A novel method for creating charged polymer particles in non-polar organic solvents is demonstrated. A small amount of an oleophilic tetraalkylammonium tetraphenylborate group is incorporated into a poly(methyl methacrylate) particle to provide ionic groups which dissociate in low permittivity solvents.

Conventional wisdom has it that ions should play no role in ultra-low dielectric liquids ($\epsilon_r < 4$) because the attraction between oppositely-charged molecular ions far exceeds the available thermal energy. Despite this argument, particle charging in non-polar solvents was documented first in 1861, and it has been repeatedly rediscovered over the intervening century and a half. Indeed the generation and control of charge in oily solvents is at the heart of a diverse range of technologies from the prevention of flow electrification in petroleum handling, through the operation of air-born drug delivery systems, to toner technology. Interest has increased considerably in the last decade as a result of the development by Jacobson and others of electrophoretic particle displays (EPDs). EPDs offer several desirable characteristics - low power consumption, intrinsic bistability, and high contrast - which make them ideal candidates for electronic paper. An electrophoretic display works on the principle that a highly scattering or absorbing particle when suspended in a low polarity medium becomes electrically charged. The particles are then transported and packed against an oppositely-charged electrode under the influence of an electric field, to generate a switchable bistable change in contrast. The magnitude of the charge on the particle is a crucial factor in determining the switching speed of this display and in circumventing problems of particle clustering, agglomeration and lateral migration which limit the lifetime of the display. Developing and understanding methods to control particle chargeability is essential to fully exploit the potential of this technology.

The difficulty of charge generation in a non-polar solvent can be understood from a consideration of the Bjerrum length ($\lambda_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T}$), the characteristic distance at which the Coulombic interaction between ions in a medium with relative dielectric constant $\epsilon_r$ becomes comparable to the thermal energy ($k_B T$) of the system. Whilst in water at room temperature the Bjerrum length is typically tens of nanometres - if they are to remain stable. Previously-described approaches to achieving this are illustrated in Fig. 1. The simplest route (Fig. 1 (a)) is to add certain surfactants with ionizable groups such as sodium bis(2-ethylhexyl) sulfosuccinate (AOT) to particle suspensions. Particles charge efficiently as surfactant ions adsorb onto the surface of particles and the accompanying counterions are solubilized inside reverse micelles. Alternatively, nonionic surfactants or copolymers may be added to generate association structures such as micelles (Fig. 1 (b)), which enhance the dissociation of surface groups by stabilizing counterions in solution. A third option (Fig. 1 (c)) is to physically cage a low molecular weight hydrophobic salt within the body of the particle. A selection of hydrophobic salts which have been used previously is illustrated in Fig. 2 (a).

Despite effecting a degree of charging, all of these approaches suffer from a number of shortcomings. With surfactants, for instance, the particle charge is not fixed as the charge-producing species is only physically adsorbed. Desorption of surfactant with increasing particle concentration, or in the case of particles with opposite signs, exchange of surfactant between different particles generates complex concentration and/or time-dependent charge effects. Furthermore the large number of charge carriers in solution produced by the presence of excess surfactant results in electro-hydrodynamic instabilities, which limit the lifetime of an electrophoretic display. Whilst the...
incorporation of physically-trapped salts do not suffer from these limitations, they are relatively inefficient and generate low levels of particle charge, as the data presented below illustrates.

In this communication we demonstrate a new approach to the control of particle charge in ultra-low dielectric solvents. Our design relies simply on the covalent incorporation of a small amount of highly oleophilic ionic groups into the particle. Partial dissociation of the ionic groups occurs as these particles are suspended in low-dielectric media \((\varepsilon_r < 4)\), generating charged nearly monodisperse colloids. Large, bulky ionic groups reduce the energy barrier to ionization and generate substantial particle charges.

