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ORIGINAL CONTRIBUTIONS

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Characterisation by X-ray photoelectron spectroscopy of surface layers of poly(vinyl alcohol) on particles formed by dispersion polymerisation of divinylbenzene

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Abstract Well-defined dispersions of polydivinylbenzene in methanol and a binary liquid mixture of methanol and water were stabilised by samples of partially hydrolysed poly(vinyl alcohol) (PVOH). Mean particle diameters in the range 0.3–1.0 μm were produced in dispersion polymerisations. In order to assess surface coverage by PVOH, alcohol groups in the stabilising surface layer were derivatised with trifluoroacetic anhydride. Characterisation of trifluoroacetate groups by X-ray photoelectron spectroscopy permits the quantitative determination of atomic fluorine. The relative concentrations of surface fluorine are in agreement with expectation based on the degrees of hydrolysis of 35 mol% and 72.5 mol% of the PVOH stabilisers. Treatments based on broadscan and high-resolution spectra permit reasonable estimates of the layer thickness for PVOH chains collapsed onto the surface of dry particles. Calculations of the area occupied per PVOH chain are consistent with estimates for other stabilising chains in hydrocarbon media.

Introduction

Heterogeneous processes for radical polymerisation are performed by dispersing a non-aqueous monomer in water to produce a water-insoluble particulate product [1]. In a suspension process, a protective colloid, also known as a suspension stabiliser or suspending agent, is added to hinder coalescence of monomer droplets and adhesion of polymerizing particles. In an emulsion process, a surfactant is incorporated to enhance the colloid stability of the polymerizing particles and of the final emulsion. Partially hydrolysed poly(vinyl alcohol) (PVOH) prepared from poly(vinyl acetate) (PVAc) was used as polymeric stabiliser in both suspension and emulsion processes, and PVOH is typically used in these processes with a degree of hydrolysis (DoH) exceeding 80 mol% [2, 3].

Our studies have focused on the potential of PVOH to operate as a stabiliser, protecting particles formed by precipitating polymer during dispersion polymerisation. It was demonstrated that PVOH with a DoH of 35 mol% was an effective stabiliser in the dispersion polymerisation of styrene (STY) with alcoholic media as diluent [4]. The term dispersion polymerisation defines a process which initially is homogeneous, i.e. monomer, initiator and polymeric dispersant are dissolved in the diluent, but which transforms to heterogeneous due to polymer precipitating on polymerisation. This definition was originally formulated for dispersions produced in non-polar media, giving polymer particles ranging from 0.1 μm to 1.0 μm in size [5]. Since then, investigations have been directed to dispersions produced in polar media such as alcohols and binary mixtures of alcohol and water [6, 7]. A stabiliser in dispersion polymerisation must be soluble in the diluent; and so by adjusting the DoH in PVOH and the composition of the diluent to retain solubility, it is possible to control the concentration of hydroxyl groups in the surface layer of the stabiliser in the resulting polymer particles. The presence of hydroxyl groups at particulate surfaces is an attractive feature. Facile organic chemistry, then, permits conversion to an appropriate surface functionality for a range of applications, e.g. solid phase organic synthesis, polymer-supported reagents and catalysts, separation media, and medical diagnostics [8, 9].

In view of the availability of hydroxyl groups for modification of the surface characteristics of particles, it follows that the development of a suitable methodology based on chemical modification will enable the concentration of PVOH surrounding a particle to be determined. Previously, experimental vapour-phase chemical derivatisation of flat surfaces containing hydroxyl groups permitted characterisation of the hydroxyl concentration by X-ray photoelectron spectroscopy (XPS) [10, 11]. In this experimental procedure, the alcohol groups are derivatised by reaction with trifluoroacetic anhydride (TFAA), and then XPS is used to measure the resulting surface concentration of fluorine. Here, the aim is to extend this method for flat substrates to spheres in order to characterise the stabilising dispersant layer of PVOH present on dry particles following dispersion polymerisation. We report successful dispersion polymerisations of divinylbenzene (DVB) with a PVOH stabiliser (DoH = 35.0 mol%) dissolved in methanol and a PVOH stabiliser (DoH = 72.5 mol%) dissolved in aqueous methanol, in which a range of mean particle diameters is produced as a function of the concentration of dispersant. Outcomes of the XPS characterisation are new results for the thickness of the PVOH surface layer on dry particles and the surface area occupied per PVOH chain.

