Synthesis and Characterization of Polypyrrole-Coated Poly(Alkyl Methacrylate) Latex Particles

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Polypyrrole (PPy) has been deposited from aqueous solution onto two types of near-monodisperse poly(alkyl methacrylate) latexes and the resulting composite particles have been extensively characterized using SEM, DCP, XPS, FTIR, and electrical conductivity measurements. Poly(methyl methacrylate) (PMMA) latex is more difficult to coat than the polystyrene latexes previously reported by our group in that the deposited PPy overlayer is much less uniform. This difference is most likely related to the greater hydrophilicity of the PMMA surface. The poly(*n*-butyl methacrylate) (PBMA) latex has intermediate hydrophobic character, and, as a result, PPy overlayers on this substrate are somewhat more uniform than those obtained for PMMA particles. The PPy-coated PBMA latex is an interesting model system for understanding the behavior of PPy-coated film-forming latexes such as DSM's ConQuest (PPy-coated polyurethane particles). The lightly cross-linked outer shell of PPy hinders film formation significantly but conductive films can be obtained in the presence of coalescence aids such as *N*-methyl pyrrolidone. This cosolvent acts as a plasticizer for the PBMA latex and allows a reasonable degree of film formation at ambient temperature.

Introduction

Over the last fifteen years or so there has been increasing interest in the deposition of air-stable organic conducting polymers such as polypyrrole (PPy), polyaniline (PANi), or poly(3,4-ethylenedioxythiophene) (PEDOT) onto colloidal/particulate substrates. As far as we are aware, the first report 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 deposition of PPy in the presence of an aqueous dispersion of film-forming latex particles.[1] Other early examples included the synthesis of PPy-sulfonated polystyrene latex composites[2] and the deposition of PPy onto large, noncolloidal polyolefinic particles of either 10- or 35-μm diameter.[3] These coated particles were mixed with uncoated polyolefinic particles to produce composites that exhibited relatively low percolation thresholds after melt processing. More recent work has involved the controlled deposition of conducting polymers onto colloidal sols such as silica[4] or haematite[5] or various organic latexes.[6−9] At Sussex we have used polystyrene (PS) latex as a model high T_g polymeric substrate, mainly because this material can be readily prepared in the form of near-monodisperse microspheres over a wide range of particle diameters using either emulsion or dispersion polymerization techniques. In a series of papers our group has described the synthesis of PPy-, PANI-, and PEDOT-coated PS latexes.[10−13] In each case sterically stabilized latex particles were employed as colloidal substrates and considerable care was taken to ensure that the conducting polymer overlayer remained within the steric stabilizer layer thickness in order 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

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found to be extremely useful in assessing the relative uniformity (or otherwise) of the conducting polymer overlayers.[11b,12b,13b] An interesting, albeit esoteric, application for these core−shell microparticles was recently established in collaboration with Burchell and co-workers.[14] Because of their electrically conductive overlayer, these coated latex particles easily acquire a high surface charge and hence can be accelerated up to hypervelocities (>1 km sec^{-1}) using a Van de Graaf instrument. Given their high carbon contents, low densities, and narrow particle-size distributions, these conducting polymer-coated latexes are proving to be excellent mimics for organic-based micro-meteorites.[15] This ongoing work is expected to have important implications for the calibration of the cosmic dust analyzer (CDA) that is one of twelve detectors on the CASSINI space probe.[16] The CDA is currently analyzing the composition of micro-meteorites as CASSINI travels through the Solar System. In addition, on CASSINI's arrival at Saturn in 2004, it is anticipated that the CDA instrument will allow determination of the chemical composition(s) of the microscopic dust particles that comprise Saturn's rings.

In the early 1990s workers at DSM Research patented the synthesis of PPy-coated, film-forming latexes in which the latex substrate was typically based on either polyurethane, poly(vinyl acetate), or alkyd resins.[17] These composite materials are being marketed under the "ConQuest" tradename and have potential applications as anti-static and anti-corrosion coatings. In an effort to understand the behavior of these film-forming latexes both our group[18] and also Huijs and co-workers[19] prepared poly(*n*-butyl methacrylate) (PBMA) particles as a model colloidal substrate. PBMA latex has a minimum film-forming temperature that is around ambient temperature, i.e., somewhat higher than conventional film-forming latexes but much lower than high T_g materials such as PS or poly(methyl methacrylate) (PMMA) latex. In principle, this should enable the film formation process to be studied in some detail. In both studies relatively large PBMA particles were targeted because this was expected to aid their morphological characterization.

In this paper we summarize our recent results concerning the synthesis and characterization of near-monodisperse poly(alkyl methacrylate) latexes with ultrathin overlayers of PPy (Figure 1). In particular, the uniformity of the conducting polymer overlayers deposited onto nonfilm-forming PMMA and film-forming PBMA latexes of similar particle diameters was compared, and the extent to which this shell affected the film-forming properties of the encapsulated PBMA latex core was investigated.

