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A new method for stabilising conducting polymer latices using short chain alcohol ethoxylate surfactants

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This study involves the investigation of a new method for the preparation of colloidally stable poly(3,4-ethylenedioxythiophene) (PEDT) dispersions. Our experimental data show for the first time that a relatively short-chain alcohol ethoxylate surfactant ($C_{16}E_{16}$, where C and E represent the methylene and ethylene oxide groups, respectively) can be used to stabilise a conducting polymer dispersion. The principle techniques used to study the PEDT dispersions are photon correlation spectroscopy, transmission electron microscopy and electrical conductivity measurements (of pelletised samples). Microanalytical data are also presented. The oxidant (ammonium persulfate, APS) oxidises the surfactant and monomer simultaneously during dispersion synthesis causing production of surfactant aggregates and conducting polymer particles, respectively. The oxidation results in control samples of surfactant solution becoming turbid. The anionic surfactant aggregates adsorb onto the growing PEDT particles and provide electrosteric stabilisation for the PEDT dispersions. The effect of several key parameters on the hydrodynamic diameter for the PEDT particles are investigated, *e.g.*, APS and surfactant concentration. Stable dispersions result only when critical concentrations of the APS and surfactant are exceeded. The electrical conductivity for PEDT samples increases with decreasing amount of surfactant used during preparation. A maximum conductivity of 0.016 S cm^{-1} was measured.

Introduction

Most polymers are electrically insulating. A new family of electrically conducting polymers emerged in the late 1970's. The major advance in the area of electrically conducting polymers resulted from the pioneering work of Shirakawa, MacDiarmid and Heeger and co-workers,[1] which led to their recent award of the Nobel Prize for chemistry. Electrically conducting polymers offer much promise for improving electronics and providing new functional materials. However, their insolubility in most solvents has delayed widespread application. An alternative approach for improving the tractability of conducting polymers involves their preparation as water-based dispersions. There are considerable environmental and economic advantages of using this route for large-scale production of conducting polymers. In this work we show that stable poly(3,4-ethylenedioxythiophene) (PEDT) dispersions can be prepared using relatively short-chain, non-ionic surfactants. (The structure of the EDT monomer is shown in Fig. 1.) Pressed powders isolated from some of these dispersions have good electrical conductivity.

Most of the electrically conducting dispersions reported in the literature have concerned poly(pyrrole) (PPy). Vincent[2] and Armes[3] and their co-workers pioneered this research and have established various methods whereby long-chain polymers provide steric stabilisation for conducting polymer dispersions. Recently, we have extended these processes to show that it is possible to prepare conducting PPy dispersions stabilised by temperature responsive copolymers.[4] In addition, it has also proven possible to use swollen cross-linked latex particles (microgels) as a matrix for the growth of a conducting polymer phase.[5]

There are relatively few examples of studies involving conducting PEDT dispersions. Armes *et al.* investigated PEDT coated latex particles[6,7] and have noted that this monomer has a relatively low efficiency for oxidative polymerisation[8] (*cf.* PPy). Much of the work published concerning PEDT has resulted from Jonas *et al.*[9–12] at Bayer AG. This company markets a number of conducting polymer products based on EDT.[13,14] Their PEDT dispersion (Baytron P) appears to be stabilised by poly(styrenesulfonate). PEDT is considered to be a superior electrically conducting polymer (*cf.* PPy) because of its improved environmental stability.[11] PPy films generally have poor environmental stability of the conductivity under ambient conditions.[15]

Electrically conducting polymer dispersions are prepared in the presence of appreciable ionic strengths due to the ionic nature of the oxidants employed. The ionic screening present during oxidative polymerisation is more than sufficient to suppress electrostatic stabilisation. Therefore, steric stabilisation must be present if colloidally stable dispersions are to be prepared. Long chain polymeric stabilisers are traditionally used to provide this stability. The particles have a core-sheath morphology, *i.e.*, a conducting particle core and a non-conducting, stabilising sheath.