Experimental

Chemicals

Azobis(isobutyronitrile) (Fluka) as initiator was recrystallised from methanol before use. Divinylbenzene monomer (Aldrich) was 55% DVB (mixture of isomers with 45% 3- and 4-ethylvinylbenzene by volume), and was purified by passing through an inhibitor column (Aldrich) to remove the dissolved *p*-*t*-butylcatechol. Methanol (laboratory grade Carless Solvents) was used as received and water was triply distilled. Partially hydrolysed PVOH (35 mol%, number average molecular weight $M_n = 104{,}400$) was supplied as a solution under the trade name Alcotex 359B (Harlow Chemical Company Ltd). This solution consisted of polymer (26% by weight), methanol (65%) and methyl acetate (9%) and was used as received. Partially hydrolysed PVOH (72.5 mol%, $M_n = 52{,}300$) was supplied in pellet form under the trade name Alcotex 72.5 (Harlow Chemical Company Ltd) and was used as received.

Dispersion polymerisation

Particles of polydivinylbenzene (PDVB) were prepared by dispersion polymerisation by a well-established method [4]. A sample of Alcotex 359B or 72.5 was added to the reactor. The diluent was methanol for Alcotex sample 359B and methanol:water (75:25, w/w) for Alcotex sample 72.5. Values of [PVOH] were in the range 0.85–4.89% w/w. This dispersion medium was heated to reflux with stirring after introducing a flow of nitrogen and left overnight. A mixture of monomer (in the range 0.9–10.0% w/w), solvent and initiator (in the range 0.05–2.35% w/w) was added, as one shot, to the reactor and the polymerisation was performed for 24 h. The dispersions produced were subjected to redispersion cycles using quantities of diluent as employed in the polymerisation, in order to remove any unconverted monomer, unadsorbed stabiliser, or initiator residues. Particles were sedimented with an MSE High Speed 25 centrifuge operating at 7,000 rpm for 15 min. The clear supernatant fluid above the sedimented particles was carefully removed and then replaced with fresh diluent. Particles were then redispersed, and the sedimentation-separation-redispersion procedure repeated five times.

Particle characterisation

Scanning electron microscopy (SEM) was used to assess particle shape, size, and distribution, and to determine number average particle diameter. Samples were prepared by placing one drop of clean dispersion on to glass covers attached to aluminium metal stubs, which were then sputtered with gold after evaporating to dryness. Samples were examined at suitable magnifications using a Cambridge Stereoscan 360 instrument equipped with a Link AN1000 energy dispersive spectrometer and a Microspec WDXZA wavelength dispersive spectrometer. The particle size and distribution were also analysed using a Malvern Mastersizer instrument. Results for mean particle diameter D by both techniques were in good agreement.

Vapour-phase chemical derivatisation

Particles were prepared for derivatisation by spraying the purified dispersion onto a chromic acid cleaned glass plate. Several layers were required to produce a complete covering of a microscope slide. Films of PVOH dispersant alone, in the absence of particles, were also prepared by solution casting onto a cleaned glass plate. Vapour-phase derivatisations can be affected by adsorbed water vapour and contaminants present in air; and so a purpose-built chemical derivatisation apparatus was used for the derivatisation reactions [10, 11]. Samples were evacuated overnight to remove any contaminants. TFAA (99+%, Aldrich) was purified by performing three freeze-thaw cycles before derivatisation. TFAA was allowed to react with a dry sample of polymer particles, or dispersant films, for ~2 h and then, the samples were evacuated once again overnight before performing XPS characterisation.

