is not unexpected since the PPy content is below the critical value of 16 vol % that is required for a percolation mechanism.[10b] More efficient electrical conduction occurs in the case of PPy-coated PMPV particles because the electrons can flow with lower resistance between adjacent particles via the conductive pathway provided by the PPy overlayers, without "seeing" the underlying electrically insulating PMPV latex cores.[10b]

In previous studies the core−shell nature of conducting polymer-coated latexes has been readily verified by solvent extraction of the latex core, followed by examination of the morphology of the insoluble PPy residues.[10c] Thus, extraction of linear polystyrene from PPy-coated polystyrene latex using THF leads to insoluble PPy residues with a well-defined "broken eggshell" morphology. However, this solvent extraction approach is not suitable for the present study because the PMPV latex is highly cross-linked and hence cannot be extracted. In view of this problem, we conducted XPS and Raman studies in order to gain further evidence for the presumed core−shell morphology of the PPy-coated PMPV latex particles.

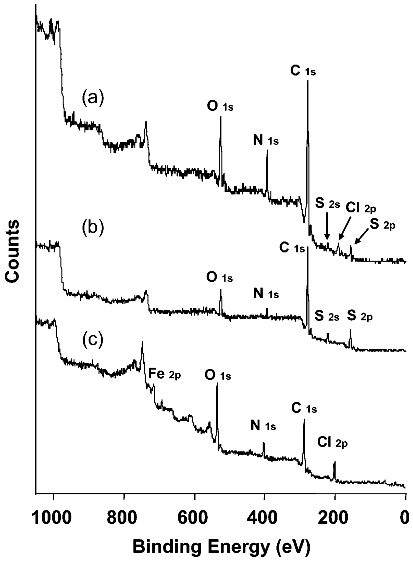

Figure 6. XPS survey spectra obtained for (a) PPy-coated PMPV latex particles, (b) PNVP-stabilized PMPV latex particles, and (c) PPy bulk powder.

Figure 6 shows the XPS survey spectra of (a) PPy-coated PMPV composite particles, (b) PNVP-stabilized PMPV latex particles, and (c) PPy bulk powder (prepared by precipitation polymerization in the absence of any PMPV latex). The O(1s) peak in the PPy bulk powder spectrum has also been observed in previous studies and is consistent with partial overoxidation of the PPy backbone.[31] The spectrum of the PPy-coated PMPV particles contains peaks that are assigned to Cl(2p) (at 197.5 eV), S(2p), and S(2s), in addition to C(1s), N(1s), and O(1s) signals. A surface doping level of 23% can be estimated for the PPy-coated PMPV particles from the Cl/N atomic ratio. This value is in reasonable agreement with the normally accepted doping range of 25−33% for PPy, particularly if the likelihood of surface oxidation and concomitant loss of dopant species is taken into account.

The surface S/N atomic ratio of the PPy-coated PMPV latex particles was determined to be 0.22, which is significantly lower than the value of 1.45 obtained for the PMPV latex particles, as shown in Table 2. This is consistent with partial obscuration of the underlying PMPV latex surface (and hence sulfur signal) by the PPy overlayer. The sulfur signal does not completely disappear because the XPS sampling depth can be up to 10 nm, which is greater than the estimated PPy overlayer thickness of 8 nm (assuming a perfectly uniform coating). Moreover, SEM studies suggest that the PPy coating is somewhat patchy; thus, completely efficient obscuration of the sulfur signal is unlikely.[10] Despite their nonuniform PPy coatings, our preliminary studies confirmed that these new sulfur-rich latexes acquire sufficient surface charge to allow their efficient acceleration up to the hypervelocity regime (see below).[17b] This is an essential prerequisite if these particles are to become useful mimics for understanding the behavior of sulfur-based micrometeorites.

The Raman spectroscopy studies are summarized in Figure 7. The spectrum of uncoated PMPV latex is shown in Figure 7a. There are several strong signals that are characteristic of PMPV at approximately 1070 cm^{-1} (ν_1 ring-breathing mode), 1570 cm^{-1} (ν_{9b} ring stretch), and 620 cm^{-1} (ν_{6b} ring

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(31) Maeda, S.; Armes, S. P. *J. Mater. Chem.* **1994**, *4*, 935.

(32) In our previous FT-Raman studies we demonstrated that *complete* attenuation of Raman bands due to underlying polystyrene latex particles can be achieved (see ref 10c and also Cairns, D. B. Ph.D. Thesis, University of Sussex, 1999). However, in the present study a shorter wavelength laser was used to acquire the Raman spectra (514.5 nm vs 1064 nm). This higher energy laser is more penetrating and hence increases the effective sampling depth for these strongly absorbing materials.

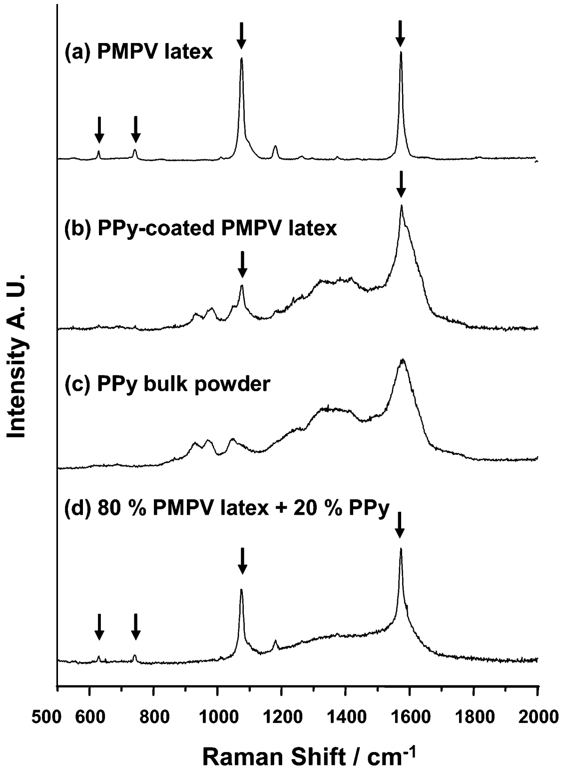

Figure 7. Raman spectra recorded for (a) PNVP-stabilized PMPV latex particles, (b) PPy-coated PMPV latex particles, (c) PPy bulk powder, and (d) an 80/20 w/w admixture of PPy bulk powder and PNVP-stabilized PMVP latex particles.