There have been a few reports involving the chemical synthesis of conducting polymers in the presence of surfactants. Kudoh *et al.*[16] chemically polymerised EDT in the presence of sodium alkylnapthalenesulfonate. The product appeared not to be colloidally stable. Kudoh[17] also prepared PPy in the

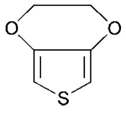

Fig. 1 The structure of EDT.

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presence of the same surfactant. The latter report indicated that colloidally stable dispersions were obtained.

An alternative approach for stabilising latexes is to use small species that self-assemble in solution to give aggregates providing optimum steric stabilisation at a minimum sheath thickness. This work reports the first step toward achieving this goal. Here, a short-chain alcohol ethoxylate surfactant provides steric stabilisation to PEDT dispersions even though the individual chains are too small to confer dispersion stability as individual monomers or normal micelles. The oxidative conditions used during PEDT conversion produce relatively large aggregated surfactant species that adsorb to the growing PEDT surface and facilitate steric stabilisation.

Experimental

Reagents

EDT and $C_{16}E_{16}$ were gifts from Bayer AG and Ecolab LTD, respectively, and were used as received. The composition of $C_{16}E_{16}$ material was investigated using ^{1}H NMR and microanalysis (later) and was satisfactory. Ammonium persulfate (APS) was purchased from Aldrich (98%). Water was of Milli-Q quality.

Dispersion preparation

The PEDT dispersions were prepared at room temperature in the presence of air. In a typical preparation EDT (1.50 g) and $C_{16}E_{16}$ (1.38 g) were added to 200 ml of water and emulsified using a Silverson SL2T laboratory mixer operated at 6000 rpm. APS (13.5 g) dissolved in 50 ml water was then added and the emulsion gently stirred for a period of *ca.* 24 h. The emulsion appearance changed from white to dark blue–black during this time. The product was then dialysed extensively against water and stored at 4 °C. Powders were isolated by freeze-drying. The APS : EDT mole ratio used was 5.64 unless otherwise stated.

Physical measurements

Photon correlation spectroscopy (PCS) data were obtained using a NOVA 901 instrument (Group Scientific) and a scattering angle of 90°. The Stokes–Einstein equation was used to calculate the hydrodynamic diameter. The coefficient of variation for the PCS measurements was 3.5%. Electrophoretic mobility data were obtained using a Malvern Zetamaster instrument. A Philips CM100 instrument operated at 80 kV was employed to obtain TEM data. A Cary 2200 UV-Vis spectrophotometer was used to collect optical and turbidity data. Particle aggregation for the oxidised surfactant solution was detected from the wavelength (λ) dependence of the turbidity (τ) using the wavelength exponent (n).[18] The latter is obtained from the magnitude of the gradient for a plot of log (τ) *vs.* log (λ). The conductivity of the pressed pellets of freeze-dried dispersions was measured using the four-point probe method. Microanalytical data were provided by the University of Otago (NZ) microanalytical service. Samples for microanalysis were dried under vacuum over P_2O_5 in order to remove water prior to analysis.

Results and discussion

PEDT dispersion preparation and properties

A key criteria for assessing dispersion stability is the extent of aggregation present in the system. The dispersions prepared by the method given in the experimental section consisted of isolated (non-aggregated) particles provided there were adequate concentrations of oxidant or surfactant present. The dispersions were generally dark blue–black and remained in the dispersed state during long term storage (*i.e.*, over more than 6 months at *ca.* 4 °C). The particles have a density significantly greater than water and sedimentation was observed over a period of months under quiescent conditions. In a number of cases there was evidence of irridescence on the bottom of the storage flasks. This phenomenon is occasionally observed for latex dispersions, but we are not aware of any reports of irridescence for conducting polymer dispersions.

The particle size of the dispersions was investigated using a range of conditions that are discussed in detail below. Diameters in the range of 160–180 nm were mainly found. These values are in the range expected from the literature. Bayer[14] report that their PEDT dispersion (Baytron P) has a particle size less than 200 nm. Markham *et al.*[2] and Saunders *et al.*[4] reported particle sizes for PPy dispersions in the range of 250 to 350 nm.