X-ray photoelectron spectroscopy

The XPS was performed on a VG ESCALAB Mk 1 spectrometer using a non-monochromatised Al-Kα X-ray source (1486.6 eV), at a pressure of $\sim 10^{-7}$ mbar, as described elsewhere [10, 11]. All spectra were recorded with an X-ray power of 200 W (10 kV, 20 mA) and in the constant analyser energy (CAE) mode. Broadscan spectra were gained at a pass energy of 100 eV with a 10-mm slit and high-resolution spectra were gained at a pass energy of 20 eV with a 4-mm slit. All spectra were obtained at a take-off angle of 90° with respect to the sample surface and charge referenced to the carbon 1s peak at a binding energy of 284.6 eV. The high-resolution spectra deconvolution was achieved using a modified van Cittert deconvolution algorithm to remove lineshape broadening effects of the Al-Kα line. Quantification of the stabilising layer was achieved by measurement of the peak areas after the subtraction of a Shirley-type background, with appropriate corrections also being made for photoelectron cross-sections [12], inelastic mean-free paths [13], energy analyser transmission [14], and angular asymmetry in photoemission [15], as required. Re-analysis by XPS after the initial analysis showed no significant changes in surface composition, indicating that no significant radiation damage had occurred.

Results and discussion

Dispersion polymerisations with polymeric stabilisers such as poly(N-vinyl pyrrolidone) (PVP) and poly(acrylic acid) (PAA), rather than a polymerisable stabiliser such as a macromonomer, have been directed to producing micron-sized particles [7]. The production of cross-linked particles has been investigated for copolymerisation of STY and DVB, in which STY is the major monomeric component [16]. Previously, Li and Stover [17] and Hattori et al. [18] reported dispersion polymerisations of DVB (55%) with PVP as stabiliser. Examples of PDVB particles stabilised with Alcotex PVOH samples 72.5 and 359B are shown in Fig. 1. Both micrographs indicate spherical particles, indicating that the conditions for dispersion polymerisation are satisfactory. The size distribution in Fig. 1a appears to be close to monodisperse, which was confirmed by distribution parameters determined from Mastersizer data. Number average diameter for dispersion LA186 estimated from Fig. 1a was 0.33 µm in good agreement with the mean particle diameter 0.37 µm calculated from the Mastersizer distribution. It is indicated that the particle size distribution in Fig. 1b is somewhat more polydisperse for dispersion LA382, and the mean particle diameter was estimated to be 0.73 µm (SEM) and 0.81 µm (Mastersizer). Mean particle diameters obtained from Mastersizer distributions are included in Table 1 for particles studied by XPS.

The surface composition of polystyrene particles (D > 1 µm) produced by dispersion polymerisation has been determined by XPS, and concentrations of adsorbed PVP [19, 20] and PAA [21, 22] stabilisers have been estimated. Although treatments of XPS data are well developed for flat substrates, Sheng and Sutherland [23] considered a model for data treatment in XPS characterisation of spherical particles (D < 1 µm) having a uniform overlayer. Their general model takes into

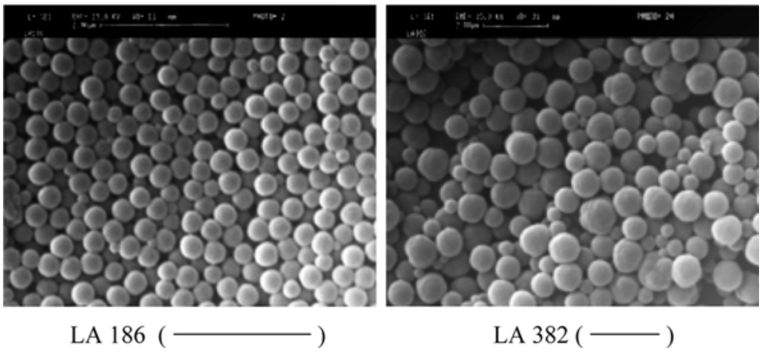

LA 186 (———————)   LA 382 (————)