Non-polar ionic particles were prepared by dispersion polymerization of a mixture of monomers (methyl methacrylate (MMA), and methacrylic acid (MAA)) and a specially-prepared ionic monomer (labelled 1 in Fig. 2 (b)) in a mixed hexane/dodecane medium using a poly(12-hydroxy stearic acid)-poly(methyl methacrylate) copolymer \([\text{P(HSA-co-MMA)}]\) as a stabilizer. For the resulting particles to charge the ionic monomer must fulfil two conditions: First, its constituent ions should be as large and bulky as feasible to aid ionization and secondly, the polymer chains need to be physically compatible with the non-polar solvents to allow easy ion separation, as ions generated within the matrix must diffuse to the surface for the particle to display a net charge. Most simple electrolytes such as \(\text{KBr}\) or short-chain quaternary ammonium salts such as \((\text{CH}_3)_2\text{NBr}\) are sparingly soluble in typical non-polar solvents such as cyclohexane \((\varepsilon_r = 2)\). Studies however have shown that increasing the carbon chain length of quaternary ammonium electrolytes to \(\varepsilon_r = 6\) or greater significantly increases the solubility in non-polar solvents. For instance, the salt tetrakis(decyl)ammonium tetraphenylborate \((\text{TPB})\) anion, \([\text{B(C}}_6\text{H}_{12}\text{Br}_4]\), has a surprisingly high solubility of 0.045 mol dm\(^{-3}\) in cyclohexane. This solubility can be significantly increased by making the \(\text{TPB}\) anion more hydrophobic by fluorination of the phenyl ring. The \text{para-}fluorinated analogue of tetrakis(decyl)ammonium tetraphenylborate, for instance, has a solubility\(^{24}\) in excess of 0.25 mol dm\(^{-3}\) in cyclohexane. Motivated by these observations we selected a tetraalkylammonium group with a \(\text{C}_8\)-alkyl chain as an oleophilic cation and tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate (TFPB)\(^{22}\) as an oleophilic anion.

An acrylic monomer (I) containing both of these functionalities was prepared by alkylation of \(3\text{-}(n\text{-hexyl})\text{amine}\) by 3-bromo-1-propanol, followed by esterification of the hydroxy group with methyl acryloyl chloride, and finally ion exchange with Na-TFPB, following a procedure similar to that reported elsewhere.\(^{21}\) Polymer particles containing either the ionic monomer or one of the hydrophobic salts shown in Fig. 2 were prepared by dispersion polymerization. The reaction conditions used are given in Table 1, and are based on a single-pot, two-stage synthesis of PMMA colloids developed previously.\(^{18,22}\) In this work, the weight ratio of monomer in the reaction mixture was kept constant at 50 wt% and the only parameter varied was the amount of the charging species. In a typical example, the apolar monomers (MMA and MAA), the polymeric comb stabilizer, initiator, chain transfer agent and the ionic monomer (I) were dissolved in a low-boiling point mixture of hexane and \(n\)-dodecane in a 250 ml three-necked round-bottomed flask and refluxed under nitrogen at 80 °C for two hours to nucleate and grow particles. In the second stage, the \(\text{P(HSA-co-MMA)}\) stabilizer was chemically bonded to the surface of the particles to prevent any possible desorption, by heating the mixture at 120 °C for 20 h in the presence of \(\sim 0.2\text{ wt%}\) diethylene glycol. After completion, the reaction mixture was cooled, filtered through tightly packed glass wool to remove large aggregates, and washed by centrifugation. The supernatant was replaced with \(n\)-dodecane which had been dried by contact with molecular sieves. The process of centrifugation and redispersion was repeated at least three times to remove all water and unwanted reaction products. Examples of the particles prepared are shown in Fig. 3. Full details of all synthetic procedures are available in the ESI.\(^{\dagger}\)

The radii of the resulting particles were determined by multi-angle static light scattering using a laser light scattering photometer from Malvern Instruments fitted with a vertically-polarized diode laser at 532 nm. The measured data were fitted numerically to the scattering expected from a Gaussian distribution of uniform spheres of mean radius \(R\) and size polydispersity \(\sigma_R\). The charge on a large number of isolated individual particles were measured in dry \(n\)-dodecane from their motion in an external sinusoidal electric field using an optical tweezer technique\(^{25}\) capable of detecting particle charges of the order of a few elementary charges. The optical trap was generated from a tightly focused diode pumped Nd\(^{3+}\):YAG laser operating at 1064 nm. At the chosen wavelength adsorption and heating of the suspension is negligible. An oscillatory electric field of amplitude

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomers</td>
<td>MMA 31.9</td>
</tr>
<tr>
<td></td>
<td>MAA 0.65</td>
</tr>
<tr>
<td>Charging species</td>
<td>Various(^a)</td>
</tr>
<tr>
<td>Dispersion medium</td>
<td>Hexane 20.3</td>
</tr>
<tr>
<td></td>
<td>(n)-dodecane 10.1</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>(\text{P(HSA-co-MMA)})(^c) 1.63</td>
</tr>
<tr>
<td>Initiator</td>
<td>AIBN(^d) 0.26</td>
</tr>
<tr>
<td>Chain transfer agent</td>
<td>Octanethiol 0.16</td>
</tr>
</tbody>
</table>