Fig. 2 shows a transmission electron micrograph for a representative PEDT dispersion. The deposited particles exhibit hexagonal close packing. This is unusual for conducting polymer dispersions where a higher degree of polydispersity is normally observed. It must be noted that there is evidence of smaller particles with a size less than 20 nm. Mandal *et al.*[19,20] reported the preparation of nanoparticles for PPy and polyaniline. Our TEM data for related preparations (not shown) invariably showed two populations of particles; one with a size in the range of 150–200 nm as well as smaller particles. This indicates secondary nucleation. PCS determines the z-average particle size[21] which is dominated by the larger particles. The presence of the smaller particles is not considered significant for the diameters determined *via* PCS in this work.

The electrophoretic mobilities of a number of dispersions were measured. The mobilities were of the order -3×10^{-8} m^2 V^{-1} s^{-1}. The negative sign could originate from adsorbed inorganic anions, *e.g.*, SO_4^{2-}. These anions would be produced as a consequence of oxidation by $S_2O_8^{2-}$ and are likely to be incorporated into PEDT as a consequence of charge neutralisation. It is well known that conducting polymers scavenge anionic species during oxidative polymerisation.[4] An additional explanation is that anionic surfactant aggregates are produced during the reaction which adsorb to the growing particles. The presence of adsorbed ionic polyelectrolyte sheaths is well known to strongly modify the sign and magnitude of the mobility for latex particles.[22]

Effect of oxidant concentration

The first experimental parameter investigated in detail was the effect of oxidant concentration. The dispersions were prepared and purified by dialysis and the yield recorded as a function of APS concentration employed. The yield is expressed in terms of

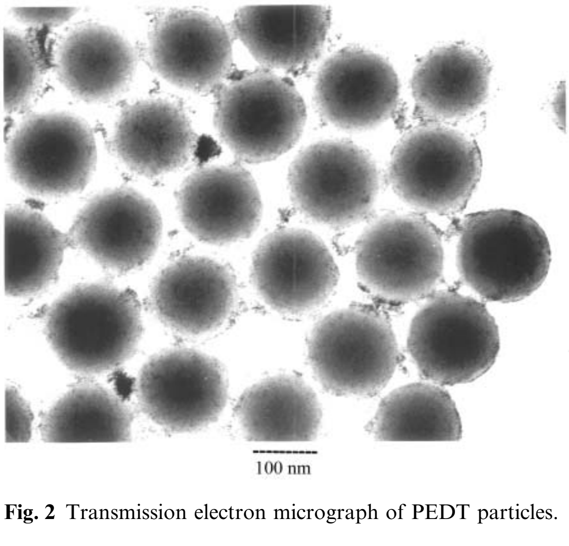

Fig. 2 Transmission electron micrograph of PEDT particles.

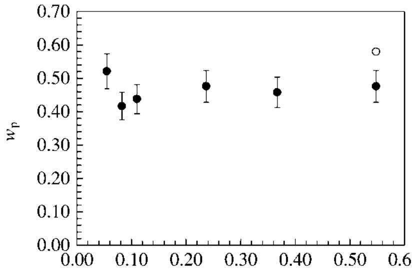

Fig. 3 Effect of APS concentration on the yield of dialysed PEDT dispersions (●). A datum point for a control sample which did not contain EDT (○) is also shown for comparison. The APS : EDT mole ratio increases from 1.04 ([APS] = 0.044 M) to 13.04 ([APS] = 0.548 M) for these data.

the weight fraction of product (w_p) [eqn. (1)],

$$w_p = \frac{m_p}{m_{EDT} + m_s} \tag{1}$$

where m_p, m_{EDT} and m_s are the mass of purified (dried) product, mass of EDT used and mass of $C_{16}E_{16}$ initially added, respectively. The results appear in Fig. 3. The yield of dialysed product is not strongly dependent on APS concentration. An important result was obtained when a control sample containing only APS and $C_{16}E_{16}$ was prepared in the absence of EDT, allowed to react and then dialysed. The product for this sample was a white, turbid dispersion. The value for w_p for the control sample is greater than for the dispersions prepared using EDT because the conversion efficiency of EDT to PEDT is low (see below). The turbidity of the control sample (no added EDT) was attributed to surfactant aggregates that formed as a consequence of oxidation. This is discussed later.