Fig. 1 Examples of scanning electron micrographs of PDVB particles stabilised with Alcotex 72.5 and 359B, micrographs LA 186 and LA 382 respectively, with 2 µm bar mark in parentheses

Table 1 Results for PDVB particles stabilised by Alcotex 72.5 (a) and Alcotex 359B (b)

Dispersion	[PVOH] % w/w	D (μm)	*d* (nm)	A (nm^2)
LA 186[a]	4.89	0.37	2.97	16.8
LA 187[a]	4.11	0.38	2.76	18.3
LA 188[a]	3.31	0.39	2.75	18.3
LA 189[a]	2.50	0.38	2.49	20.2
LA 190[a]	1.68	0.42	2.11	23.8
LA 191[a]	0.85	0.52	1.61	31.1
LA 370[b]	1.06	0.93	1.29	93.3
LA 371[b]	1.45	0.79	1.45	82.5
LA 372[b]	1.84	0.68	1.53	78.9
LA 373[b]	2.40	0.57	1.86	64.8
LA 374[b]	3.10	0.51	1.80	67.0

account particle size, the range of path lengths of photoelectrons passing through the adsorbed surface layer and the fact that substrate and adsorbed layer will have different attenuation lengths. The situation here is simpler than the general case. Given the range of particle diameters used in this work the relative intensities of peaks from the adsorbed layer and substrate will be independent of particle size, for a fixed coating thickness. This situation has been investigated [24] and Eq. 1 shown to apply.

$$\frac{I_\mathrm{F}}{I_\mathrm{C}}=\frac{\mathrm{rsf}_\mathrm{F}\lambda_{\mathrm{L/F}}n_{\mathrm{L/F}}\int_0^{\pi/2}\cos\theta\sin\theta\left(1-\exp\left(\frac{-d}{\lambda_{\mathrm{L/F}}\sin\theta}\right)\right)\mathrm{d}\theta}{\mathrm{rsf}_\mathrm{C}\lambda_{\mathrm{C/C}}n_{\mathrm{C/C}}\int_0^{\pi/2}\cos\theta\sin\theta\exp\left(\frac{-d}{\lambda_{\mathrm{L/C}}\sin\theta}\right)\mathrm{d}\theta+\mathrm{rsf}_\mathrm{C}\lambda_{\mathrm{L/C}}n_{\mathrm{L/C}}\int_0^{\pi/2}\cos\theta\sin\theta\left(1-\exp\left(\frac{-d}{\lambda_{\mathrm{L/C}}\sin\theta}\right)\right)\mathrm{d}\theta}\tag{1}$$

where I represents the intensity of the peak and rsf is the relative sensitivity factor; including the photoelectron cross-sections, energy analyser transmission and angular asymmetry in photoemission. Symbol λ is the inelastic mean-free path, n the number density, d is the layer thickness and θ is the take-off angle. Subscript F signifies fluorine, C carbon, L/F fluorine present in the stabilising layer, L/C carbon in the surface layer and C/C carbon in the particle core. The numerator, in the above expression, is proportional to the number of fluorine 1s photoelectrons detected from the adsorbed layer. The denominator has two terms which must be summed to estimate the total number of carbon 1s photoelectrons detected (I_c). The first term represents the number of photoelectrons from carbon atoms in the particle. These electrons pass through the coating and are attenuated as a result. The second term represents photoelectrons from carbon atoms in the adsorbed surface layer, and is, consequently, similar in form to the numerator.