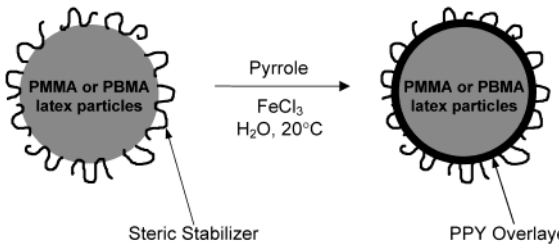

Figure 1. Schematic representation of the coating of poly(alkyl methacrylate)-based latex particles with a thin overlayer of polypyrrole.

Experimental Section

Materials. *n*-Butyl methacrylate (BMA; Aldrich) was purified by passing it through a column of activated basic alumina to remove the inhibitor. Poly(*N*-vinyl pyrrolidone) (PVP) with a nominal molecular weight of 360 000 was obtained from BDH and used without any further purification. Pyrrole was kindly donated by BASF and purified by passing it through a column of activated basic alumina prior to storage at −15 °C before use. Azo-*iso*-butyronitrile (BDH) and *N*-methyl pyrrolidone (NMP) (Aldrich) were used without any further purification. A near-monodisperse PMMA latex, prepared by dispersion polymerization in an alcohol-water mixture using PVP as a polymeric stabilizer, was supplied by Dr. F. Louwert of Agfa, Belgium.

PBMA Latex Synthesis. Methanol (800 mL) and water (200 mL) were added in turn to a 2-L round-bottomed flask fitted with a condenser and a mechanical stirrer. The PVP steric stabilizer (20.0 g) was then added and allowed to dissolve. After the reaction vessel was heated to 75 °C under a nitrogen blanket, it was purged with a stream of nitrogen for 4 h at 75 °C. A solution of azo-*iso*-butyronitrile initiator (1.00 g) predissolved in BMA monomer (100 g) was then added to the reaction vessel. The mechanical stirrer was set at a constant speed of 2000 rpm. The polymerization was allowed to proceed for 24 h before cooling to room temperature. The resulting latex particles were then purified by repeated centrifugation−redispersion cycles, replacing successive supernatants with a 50:50 w/w % methanol/water solution.

Latex Characterization. The particle-size distribution and colloid stability of the two latexes were determined using disk centrifuge photosedimentometry (DCP). All measurements were carried out using a Brookhaven BI-DCP instrument, operating in the line start mode. Samples for DCP analysis were prepared by adding a few drops of the dispersed latex to 3 mL of a 1:2 v/v % methanol/water mixture. The centrifugation rate was 4000 rpm. The solid-state densities of the dried latex particles were determined by helium pycnometry. Preliminary studies indicated that both latexes had relatively narrow particle-size distributions, and DCP measurements yielded weight-average particle diameters of 995 ± 23 nm for the PBMA latex and 724 ± 35 nm for the PMMA latex donated by Agfa. Scanning electron microscopy (SEM) studies on the dried latexes were also in good agreement with these values (Figure 2). The latexes were also analyzed by FTIR spectroscopy using a Nicolet Magna Series II spectrometer (KBr disk, 64 scans, 4 cm^{-1} resolution). The microanalytical nitrogen content of the PBMA latex was consistent with a PVP stabilizer content of 1.5% by mass. Assuming that this PVP stabilizer is all located at the surface of the latex particles, it is possible to calculate the adsorbed amount of PVP, Γ, to be around 2.6 mg m^{-2}.

Deposition of PPy onto Latex. $FeCl_3 \cdot 6H_2O$ oxidant (0.9 g) was dissolved into an aqueous dispersion of either the PBMA or PMMA latex of known concentration, in a screw-cap bottle with magnetic stirring. Pyrrole (0.10 mL) was added via syringe, and the polymerization was allowed to proceed for 24