The variation of particle size with APS concentration was investigated and the data appear in Fig. 4. The data show a clear increase in particle size with decrease in APS concentration. Such an observation would be expected if a mechanism related to surfactant-free emulsion polymerisation were operative.[23] Adaption of this mechanism to the present system would envisage growing nuclei that are electrostatically stabilised by anionic residues from the oxidant (*e.g.*, SO_4^{2-}). According to this type of mechanism, a decrease in oxidant concentration would result in a decrease in the surface charge density of charged groups giving rise to greater aggregation during particle formation and larger particles in the final product. This electrostatic-based mechanism would seem to be further supported by the experimental observation that addition of $(NH_4)_2SO_4$ results in an increased particle size (Fig. 4), *i.e.*, increased aggregation during particle nucleation due to greater screening.

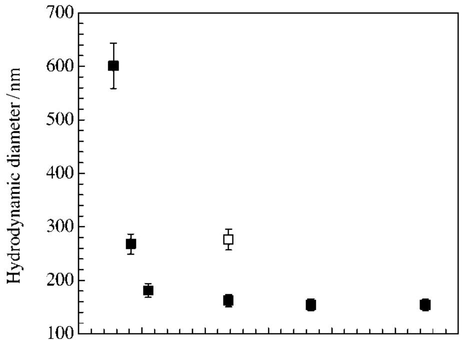

Fig. 4 Variation of the hydrodynamic diameter of PEDT dispersion (■) with APS concentration. The effect of added electrolyte was tested (□) by adding the appropriate mass of $(NH_4)_2SO_4$ to the aqueous phase to achieve an $(NH_4)_2SO_4$ concentration of 0.31 M prior to addition of APS.

The electrostatic mechanism proposed in the preceding paragraph has a serious flaw: the high ionic strengths present due to the oxidant. DLVO calculations (not shown) using the ionic strengths resulting from the oxidant (invariably greater than 0.1 M) and zeta potentials calculated from the mobility data (smaller than −40 mV) show that there could not be any significant electrostatic barriers to aggregation present for the particles under the conditions used to prepare these PEDT dispersions. This is why steric stabilisation is required during preparation of conducting polymer dispersions.[5,24] A non-electrostatic mechanistic explanation must be sought which involves steric stabilisation. This is discussed in detail below.

Effect of surfactant concentration

The effect of $C_{16}E_{16}$ concentration used during synthesis was also investigated. Fig. 5 shows the variation of w_p with $C_{16}E_{16}$ concentration. Data for control samples (*i.e.*, no added EDT) are also shown. A sample containing EDT but no added $C_{16}E_{16}$ was also prepared. The value of $w_p = 0.13$ for this sample corresponds to an EDT conversion efficiency of 13%. Corrardi and Armes[8] reported comparable yields for their PEDT powders. In our work the mass of PEDT (m_{PEDT}) isolated in the absence of $C_{16}E_{16}$ was 0.19 g. Addition of this value to the mass of $C_{16}E_{16}$ used for each preparation shown in Fig. 5 allowed the theoretical curve for w_p to be calculated (shown in the figure). The good agreement with this curve and the experimental data points indicates that the efficiency of EDT conversion is independent of $C_{16}E_{16}$ concentration.

The yield data for the control samples (no EDT) allow an estimate to be made for the mass of excess surfactant present within the PEDT dispersions. This unbound surfactant species is considered to be also present in the respective PEDT dispersion and has a mass, m_{su} (the subscript "su" indicates unbound surfactant). For a given $C_{16}E_{16}$ concentration used to prepare a PEDT dispersion, the mass of surfactant bound to the PEDT particles (m_{sb}) and the total mass of surfactant recovered in the PEDT dispersion ($m_{s(T)}$) are related to m_{su}, m_p and m_{PEDT} by eqns. (2) and (3).

$$m_{s(T)} = m_p - m_{PEDT} \tag{2}$$

$$m_{sb} = m_{s(T)} - m_{su} \tag{3}$$

The values for $m_{s(T)}$ and m_{sb} permit the ratio of PEDT to total surfactant ($R_{PEDT/s(T)}$) and the ratio of PEDT to bound surfactant ($R_{PEDT/sb}$) to be calculated. Values for these parameters appear in Table 1. These data show that the proportion of bound surfactant and total surfactant present increases with increasing $C_{16}E_{16}$ concentration used during dispersion synthesis.