A broadscan XPS spectrum for PDVB particles stabilised with Alcotex 72.5 is shown in Fig. 2. In the interpretation of spectroscopic data, in order to consider surface coverage by a stabiliser, the extent of TFAA derivatisation has to be established before adsorption on particles. The percentage derivatisation for pure stabiliser was calculated from results obtained from the broadscan spectra before and after derivatisation of each PVOH stabiliser alone. In this case the percentage composition from XPS was used, specifically the carbon and fluorine percentages. High-resolution spectra for both PVOH stabilisers after derivatisation provided sufficient resolution of the peaks, which may be analysed according to the text associated with Eq. 2. The areas under the peaks associated with the acetate groups and the fluorinated acetate groups were analysed to determine the extent of reaction for the derivatisation. Both broadscan and high-resolution spectroscopic methods gave good agreement, and the average values for pure

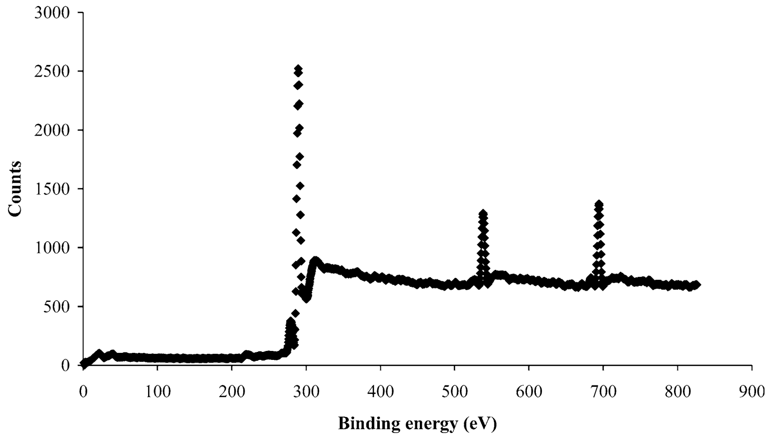


Fig. 2 A broadscan XPS spectra of derivatised PDVB particles stabilised with Alcotex 72.5, with major peaks at ~280 eV (carbon), ~530 eV (oxygen), ~680 eV (fluorine)

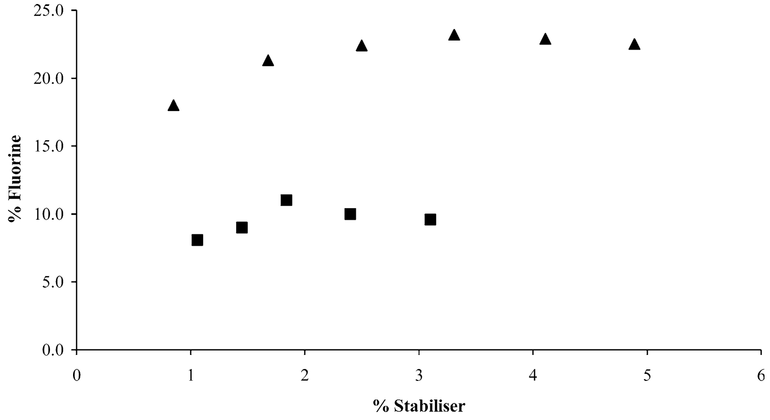


Fig. 3 Percentage fluorine for derivatised PDVB particles stabilised by Alcotex 72.5 (*filled triangle*) and Alcotex 359B (*filled square*) versus stabiliser (% w/w) in dispersion polymerisations of 55% DVB

Alcotex samples 359B and 72.5 were 85.5% and 75.5% derivatisation, respectively, which are in reasonable agreement with the conversion of 80% quoted by Sutherland et al. [10]. The percentage conversions obtained for pure PVOH stabilisers were used as correction factors for calculating complete derivatisation in analysing data for particles dispersed with the same stabiliser.