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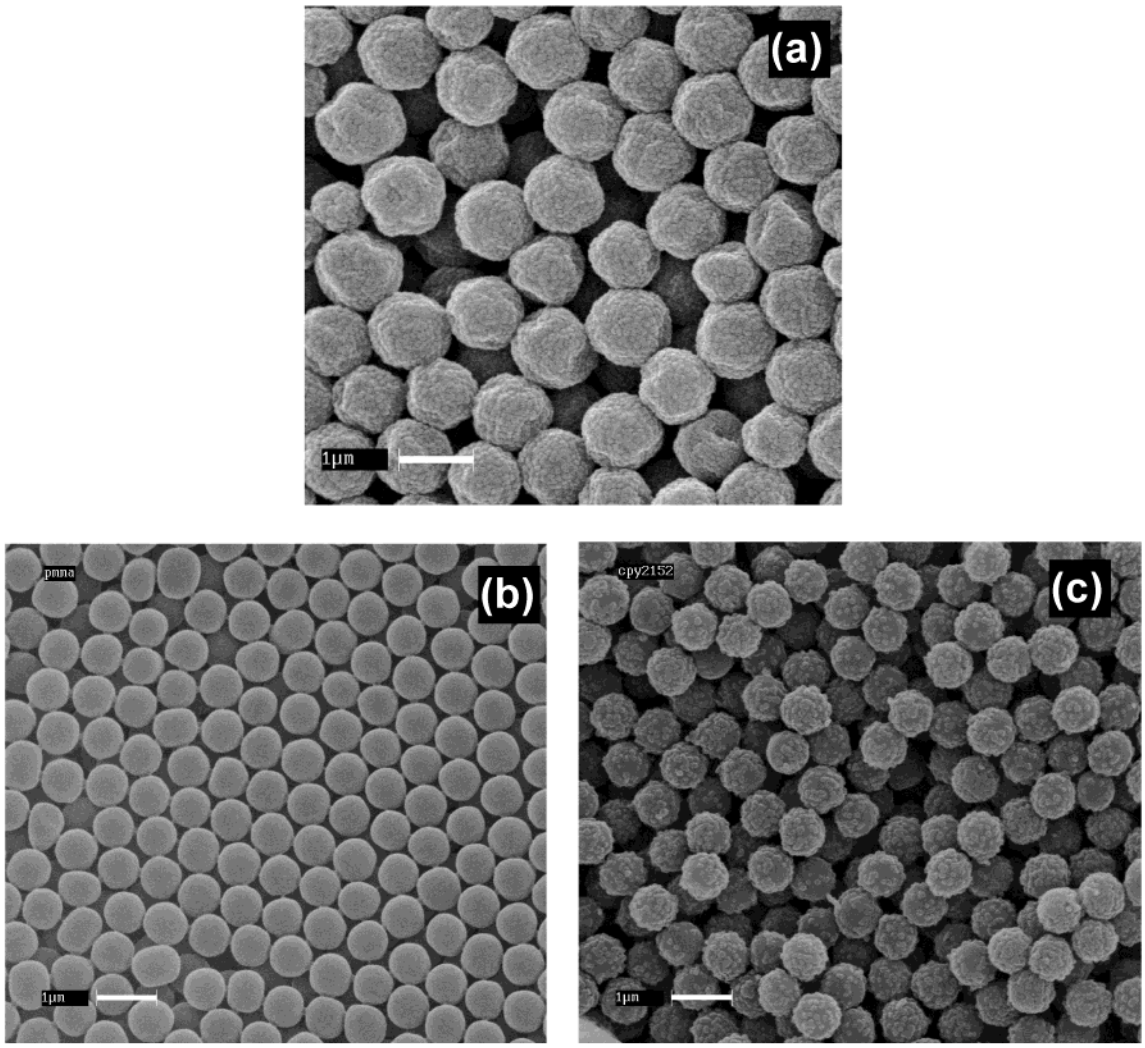

Figure 2. Typical SEM images of (a) PPy-coated PBMA latex (9.9 wt. % PPy); (b) uncoated PMMA latex; and (c) PPy-coated PMMA latex (10.5 wt. % PPy).

h. The coated latex particles were then 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) produced during the pyrrole polymerization.

Characterization of PPy-Coated Latexes. CHN microanalyses were determined for each of the freeze-dried PPy-coated latexes. The PPy loadings of each of the coated latexes were determined by comparing their nitrogen contents to that of the uncoated PBMA ($N = 0.16\%$) or uncoated PMMA ($N = 0.0\%$), and conventional PPy bulk powder ($N = 16.5 \pm 0.5\%$) synthesized in the absence of any latex particles. CHN microanalyses were carried out at an independent laboratory (Medac Ltd at Brunel University, UK). DCP studies were carried out on all coated latexes, as described earlier. The centrifugation rate ranged from 1000 to 4000 rpm and was varied according to the particle density and the degree of aggregation perceived by visual inspection. Electrical conductivity measurements were carried out on compressed pellets of dry powders using a homemade four-point probe apparatus. The PPy-coated latexes were examined in turn by SEM. The sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold to prevent sample-charging problems. XPS spectra were recorded using a VG Scientific ESCALAB MKII system.

Film-Formation Experiments. *N*-Methyl pyrrolidone (NMP) was added as a cosolvent to an aqueous dispersion of one of the PPy-coated PBMA latexes (8.3% PPy mass loading). Two films were cast using varying amounts of NMP: (i) 25 wt. % and (ii) 75 wt. % (relative to the PBMA content). After 2 h, several drops of the black dispersion were placed on a glass microscope slide and allowed to dry under ambient conditions overnight. The conductivities of the dried films were assessed using the four-point probe technique.