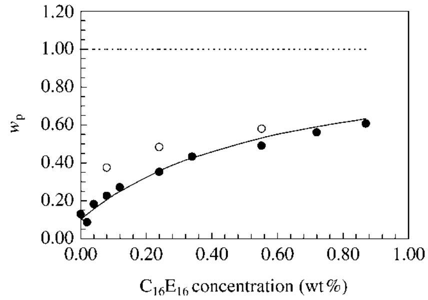

Fig. 5 The yield of PEDT dispersion as a function of $C_{16}E_{16}$ concentration used during synthesis (●). Data obtained in the absence of EDT are also shown (○). The curve shown is based on the sum of the PEDT mass obtained in the absence of $C_{16}E_{16}$ and the mass of $C_{16}E_{16}$ used during synthesis (see text).

Table 1 Gravimetric and conductivity data for poly(EDT) dispersions[a]

$C_{16}E_{16}$ conc. (wt%)	Dispersion yield/g	$m_{s(T)}$	w_p for dispersion	$R_{PEDT/s(T)}$	PEDT (wt%) in dispersion	w_p for control[b]	$R_{PEDT/sb}$	Bound surfactant (wt%)[c]	Conductivity/S cm^{-1}
0	0.194	0	0.130	—	100	—	—	—	—
0.020	0.135	0	0.087	—	—	—	—	—	—
0.040	0.292	0.097	0.182	2.00	67	—	—	—	—
0.080	0.386	0.191	0.227	1.02	50	0.375	1.66	61	0.016
0.120	0.490	0.296	0.272	0.66	40	—	—	—	0.012
0.240	0.740	0.546	0.352	0.36	26	0.483	0.76	47	9.3×10^{-5}
0.340	1.018	0.823	0.433	0.24	19	—	—	—	6.8×10^{-6}
0.552	1.412	1.217	0.490	0.16	14	0.580	0.46	34	—
0.720	1.850	1.66	0.561	0.12	11	—	—	—	—
0.870	2.230	2.04	0.607	0.10	9	—	—	—	—

[a] See text for description of parameters. [b] The control experiment did not contain added EDT. [c] This is the percentage of surfactant adsorbed to the particles.

Microanalytical data were obtained for selected PEDT dispersions and these appear in Table 2. The data for as-received $C_{16}E_{16}$ give reasonable agreement with the theoretical values. It appears as though reaction with APS causes a decrease in the oxygen content of the surfactant. This would be consistent with a decrease in hydrophilicity. Cleavage of ethylene oxide chains is possible within oxidised alcohol ethoxylate surfactants.[25,26] In order to obtain compositional information about the dispersions, it was assumed that the surfactant aggregates present had the same structure as in the control (*i.e.*, $C_{48}H_{101}O_{15}$). Making the reasonable assumption that SO_4^{2-} is the only anionic species incorporated into the PEDT dispersion, the compositions of the two dispersions were calculated. Each calculation relied on solving three simultaneous equations based on the experimental %C, %H and %O values and the general empirical formula for the repeat unit of $(EDT)_{1.00}(SO_4^{2-})_x(C_{48}H_{101}O_{15})_y$. The compositions deduced appear in Table 2. These data allow calculation of the %PEDT in the product, which agree well with those determined from $R_{PEDT/s(T)}$ in Table 1. The compositions indicate a constant level of SO_4^{2-} incorporated. This is not surprising given that identical APS concentrations were used for dispersion synthesis in each case.