Interpretation of a broadscan spectrum according to Eq. 1 permits the determination of the atomic fluorine percentage by weight, and results for particles stabilised by both Alcotex samples in Table 1 as a function of particle diameter are displayed in Fig. 3. It is concluded that there is about twice as much fluorine present on particles stabilised by 72.5% hydrolysed PVOH as those stabilised by 35% hydrolysed PVOH, in agreement with expectation based on the DoH of these stabilisers. From Eq. 1 and a broadscan spectrum the surface layer thickness d can be calculated, and results for Alcotex 72.5 as stabiliser are given in Fig. 4. It is estimated that the average error for repeat measurements of *d* for particles in Fig. 4 is 0.16 nm. From the stabilising layer thickness, and knowing the DoH and the molecular weight of the PVOH stabiliser, the surface area A occupied per stabiliser chain on a PDVB particle can be calculated, and these results are also plotted in Fig. 4. Repeat measurements for A demonstrated reasonable agreement for particles in Fig. 4 with an average error of 1.36 nm^2 . Computed results for *d* and A for PDVB particles stabilised by Alcotex 359B are displayed in Fig. 5. The average error for *d* and A for repeat measurements for particles in Fig. 5 was estimated to be 0.14 nm and 6.46 nm^2, respectively.

The results for surface layer thickness in Table 1 indicate that *d* increases as the particle diameter D decreases. The decrease in D for particles in these dispersion polymerisations was accomplished by controlled increases of [PVOH]. Ranges of concentration for the stabilisers in Table 1 were 0.85–4.89% w/w and 1.06–3.10% w/w for Alcotex 72.5 and 359B, respectively. A possible explanation for the trend in the data for d is that some adsorbed stabiliser is covalently anchored to particles due to chain transfer reactions between propagating PDVB radicals and PVOH, and the incidence of chain transfer will rise as [PVOH] increases. The higher *d* values for Alcotex 72.5 than for Alcotex 359B of higher molecular weight might appear surprising, but may result from somewhat different concentrations of stabilising units in PVOH as a function of DoH during dispersion polymerisation. Model calculations based on DoH and molecular weight (Mn) show that the number

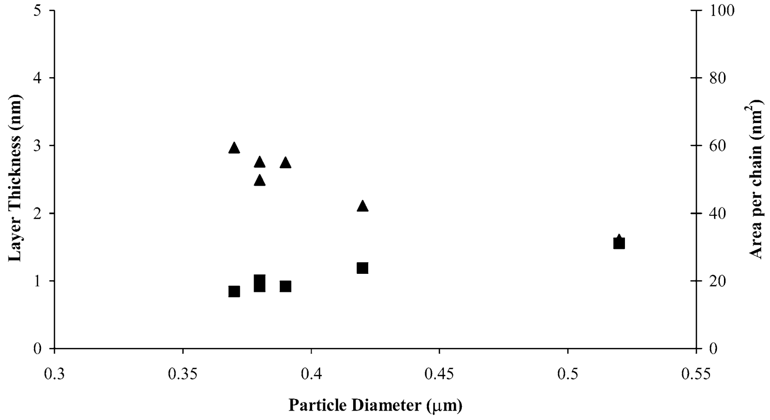
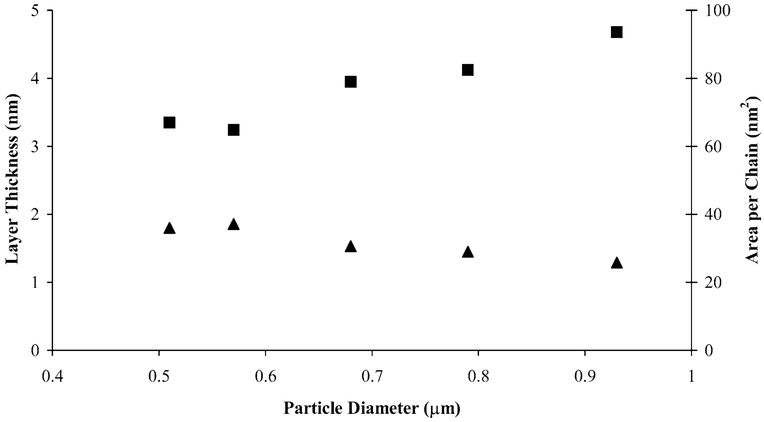