Results and Discussion

Apart from the recent studies by Huijs and co-workers[19] mentioned earlier, there has been relatively little work on the deposition of conducting polymers onto poly(alkyl methacrylate) latex particles. Omastova and co-workers[8] reported the synthesis of PPy−PMMA latex composites, where the PMMA latex diameter was only 100 nm. However, the small size of the PMMA latex precluded morphological studies of the PPY component, and the colloidal stability of these composite particles was not discussed. In this context it is interesting to note that Cairns et al.[12] were unable to coat PS latex of similar dimensions with PPy overlayers. Instead of the expected core−shell particle morphology, colloidally stable aggregates of heteroflocculated PS latex and 5−10-nm PPy nanoparticles were obtained. In retrospect, it seems likely that similar heterofloccs, rather than genuine core−shell particles, were obtained by Omastova and co-workers.

The synthesis of PPy-coated poly(alkyl methacrylate) latexes is summarized in Table 1. The pyrrole monomer

Table 1. Summary of the PPy Loadings, PPy Overlayer Thicknesses, and Colloidal Stabilities of the PPy-Coated PBMA Latexes and the PPy-Coated PMMA Latexes

latex type	latex surface area (m^2)	theoretical PPy loading (wt %)	actual PPy loading (wt %)[a]	calculated PPy overlayer thickness (nm)	colloid stability of PPy-coated latex[b]
PBMA	15.1	3.5	4.6	3.4	stable
	11.4	5.2	5.6	7.1	stable
	7.5	6.8	6.1	7.7	stable
	6.8	7.4	8.3	10.7	stable
	4.7	10.5	9.9	13.0	stable
	4.0	12.1	13.4	18.1	stable
	2.8	15.5	16.6	23.0	floc'd
	2.3	18.9	18.4	25.9	floc'd
	1.6	25.1	24.5	36.5	floc'd
	1.1	30.6	32.8	53.2	unstable
	0.6	51.1	52.3	107.8	unstable
PMMA	40.1	1	1.1	1.1	unstable
	13.1	3	3.3	3.3	unstable
	7.7	5	5.6	5.8	unstable
	5.4	7	7.6	8.0	unstable
	4.1	9	9.6	10.3	unstable
	3.6	10	10.5	11.4	unstable
	3.0	12	12.8	14.2	unstable
	2.3	15	16.1	18.3	unstable
	1.8	18	19.1	22.3	unstable
	1.2	25	26.4	32.9	unstable
	0.6	40	41.7	60.8	unstable

[a] Determined by reduced nitrogen content using CHN microanalysis. [b] Determined by disk centrifuge photosedimentometry.

and $FeCl_3$ oxidant concentrations were kept constant in all PPy syntheses. Systematically decreasing the latex surface area that was available for PPy deposition led to a monotonic increase in the PPy loading, as expected. 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 thicknesses were calculated using a previously published formula,[10a] assuming a uniform core−shell particle morphology and using helium pycnometry densities of 1.19, 1.06, and 1.46 g cm^{-3} for the PMMA, PBMA, and PPy components, respectively. Because the minimum grain size of the deposited PPy nuclei is believed to be around 5−10 nm,[12,20] mean thicknesses below this threshold are merely nominal. Thus, for PPy mass loadings lower than 5% (see Table 1), only patchy, submonolayer deposition is expected, rather than a uniform PPy shell. This grain size problem apparently was not recognized by Huijs and co-workers, who claim that uniform overlayers of PPy are obtained even at overlayer thicknesses of only 1 nm.[19] The final column in Table 1 refers to the colloid stability of the coated latex, as judged by visual inspection. In the case of the PBMA latex particles, colloidally stable dispersions were obtained for thin PPy overlayers (up to 18 nm). Flocculated particles were observed for PPy overlayers of 23−36 nm, and unstable agglomerated dispersions were obtained for thicker overlayers. These observations can be rationalized by comparing the PPy overlayer thickness to the thickness of the PVP stabilizer, which has been estimated to be around 20−30 nm by Yamamoto and co-workers.[7] In contrast, the PPy-coated PMMA latex was agglomerated at all PPy loadings investigated. This suggests that either the PVP stabilizer layer is very thin for this particular latex, or that the PPy overlayer is very nonuniform (globular), which would favor increased particle aggregation at a given loading. There is reasonable experimental evidence to support the second hypothesis (see below).