Fig. 6 shows the variation of particle size with surfactant concentration used during synthesis. Dispersions prepared with low $C_{16}E_{16}$ concentrations show an increased particle size. At $C_{16}E_{16}$ concentrations less than 0.02 wt% extensive aggregation occurred. The APS concentration used for these preparations was fixed at 0.24 M. A steric stabilisation mechanism must be operative. The increase in hydrodynamic diameter observed at low $C_{16}E_{16}$ concentrations could be explained by a decrease in the sheath thickness and surface coverage of the surfactant aggregates adsorbed onto the PEDT particle surface during growth. The dispersed phase is expected to contain greater than 80 wt% of PEDT when the $C_{16}E_{16}$ concentration used is less than or equal to 0.02 wt% Presumably, at concentrations of surfactant significantly below this value the steric stabilisation afforded by the surfactant aggregate sheath is compromised, leading to excessive aggregation during particle growth. It is important to note that electrophoretic mobility measurements on the surfactant aggregates (after oxidation with APS) revealed that they were negatively charged at the pH of preparation (4.0). These measurements were made over a pH range of 2–8. The growing PEDT polymer chains will be positively charged and therefore adsorption of the anionic surfactant aggregates onto the PEDT particles is favoured.

Fig. 7 shows the variation of conductivities of pelletised powders of several of the PEDT dispersions as a function of

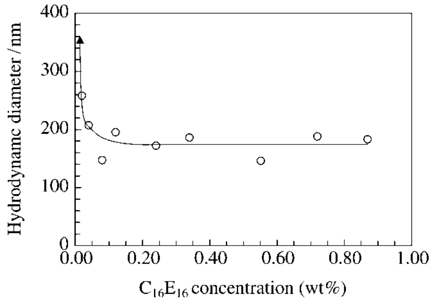

Fig. 6 Variation of the hydrodynamic diameter for PEDT dispersion with $C_{16}E_{16}$ concentration.

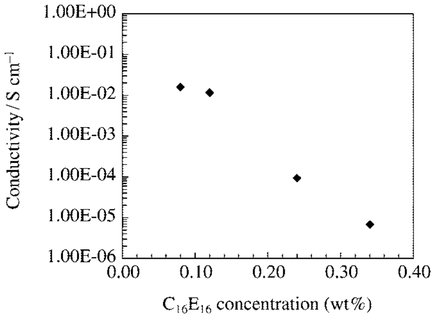

Fig. 7 Conductivity of pelletised powder samples obtained from PEDT dispersions as a function of the $C_{16}E_{16}$ concentration used during dispersion synthesis.

Table 2 Microanalytical data for $C_{16}E_{16}$, PEDT and selected poly(EDT) dispersions

			Found			Calculated			
Sample	$C_{16}E_{16}$ Conc. (wt%)	Formula[a]	%C	%H	%O[b]	%C	%H	%O	%PEDT[c]
$C_{16}E_{16}$[d]	100	$C_{48}H_{101}O_{16}$	61.7	10.9	27.4	60.9	10.44	28.8	100
$C_{16}E_{16}$[ef]	100	$C_{48}H_{101}O_{15}$	63.1	11.2	25.4	62.8	11.09	26.1	100
PEDT	0	—	47.4	4.1	—	—	—	—	—
PEDT	0.080	$EDT_{1.00}(SO_4^{2-})_{0.52}(C_{48}H_{101}O_{15})_{0.17}$	51.4	6.4	—	51.0	6.37	—	47 (50)[g]
PEDT	0.340	$EDT_{1.00}(SO_4^{2-})_{0.47}(C_{48}H_{101}O_{15})_{0.67}$	58.4	9.1	—	58.4	9.21	—	22 (19)[g]

[a] EDT corresponds to the repeat unit of PEDT (*i.e.*, $C_6H_4O_2S$). [b] Calculated by difference. [c] Based on microanalytical data. [d] As supplied. [e] After treatment with APS (see text). [f] Sample contained 0.3% S. [g] The values in brackets are taken from Table 1.

$C_{16}E_{16}$ concentration. It is clear that lower concentrations of surfactant used during dispersion preparation result in higher conductivities for the isolated solid. This is entirely reasonable since $C_{16}E_{16}$ is non-conducting and acts as a barrier to charge transport between PEDT particles. The maximum value for the conductivity is 0.016 S cm^{-1}. Thus, the new synthetic method introduced here is capable of producing colloidally stable dispersions whose deposited solids have good conductivity.