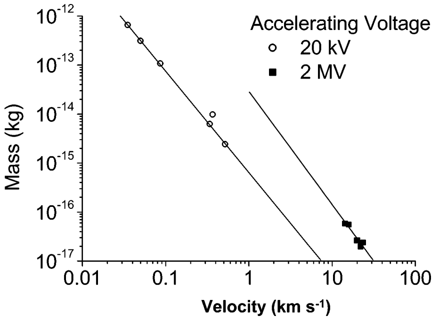

Figure 8. Mass vs velocity plot obtained for PPy-coated PMPV latex particles electrostatically accelerated using two different applied voltages (20 kV and 2 MV). The two data sets were fitted separately.

deformation). A spectrum of the PPy-coated PMPV latex is shown in Figure 7b. The PPy loading on this latex is around 11.5% by mass and this Raman spectrum is very similar to that obtained for PPy bulk powder (see Figure 7c), even though weak signals attributable to the underlying PMPV latex were observed at 1070 and 1570 cm^{-1}. A heterogeneous admixture comprising 20% PPy bulk powder and 80% *uncoated* PMPV latex by mass was also prepared as a reference material. The Raman spectrum of this admixture is shown in Figure 7d. Clearly, there is no possibility of a "core−shell" type morphology for such an admixture. Thus, the bands due to the PMPV latex at 1070, 1570, and 620 cm^{-1} are now prominent, even though this reference material has a somewhat lower PMPV content (80%) than that of the PPy-coated PMPV latex (90%). In summary, the reasonably efficient attenuation of the Raman signals expected for the PMPV latex in Figure 7b is consistent with a PPy-coated PMPV particle morphology. However, the PPy coating appears to be somewhat patchy, rather than perfectly uniform, since complete obscuration of the underlying latex component is not achieved. Thus, these Raman observations support the SEM and conductivity data.

The mass vs velocity data obtained from the two sets of electrostatic acceleration experiments are shown in Figure 8. With the 20 kV voltage field, six events were measured and the corresponding apparent particle diameters ranged from 1.5 to 10 μm. The calculated particle charge ranged from 1.6 to 3.3 × 10^{-14} C with the charge per unit surface area ranging from 0.07 to 2.3 × 10^{-3} C m^{-2}. Given the high particle masses that are calculated, the latex particles in this low-voltage experiment were almost certainly accelerated as aggregates or clumps, rather than as single discrete particles. This interpretation is consistent with their relatively low (<1 km s^{-1}) velocities. In contrast, using the high-voltage (2 MV) accelerator led to calculated particle diameters that were consistent with the acceleration of individual particles (i.e., 0.30−0.44 μm) and hypervelocities exceeding 20 km s^{-1} were observed. Particle charges of 2 to 3.4 × 10^{-15} C were obtained, which correspond to surface charge densities of 4.9 to 10 × 10^{-3} C m^{-2}. Two distinct regimes are apparent for the fits to the low-voltage and high-voltage data sets shown in Figure 8. However, the slopes of the power law fits are similar (within experimental error), suggesting differing charging efficiencies in addition to the change in accelerating voltage. The data set from the 2 MV accelerator gave the largest charge per unit surface area and hence a maximum surface electric field strength of 1.2 × 10^{9} V m^{-1} is calculated. The latex particles that were successfully accelerated to hypervelocities were fired at a silver target and the plasmas generated from such impacts were analyzed using time-of-flight mass spectroscopy. The analysis of these mass spectra will be discussed in a separate publication, but it is worth stating here that signals at 32 *m*/*z* corresponding to sulfur ions were observed in all spectra.

In summary, these new PPy-coated PMPV latex particles are expected to be interesting model projectiles for mimicking the behavior of sulfur-rich micrometeorites in laboratory-based hypervelocity impact experiments. Such studies should enhance our ability to interpret the cationic plasma generated by sulfur-rich micrometeorites that are believed to have struck the CDA detector that is on board the CASSINI probe and hence may ultimately provide some insights regarding the nature of the volcanic activity on Io.

Conclusions

Submicrometer-sized, PMPV latex particles have been successfully synthesized and coated with an ultrathin layer of an organic conducting polymer (polypyrrole). The resulting composite particles were extensively characterized using helium pycnometry, SEM, XPS, FT-IR, and Raman spectroscopy and also electrical conductivity measurements. The XPS and Raman data suggest a patchy PPy shell encapsulating the PMPV latex core. Despite their relatively low pressed pellet conductivity, these sulfur-rich PPy-coated latex particles can accumulate sufficient surface charge to allow their efficient acceleration up to the hypervelocity regime (>1 km

s^{-1}) using a 2 MV van de Graaf accelerator. Thus, these new particles are expected to become useful mimics for understanding the behavior of sulfur-based micrometeorites. This work is particularly timely since planetary scientists have recently predicted the existence of sulfur-rich cosmic dust particles based on their recent observations of volcanic activity on one of Jupiter's moons (Io).

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