Provided that the latex diameter is sufficiently large, scanning electron microscopy is a powerful technique for assessing the uniformity of the PPy overlayer. A PPy-coated PBMA latex with a mass loading of 9.9% PPy is shown in Figure 2a. Control experiments with the uncoated PBMA precursor latex confirmed that a certain amount of particle coalescence occurs on drying at ambient temperature, as expected (image not shown here; see ref 18). However, the lightly cross-linked PPy overlayers hinder particle coalescence considerably under these conditions, and discrete core−shell particles are observed. The latex particle-size distribution is reasonably narrow, with a mean diameter of just under 1 μm, and the granular morphology of the PPy coating is readily apparent. This surface morphology is rather rougher than that reported for PPy-coated PS latexes,[10] but it is quite similar to that observed by Barthet et al. for PANI-coated PS latexes.[11] The uncoated, near-monodisperse PMMA particles are shown in Figure 2b and the mean number-average latex particle diameter is around 700 nm, which is in good agreement with the weight-average diameter obtained by DCP. The surface morphology of the particles is very smooth and featureless. Polymerization of pyrrole in the presence of this PMMA latex leads to core−shell particles with a rather inhomogeneous coating of PPy (Figure 2c). Note that the PPy mass loading of 10.5% is comparable to that for the PPy-coated PBMA latex shown in Figure 2a. Comparing this information with that of our earlier studies with polystyrene latexes, there is an obvious correlation between the morphology of the PPy overlayer and the surface hydrophobicity. Thus, smooth, uniform coatings were obtained on the most hydrophobic surface (polystyrene), whereas much more inhomogeneous coatings are observed on the relatively hydrophilic PMMA latex, with the PBMA latex exhibiting intermediate

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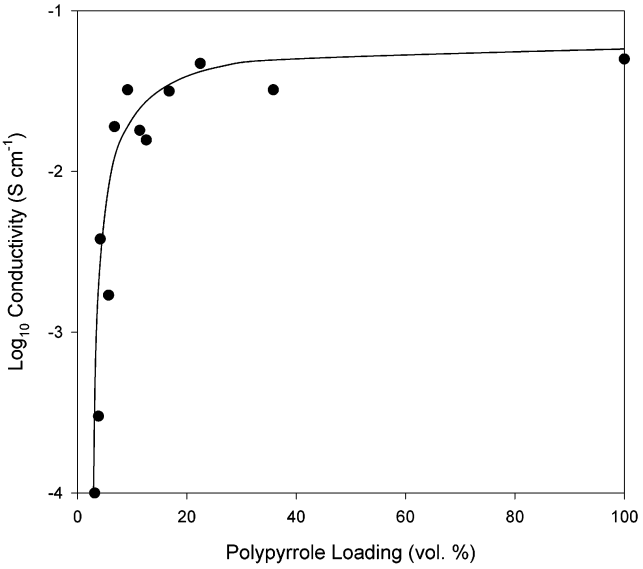

Figure 3. Variation of conductivity with PPy volume fraction for PPy-coated PBMA latex composites.

behavior. In general, these qualitative observations are consistent with the findings of MacDiarmid and coworkers, who reported that conducting polymers such as PPy and PEDOT are preferentially deposited (with improved uniformity) onto hydrophobic regions of patterned hydrophilic planar substrates.[21]

A conductivity percolation threshold curve for PPy-coated PBMA latex particles is depicted in Figure 3. A steep rise in conductivity is observed at a PPy volume fraction of around 5%, which is a little higher than that previously reported for PPy-coated PS latex.[10] Efficient electrical conduction occurs because the electrons can flow with minimal resistance between adjacent core−shell particles via the PPy overlayers and hence do not "see" the underlying, electrically insulating latex cores.[10] However, the conductivity plateau of approximately 5×10^{-2} S cm^{-1} is somewhat lower than that reported for PPy-coated PS latex. This is believed to be due to the use of 1:1 water/ethanol as a dispersion medium for the PBMA latex, which is not an ideal medium for the synthesis of high-quality PPy. Indeed, in a control experiment, the conductivity of PPy bulk powder prepared in this mixed solvent in the absence of any latex was approximately 5×10^{-2} S cm^{-1}, which corresponds closely to the conductivity plateau observed for the PPy−PBMA latex composites. Similar conductivities were obtained for PPy bulk powders prepared in water/ethanol mixtures by Digar.[22] For the PPy-coated PMMA latex (data not shown), electrical conductivities were immeasurable (<10^{-6} S cm^{-1}) for PPy volume fractions below 2.4%. Even at a loading of 5.8%, the conductivity was only 1.5×10^{-2} S cm^{-1}. All pyrrole polymerizations involving the PMMA latex were carried out in purely aqueous solution, which should lead to the formation of good-quality PPy. Thus, the reduced conductivities obtained in these syntheses are presumably related to the less uniform surface morphologies of the PPy overlayers observed by SEM on this more hydrophilic latex substrate (Figure 2).