\(^a\) Ionic monomer (I) or physically-caged hydrophobic salt. \(^b\) Mass of charging species \(W\) was varied between 0 and 2.6 g. \(^c\) Polymeric comb stabilizer prepared using procedure detailed by Anit et al.\(^{18,25}\) \(^d\) 2,2’-azo bis-isobutyronitrile.
The dramatic effect of the incorporation of ionic groups on the particle charge in \(n\)-dodecane can be seen in Fig. 4. The particle L2 contains 1.4 wt% of the ionic monomer (I) and measurements reveal a substantial positive charge of \(Z = +60e \pm 9e\) while similar particles (L1) prepared without theionic monomer are essentially neutral (\(Z = -3e \pm 4e\)). To confirm that the high charge may be attributed to the presence of dissociable oleophilic ionic groups on the particle we investigated the charge in solvents consisting of a mixture of \(n\)-dodecane (\(\varepsilon_r = 2.0\)), which is a good solvent for the TFB anion,\(^\text{22}\) and \(n\)-pentanol (\(\varepsilon_r = 15.1\)), which is a poor solvent. Both solvents are miscible in all proportions. As illustrated in Fig. 5, increasing the proportion of \(n\)-pentanol causes initially a rapid drop in the particle charge, as the growing incompatibility between the oleophilic ionic groups and the suspension medium suppresses the dissociation of ion pairs inside the particle. Interestingly, further increases in the polarity of the solvent (\(\varepsilon_r > 8\)) reverses this trend and promotes ionization, probably as a consequence of the reduction in the Bjerrum length \(\lambda_B\) with increasing dielectric constant \(\varepsilon_r\). This indicates that the high charge of the ionic particles L2 arises because of the high degree of compatibility between the hydrophobic nature of the ions in the polymer chain and the non-polar character of the suspension medium.

Finally, to demonstrate that our approach offers an improvement over existing methods of non-polar particle charging we have investigated the charge generated by the physical incorporation of hydrophobic salts under comparable experimental conditions. We expect that the magnitude of the charge will be a function of the concentration of added salt. To establish the optimum concentration, we chose as a representative material - potassium tetraphenylborate (KTPB) - and prepared PMMA particles in which the feed ratio of KTPB to the monomers MMA and MAA, was varied systematically (KTPB) - and prepared PMMA particles in which the feed ratio of KTPB to the monomers MMA and MAA, was varied systematically. To establish the optimum concentration, we chose as a representative material - potassium tetraphenylborate (KTPB) - and prepared PMMA particles in which the feed ratio of KTPB to the monomers MMA and MAA, was varied systematically.

**Fig. 3** Typical SEM images of poly(MMA-co-MAA) particles. Micrographs depict particles prepared (a) with no added charge generating species, (b) 2 wt% KTPB, (c) 3 wt% E-89, and (d) 3 wt% P-51.

\(2.6 \times 10^8\) Vm\(^{-1}\) at 17.5 Hz was applied to a pair of planar platinum electrodes, separated by 100 \(\mu\)m, between which a single particle was trapped. The particle position was followed with sub-nanometre resolution by a quadrant photodetector at a frequency of 20 kHz and Fourier transformed to detect the periodic oscillations of the trapped particle. The \(\zeta\)-potential, determined using literature values for the viscosity and dielectric constant of the solvent, was converted into the equivalent particle charge \(Z\) using the standard expression,\(^\text{26}\) \(Z = \left(\frac{\varepsilon_0 k_B T}{\kappa R}\right) R/\lambda_B\), valid in the Hückel limit \(\kappa R \ll 1\) appropriate here.\(^\text{26}\)

Typically, fifty independent particles were measured to yield estimates for the mean charge \(\bar{Z}\) and charge polydispersity, \(\sigma_Z^2 = \langle (Z - \bar{Z})^2 \rangle / \bar{Z}^2\).

The dramatic effect of the incorporation of ionic groups on the particle charge in \(n\)-dodecane can be seen in Fig. 4. The particle L2 contains 1.4 wt% of the ionic monomer (I) and measurements reveal a substantial positive charge of \(Z = +60e \pm 9e\) while similar particles (L1) prepared without theionic monomer are essentially neutral (\(Z = -3e \pm 4e\)).