Surfactant chemistry: explanation for change

A central issue in this study concerns the role of the non-ionic surfactant, $C_{16}E_{16}$. It was observed that addition of APS to an aqueous $C_{16}E_{16}$ solution resulted in an increase in viscosity. Furthermore, addition of APS to these solutions causes a turbidity increase provided the APS concentration is moderate. This is shown in more detail in Fig. 8 where the turbidity (τ) and wavelength exponent (n) are plotted for $C_{16}E_{16}$–APS–H_2O solutions after addition of the APS. The wavelength exponent is very sensitive to aggregation and exhibits a significant decrease in magnitude upon aggregation.[18] It can be seen from Fig. 8 that both τ and n exhibit strong changes when the APS concentration increases. The value for n undergoes its greatest change at APS concentrations less than 0.105 M. Above this concentration the value for n does not change significantly. This indicates that surfactant aggregation is extensive when the APS concentration reaches 0.105 M. It is important to note that the critical concentration for maximum surfactant aggregation (0.105 M) coincides with the onset of the minimum particle size for the corresponding dispersions (see Fig. 4). These data firmly establish a link between the onset of surfactant aggregation and PEDT dispersion stability.

The size of the $C_{16}E_{16}$ aggregates present at a given stage of reaction will depend on experimental parameters including the EDT and APS concentrations as well as the shear-rate. Small-angle neutron scattering would be well-suited to studying the aggregate evolution in the presence of growing PEDT particles. In the present work attempts were made to determine the size of the $C_{16}E_{16}$ aggregates prepared in the absence of EDT using PCS. The polydispersity was sufficiently high that reliable measurements could not be obtained. The larger $C_{16}E_{16}$ aggregates were observed using ultramicroscopy and had sizes of the order 1–5 μm. These aggregates are not representative of the smaller aggregates adsorbed during PEDT particle growth. The latter aggregates are much larger than normal $C_{16}E_{16}$ micelles. We do not know of any published data for micelle properties of $C_{16}E_{16}$. However, data for $C_{16}E_{20}$ are available[27] which give an aggregation number and radius of gyration of 32 and 71 Å, respectively. The c.m.c. was 0.003 wt%. Similar values for these parameters would be expected for $C_{16}E_{16}$.

It is of course vital to the understanding of the mechanism for dispersion stability to identify the processes responsible for the generation of the surfactant aggregates. Possible causes include salting out, acid cleavage, hydrogen bonding or oxidation. The origin of surfactant aggregation was investigated by adding strong electrolyte ($(NH_4)_2SO_4$), strong acid (H_2SO_4), hydrogen bonding agent (sodium tetraborate) and strong oxidant ($CeSO_4$) to aqueous $C_{16}E_{16}$ solutions. Only the addition of $CeSO_4$ caused the appearance of turbidity (*i.e.*, aggregation). Therefore, the cause of the surfactant aggregates is oxidation of the parent $C_{16}E_{16}$ surfactant. Blute *et al.*[25,26] have extensively investigated the oxidation of alcohol ethoxylate surfactants. The turbidity increase may be due to a decrease in the number of ethoxylate units per chain (chain scission) and a decrease in the effective HLB (hydrophile–lipophile balance) and cloud point.

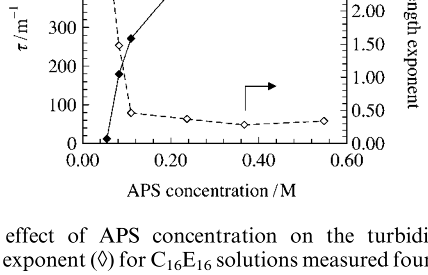

Fig. 8 The effect of APS concentration on the turbidity (♦) and wavelength exponent (◊) for $C_{16}E_{16}$ solutions measured four hours after addition of APS. Note that these systems do not contain EDT.