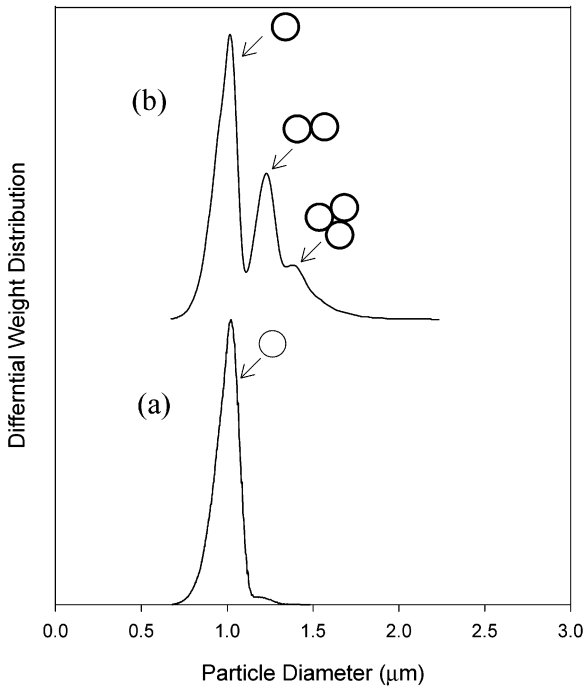

Figure 4. Weight-average diameter particle size distribution curves for (a) the uncoated PBMA latex and (b) a PPy-coated PBMA latex (PPy loading = 9.9 wt. %).

Disk centrifuge photosedimentometry (DCP) is a well-established particle sizing technique that can also be used to assess the degree of dispersion of conducting polymer-coated latexes.[10−12] In Figure 4 the DCP curves for an uncoated PBMA latex (weight-average diameter = 995 ± 23 nm) and a PPy-coated PBMA latex (9.9% PPy mass loading, which corresponds to a mean overlayer thickness of 13 nm) are presented. The size distribution curve for the coated latex clearly indicates some incipient flocculation, with a side peak and a shoulder at higher masses that correspond to the presence of doublets and triplets, respectively. This is understandable given that the PPy overlayer has a high Hamaker constant;[23] its deposition within the steric stabilizer layer inevitably reduces the effective stabilizer layer thickness and hence compromises the colloid stability of the coated latex.

FT-IR spectra of PPy bulk powder (synthesized by precipitation polymerization in the absence of any latex), the uncoated PMMA latex, and the PPy-coated PMMA latexes are depicted in Figure 5. The two strongest bands in the PMMA latex spectrum correspond to the C═O stretch at 1735 cm^{-1} and the C−O stretch at 1145 cm^{-1}. The IR spectrum of PPy bulk powder is in good agreement with its literature spectrum and confirms that this material is highly doped, as expected.[8a,24] A number of characteristic broad bands are observed, particularly those at 1550 cm^{-1} and in the 1000−1150 cm^{-1} region. At lower PPy mass loadings (e.g., 7 wt. %; spectrum not shown) there is little IR evidence for the conducting polymer component (although the dry pow-

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Table 2. XPS Elemental Compositions (in Atom %) and Surface Proportions of Conducting Polymer on the PPy-Coated PBMA Latexes

sample	C	N	O	Cl	Fe	PPy surface proportion (%)
PVP (360 000)	76.7	12.8	10.5	-	–	–
PPy bulk powder	73.0	18.6	3.0	5.2	0.0	100
PVP-stabilized PBMA latex	76.5	2.2	21.3	0.0	0.0	0.0
4.6% PPy-coated PBMA latex	68.0	9.9	15.4	4.8	0.97	41.2
5.6% PPy-coated PBMA latex	71.7	7.8	17.4	2.6	0.55	30.1
6.1% PPy-coated PBMA latex	68.1	11.3	15.1	4.7	0.83	48.7
8.3% PPy-coated PBMA latex	63.2	13.7	16.8	5.4	1.00	61.5
9.9% PPy-coated PBMA latex	60.5	15.6	13.8	8.6	1.62	71.7
13.4% PPy-coated PBMA latex	63.3	16.1	14.6	5.2	0.86	74.6
18.4% PPy-coated PBMA latex	60.1	15.8	13.9	8.7	1.49	72.0
24.5% PPy-coated PBMA latex	61.6	16.2	15.6	5.6	1.01	74.0
32.8% PPy-coated PBMA latex	62.6	17.1	11.7	7.5	1.08	80.1

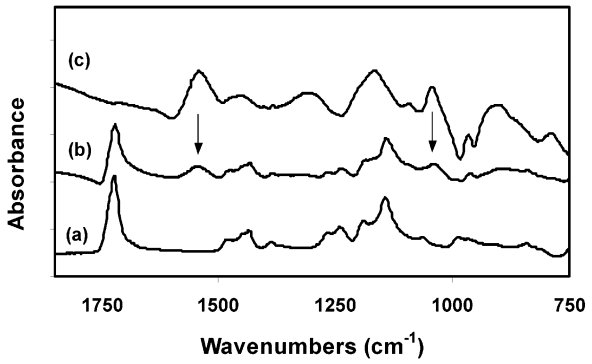

Figure 5. FTIR spectra for (a) uncoated PMMA latex; (b) PPY-coated PMMA latex with 19.1 wt. % PPy loading; and (c) PPY bulk powder.