**Fig. 4** Effect of the inclusion of the ionic monomer (I) on the particle charge. Charge distributions measured from particles synthesised with no added charge control species (L1), or with 1.4 wt% ionic monomer (L2).

**Fig. 5** Dependence of the charge of ionic monomer containing particles (L2) on the dielectric constant \(\varepsilon_r\) of the medium. Data collected in mixtures of \(n\)-dodecane and \(n\)-pentanol.
material at 3 wt% we attempted to prepare particles with each of the hydrophobic salts listed in Fig. 2. Table 2 summarizes the particle charges generated for each species, except in the case of P-51 where addition led to coagulation. Since the particles have slightly different radii, we quantify the efficiency of particle charging by the dimensionless \( \phi = Z\zeta/4R \), where \( Z \) is the charge on a particle of radius \( R \). Inspection of the data in Table 2 reveals that the surface potential generated by the ionic monomer (1) is at least of factor of two larger than that produced by the physical incorporation of a hydrophobic salt.

In conclusion, we have detailed a direct route for making charged monodisperse particles in non-polar solvents such as n-dodecane. Long-chain alkyl ammonium cations and fluorinated tetraphenylborate anions, which are sufficiently large in size to enhance their dissociation and covered with oleophilic functional groups to improve their compatibility with non-polar solvents, are incorporated inside a polymer particle. The driving force for dissociation of the ionic groups is the solubility of the weakly-coordinated ion pair in the low dielectric solvent. Our approach has several advantages: First, we produce high levels of surface charge without generating additional excess charge carriers in solution, in contrast to surfactant charging. This should limit the electrohydrodynamic instabilities which are such a troublesome feature of existing electrophoretic displays.\(^{8,11}\) Second, particles with adjustable surface charge density, suitable for the development of electrophoretic displays, could be designed rationally by tailoring the concentration of the ionic monomer used. Finally, by using other combinations of co-monomers particles with opposite signs could be prepared which should provide a route to the experimental realization of photonic crystals with a bandgap in the visible spectrum.\(^{27}\)

Acknowledgements

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References

26. Assuming a maximum charge of 100 e, a particle radius of 870 nm, and a volume fraction of 10–6, we estimate that \( k R \approx 0.01 \) so the Hückel approximation is expected to be accurate here.

Table 2 Charge and size analysis of particles synthesised with different charge generating species

<table>
<thead>
<tr>
<th>Code</th>
<th>Additive</th>
<th>Wt%(^a)</th>
<th>( e\bar{Z}\bar{r} / k_B T)</th>
<th>Charge Z/e</th>
<th>( \sigma_Z )</th>
<th>Radius R/nm</th>
<th>( \sigma_R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>—</td>
<td>—</td>
<td>0.01</td>
<td>1.4</td>
<td>0.14</td>
<td>610</td>
<td>0.05</td>
</tr>
<tr>
<td>L2</td>
<td>(1)</td>
<td>1.4</td>
<td>1.9</td>
<td>1.5</td>
<td>0.14</td>
<td>870</td>
<td>0.07</td>
</tr>
<tr>
<td>L3</td>
<td>E-89</td>
<td>3.2</td>
<td>0.7</td>
<td>0.23</td>
<td>0.14</td>
<td>590</td>
<td>0.09</td>
</tr>
<tr>
<td>L4</td>
<td>KTBP</td>
<td>3.0</td>
<td>0.8</td>
<td>0.33</td>
<td>0.14</td>
<td>780</td>
<td>0.07</td>
</tr>
<tr>
<td>L5</td>
<td>Benzoic</td>
<td>3.3</td>
<td>0.9</td>
<td>0.15</td>
<td>0.14</td>
<td>450</td>
<td>0.12</td>
</tr>
<tr>
<td>L6</td>
<td>P-51(^b)</td>
<td>3.3</td>
<td>+</td>
<td>—</td>
<td>0.14</td>
<td>490</td>
<td>0.07</td>
</tr>
</tbody>
</table>

\(^a\) Mass of additive \( W \) as percentage of monomer content. \(^b\) Dimensionless \( \zeta \)-potential. \(^c\) Charge polydispersity. \(^d\) Size polydispersity. \(^e\) Particles coagulated so unable to accurately determine charge.