A rigorous investigation of the oxidation products of $C_{16}E_{16}$ would require a comprehensive investigation in its own right. Here our investigation must be limited to procuring enough information about the aggregate species to explain their ability to stabilize PEDT dispersions. We have obtained microanalytical data, NMR, IR spectra as well as mobility *vs.* pH measurements over an extended range for the aggregates (not shown). The spectroscopic and microanalytical data indicate a minor change in composition of $C_{16}E_{16}$ upon oxidation; a small decrease in oxygen content and the presence of trace amounts of S. The electrophoresis data for the aggregates show mobility *vs.* pH behaviour that is consistent with the presence of weak and strong acid groups, with the former in the majority. Possibilities for the ionic groups are $RCOO^-$ and $ROSO_3^-$. Blute *et al.*[25,26] have shown that oxidation of alcohol ethoxylate surfactants results in chain scission and the formation of aldehydes. It is well known that in the presence of water and oxidants, aldehydes can be oxidised to carboxylic acid groups. The adsorbed aggregates probably contain a substantial proportion of water.[28] Thus, the most likely form of stabilization afforded to the dialysed PEDT dispersions by the adsorbed $C_{16}E_{16}$ aggregates is electrosteric.

Proposed mechanism for oxidant assisted steric stabilisation

Our proposed mechanism for the generation of stable PEDT dispersions in the presence of short-chain surfactant envisages PEDT polymer as well as surfactant aggregates that are generated simultaneously by oxidation. The latter species confer steric stabilisation and are effectively self-assembled during EDT polymerisation. If our oxidative mechanism is correct, it should be able to account for the effect of added $(NH_4)_2SO_4$ on the particle size (Fig. 4). The rate at which the aggregates and PEDT particles are produced will be important for PEDT dispersion stability. If the particles form much faster than the stabilising surfactant aggregates then poor dispersion stability is expected. The rate of production of reactants by oxidation is often an exponentially increasing function of the overpotential.[29] The latter is an increasing function of the reduction potential for the cathodic process. It follows that the rate of surfactant aggregate production (by an oxidation reaction) is an increasing function of the reduction potential for the $S_2O_8^{2-}/SO_4^{2-}$ half-cell. This is described by the Nernst equation [eqn. (4)],

$$\begin{aligned} E(S_2O_8^{2-}/SO_4^{2-}) = {} & E^{\circ}(S_2O_8^{2-}/SO_4^{2-}) \\ & + (RT/2F)\ln(a_{S_2O_8^{2-}}/a_{SO_4^{2-}}) \end{aligned} \tag{4}$$

where $E^{\circ}(S_2O_8^{2-}/SO_4^{2-})$ is the standard reduction potential for the $S_2O_8^{2-}/SO_4^{2-}$ redox couple (2.05 V *vs.* SHE) and $a_{S_2O_8}$ and a_{SO_4} are the activities for $S_2O_8^{2-}$ and SO_4^{2-}, respectively. This equation reveals that addition of SO_4^{2-} to an APS solution will decrease the reduction potential and hence the rate of oxidation. If the rate of surfactant oxidation were more strongly affected by the reduction potential of the $S_2O_8^{2-}$/SO_4^{2-} redox couple than EDT polymerisation, this would explain the reduced stability for PEDT in the presence of added $(NH_4)_2SO_4$ (and greater particle size observed in Fig. 4). It should be noted that stable PEDT dispersions could also be prepared in the presence of pre-formed $C_{16}E_{16}$ aggregates, which supports the above argument.

Conclusions

This work has shown that colloidally stable, conducting PEDT dispersions can be prepared by oxidative polymerisation in the presence of short chain alcohol ethoxylate surfactants. Conductivities of pelletised powders increase with decreasing concentration of surfactant used during preparation. The highest conductivity measured that corresponds to a colloidally stable dispersion was 0.016 S cm^{-1}. The new approach to conducting polymer dispersion synthesis used here (*i.e.*, using short chain surfactants) means that the use of high viscosity solutions containing long chain polymers to prepare stable dispersions is no longer necessary. Our new technique is therefore more amenable to mass production. This work has shown that the oxidising solutions used for PEDT synthesis result in the formation of a surfactant aggregate species that stabilise PEDT dispersions from flocculation. It is believed that the surfactant aggregate species provide electrosteric stabilisation for the PEDT dispersions. The data are consistent with the view that an optimum balance between emulsion stability and conductivity exists for conducting polymer dispersions. The highest conductivity (0.016 S cm^{-1}) obtained in this work corresponds to a $C_{16}E_{16}$ concentration of 0.02 wt%.

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