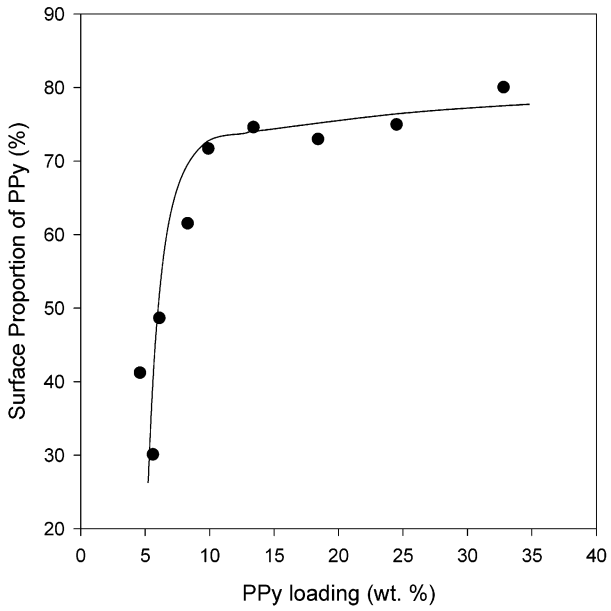

Figure 6. Relative surface proportion of PPy on the PBMA particles as determined by XPS as a function of PPy loading.

der is visibly gray), but several weak features that are characteristic of the conducting polymer component become discernible at a mass loading of 19.1% PPy (see arrows).

A summary of XPS data for a series of PPy-coated PBMA latexes, together with PPy, PVP, and PBMA latex reference materials is presented in Table 2. The surface nitrogen content of the PBMA latex is due to the PVP stabilizer used to prepare these particles. Comparing this nitrogen value with that of the PVP reference, a surface concentration of approximately 17% can be estimated. This suggests that the stabilizer overlayer is patchy in the solid state; similar conclusions were reported by Deslandes et al. for micrometer-sized, PVP-stabilized PS latexes.[25] A surface doping level of 28% can be determined for the PPy reference from the Cl/N atomic ratio, which is consistent with highly conductive material.[24] Residual levels of Fe are detected in all of the coated latexes. This is not unexpected, as $FeCl_3$ was used to polymerize the pyrrole and iron is known to complex with PVP; surface iron contamination was also observed by Perruchot et al. in their XPS study of a PPy-coated PS latex.[26] The proportion of PPy at the surface of the PBMA latex can be estimated from the nitrogen signal, although a correction for the nitrogen content of the PVP stabilizer is required. Thus, the equation used is

$$\text{PPy \%} = ([N_{\text{tot}} - N_{\text{PBMA}}]/N_{\text{PPy}}) \times 100\ \%$$

where N_{tot} is the XPS N1s signal in atom %, N_{PBMA} is the surface nitrogen content of the uncoated PBMA latex (2.2 atom %), and N_{PPy} is the surface nitrogen content of the PPy reference material (18.6 atom %). The surface proportion of PPy is summarized in the final column of Table 2 and increases with PPy mass loading, as expected. Figure 6 depicts the relationship between this XPS surface composition data and the PPy mass loadings determined by elemental microanalyses. At a PPy loading of around 20%, the surface proportion of this component is only 75%. This value should be compared with the value of 95−100% reported by Perruchot et al. for a mass loading of only 8.7% PPy on 1.8-μm PS latex.[26] Thus, XPS provides further evidence for the relatively nonuniform (patchy) PPy overlayers on poly(alkyl methacrylate) latexes, compared to more hydrophobic polystyrene substrates. However, it is emphasized that, despite this inhomogeneous coating, efficient surface charging and Van de Graaf acceleration of these PPy-coated latexes up to hypervelocities can be achieved.[27] Hence, these aliphatic polymer particles are expected to provide a very useful comparison to the

(25) Deslandes, Y.; Mitchell, D. F.; Paine, A. J. *Langmuir* **1993**, *9*, 1468.
(26) Perruchot, C.; Chehimi, M. M.; Delamar, M.; Lascelles, S. F.; Armes, S. P. *Langmuir* **1996**, *12*, 3245.
(27) Burchell, M. J.; Cole, M. J.; Armes, S. P.; Khan, M. A. manuscript in preparation, 2002.