Fig. 4 Stabilising layer thickness (*filled triangle*) and surface area per stabilising chain (*filled square*) versus mean particle diameter for PDVB particles stabilised by Alcotex 72.5

Fig. 5 Stabilising layer thickness (*filled triangle*) and surface area per stabilising chain (*filled square*) versus mean particle diameter for PDVB particles stabilised by Alcotex 359B

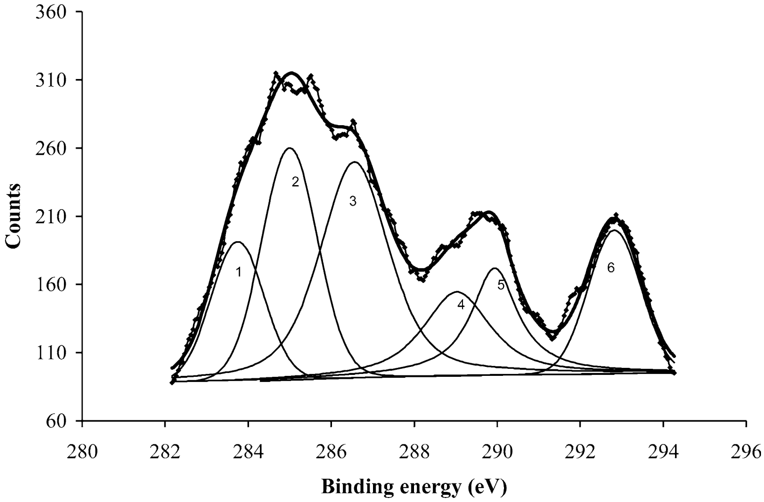


of VOH units per chain of Alcotex 72.5 is higher than for Alcotex 359B, but the number of VAc units per chain is lower. Since partially hydrolysed PVOH has a blocky architecture [4], it is envisaged that soluble sequences based on VOH units may provide longer loops and tails for stabilisation by Alcotex 72.5. Results for *d* in Table 1 are about a factor of 10 below expectation from chain dimensions according to the unperturbed root-mean-square end-to-end distance $<r^2>_o^{0.5}$ of a polymer chain extending away from the particle surface into the diluent. Literature values for the unperturbed dimensions $[<r^2>_o/M]^{0.5}$ are 0.0705 and 0.0950 nm for PVAc and PVOH (DoH = 100%), respectively [25]. By interpolation it will be presumed that values of $[<r^2>_o/M]^{0.5}$ are 0.079 and 0.088 nm for Alcotex 359B and 72.5, respectively, from which $<r^2>_o^{0.5}$ is calculated to be about 25 nm and 20 nm for these two stabilisers. Clearly, as the dispersion diluent medium is removed, the stabilising chains collapse to form a thin overlayer on dry PDVB particles.

In Figs. 4 and 5, plots indicate that the area A occupied per chain rises as the particle diameter D increases for both PVOH stabilisers. Data for A with an approximate value of 77 nm^2, for particles stabilised with Alcotex 359B, are consistently higher than the average of about 21 nm^2 of results for Alcotex 72.5 whose molecular weight (Mn), and therefore chain length, is lower. In view of the considerable reduction in the thickness of the stabilising layer as the diluent is removed, it can be hypothesised that the area occupied per chain might not be much different on drying a dispersion for XPS characterisation. Previous studies of the area occupied per chain for dispersants in hydrocarbon media by rheological methods have reported A = 50 nm^2 for poly(dimethyl siloxane) ($M_n = 50{,}000$) [26] and A = 40–48 nm^2 for ethylene–propylene copolymer ($M_n = 64{,}000$) [27].