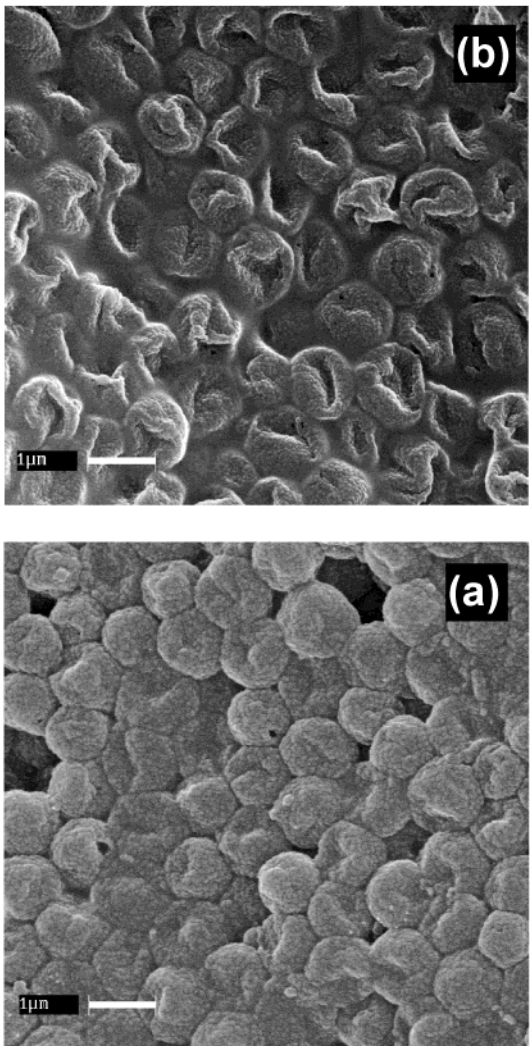

Figure 7. SEM images of the top-side of a film cast at room temperature from a PPy-coated PBMA latex with a PPy loading of 8.3 wt. % containing (a) 25 wt. % NMP; and (b) 75 wt. % NMP.

aromatic polystyrene particles already studied,[15,28] because very different ionic plasma (molecular fragments) should be generated during the hypervelocity impact. Thus the PPy-coated PMMA latexes are expected to be interesting new model micro-projectiles in laboratory-based hypervelocity impact experiments that will ultimately enhance our ability to interpret the ionic plasma generated by carbonaceous micro-meteorites detected by the CDA on CASSINI.

SEM images of the top-sides of films prepared at ambient temperature using one of the PPy-coated PBMA latexes (8.3% PPy mass loading) are shown in Figure 7. In the absence of any coalescence agent, essentially no film formation occurs (see, for example, Figure 2a) due to the relatively rigid, cross-linked nature of the PPy overlayer, and the pressed-pellet solid-state conductivity is around 3×10^{-3} S cm^{-1}. In the presence of 25% NMP cosolvent, partial coalescence is observed but the original spherical latex particles are still evident (Figure 7a). The conductivity of this film was approximately 2×10^{-3} S cm^{-1}, which suggests that the NMP cosolvent does not have a detrimental effect on the PPy. Increasing the proportion of NMP to 75% leads to more extensive deformation and additional particle coalescence (Figure 7b). This SEM image suggests that the conductive films obtained at higher temperatures[19] or with lower T_g latexes (i.e., DSM's ConQuest product, which is based on PPy-coated polyurethane latex) most likely comprise broken "egg-shells" of conductive PPy dispersed within the electrically insulating latex phase. Presumably this unusual morphology accounts for the relatively low percolation thresholds observed for these composite films.

(28) Goldsworthy, B. J.; Burchell, M. J.; Cole, M. J.; Armes, S. P.; Khan, M. A.; Lascelles, S. F.; Cairns, D. B.; Wilson, S. A.; Green, S. F.; Müller, M.; McDonnell, J. A. M.; Grün, E.; Srama, R.; Bigger, S. W. Astronomy and Astrophysics, submitted, 2002.

Conclusions

Two series of PPy-coated poly(alkyl methacrylate) latexes have been prepared and extensively characterized using SEM, DCP, XPS, FTIR, and conductivity measurements. For the PBMA latex, all the experimental evidence is consistent with the formation of a core−shell morphology, with the electrically conductive PPy component forming a granular shell. However, the PMMA latex particles are rather more difficult to coat with PPy. This difference is most likely related to the increased hydrophilicity of the PMMA substrate and leads to the deposition of a much less homogeneous conducting polymer overlayer. Nevertheless, these non-uniform PPy coatings are sufficient to enable the efficient Van de Graaf acceleration of PMMA latex up to the hypervelocity regime (>1 km sec^{-1}). Thus, the PPy-coated PMMA latex particles are expected to become interesting aliphatic-based organic micro-projectiles that will eventually aid our detection of carbonaceous micro-meteorites using the Cosmic Dust Analyzer on the CASSINI spacecraft. The PPy-coated PBMA latex is an interesting model system for understanding the behavior of PPy-coated film-forming latexes such as DSM's ConQuest (PPy-coated polyurethane particles). The lightly cross-linked outer shell of PPy hinders film formation significantly, but transparent conductive films can be obtained in the presence of coalescence aids such as *N*-methyl pyrrolidone. This cosolvent acts as a plasticizer for the PBMA latex and allows a reasonable degree of film formation at ambient temperature.

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