An example of an XPS high-resolution spectrum is shown in Fig. 6 for PDVB particles stabilised by Alcotex 72.5. This shows the curve fit and resolved contributions from all the different forms of carbon present in the derivatised stabiliser and particle core in a carbon 1s peak. There are six different forms of carbon that contribute to the carbon 1s high-resolution spectrum,. The

Fig. 6 A high-resolution XPS spectrum of derivatised PDVB particles, indicating resolved carbon 1s contributions: *1* PDVB particles, *2* stabiliser backbone CH$_2$, *3* stabiliser backbone CH, *4* acetate group C = O, *5* fluoroacetate group C = O, *6* trifluoroacetate



areas of these peaks can then be used to calculate the surface layer thickness using Eq. 2 below. Eq. 2 is a simplified version of Eq. 1. The denominator now contains one term since it is possible to identify a species in the high-resolution spectrum that is unique to the particle.

$$\frac{I_c}{I_s} = \frac{\mathrm{rsf}_c}{\mathrm{rsf}_s}\frac{n_c}{n_s}\frac{\lambda_c}{\lambda_s}\frac{\int_0^{\pi/2}\cos\theta\sin\theta\left(1-\exp\left[-\frac{d}{\lambda_c\sin\theta}\right]\right)\mathrm{d}\theta}{\int_0^{\pi/2}\cos\theta\sin\theta\left[\exp-\frac{d}{\lambda_s'\sin\theta}\right]\mathrm{d}\theta} \quad (2)$$

where I represents the intensity of the peak, rsf is the relative sensitivity factor, including the photoelectron cross-sections, energy analyser transmission and angular asymmetry in photoemission. Here, relative sensitivity factors cancel since only carbon photoelectrons are considered. In Eq. 2, the symbol n is the number density, λ the attenuation length, d the layer thickness, θ the take-off angle, subscript c denotes the surface layer and subscript s the particle core, and λ'_s is the inelastic mean free path of the substrate electrons through the coating.

A high-resolution spectrum may be curve fitted, and the areas of the resolved peaks, corresponding to intensity I for the fluorinated acetate groups and for the carbon from the particle core, are used to calculate the layer thickness d. However, the curve resolution is a laborious process, mainly because there are so many contributions and because of the number of different chemical environments present and the assignment of peak positions. These limitations include ratios such as between the acetate and fluorinated acetate groups and between the stabiliser backbone and the two acetate groups. Once the curve fitting has been achieved, then Eq. 2 may be applied to compute the surface layer thickness. For example, particles of PDVB stabilised by Alcotex 72.5 with D = 0.31 μm were analysed by the high-resolution method using Eq. 2. Results for surface layer thickness and area per stabilising chain were $d = 4.24$ nm and $A = 16.4\ \mathrm{nm}^2$, respectively, and these values are in agreement with the results shown in Fig. 4 obtained by the broadscan method using Eq. 1. These equations provide reasonable results for d, for particle diameters D < 1,000 nm. Particles stabilised with Alcotex 359B contained much less fluorine, and because carbon 1s peaks were not so well defined it was not possible to obtain an acceptable curve fit for the high-resolution spectrum for these particles.

Conclusions

The calculation of the surface coverage of PVOH stabiliser on particles of PDVB produced by dispersion polymerisation has been demonstrated. The characterisation method is dependent on the selective reaction of trifluoroacetic anhydride with the alcohol groups present in PVOH to provide trifluoroacetate groups. This chemical derivatisation then permits the quantitative characterisation of elemental fluorine on particles by XPS. Two treatments based on broadscan and high-resolution XPS spectra permit determinations of the surface layer thickness d and the area A occupied per stabiliser chain. For a series of particles produced by dispersion polymerisation in methanolic media, consistent results for d and A were calculated for particles with both a 35% and a 72.5 mol% hydrolysed PVOH as the stabiliser. Trends for the dependence of the area occupied per chain and the surface layer thickness as a function of particle diameter (D < 1 μm) were established for both stabilisers.

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