

Complexation of Microgel Particles with Small Ester Molecules as a Function of the Ionic Content of the Monomer Feed Composition

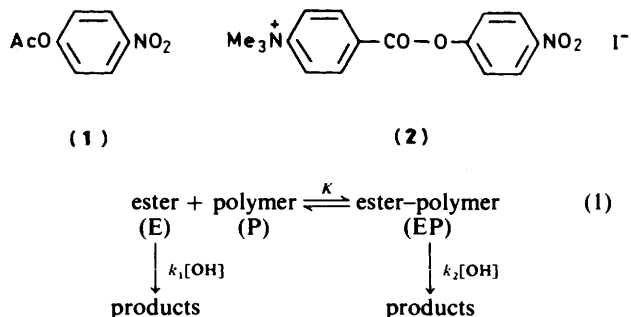
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Water-soluble, polyacrylate, internally cross-linked latex particles (microgels) form complexes with small ester molecules. The association is more favourable as the carboxy group content of the microgels increases; it does not vary significantly with the content of the ethylene dimethacrylate cross-linking comonomer present in the monomer feed in the range 2–30 mol %. The binding of the ester to the polymer is not electrostatic, as the positively charged ester 4-nitrophenyl 4-trimethylammonio-benzoate iodide is only marginally better bound than is the neutral 4-nitrophenyl acetate to the same polymer under similar conditions. The second-order rate constant for the reaction of the ester with hydroxide ion in the ester-polymer adducts is more than an order of magnitude smaller than that for reaction of hydroxide ion with the free ester; this effect also occurs with polymers prepared from neutral monomers.

The large acceleratory effects observed previously for reactions of functions attached to microgels might arise partly from partitioning of substrate into the latex particle to produce a more concentrated solution local to the reactive group.

Microgels are internally cross-linked latex particles usually formed in emulsion polymerisation with a monomer feed possessing cross-linking units.^{1–3} The term microgel is the original one for these small particles,² and has been defined by Medalia.³ Microgels were originally observed in synthetic rubber preparations where monofunctional monomer units such as styrene and butadiene become centres for unwanted cross-linking by radical reaction secondary to the chain-forming process. The diameter of the microgel sphere can be regulated by varying the composition of the monomer feed and can range from 40 to 300 nm.⁴ Microgel particles have been functionalised (with hydroxamic acid⁵ or amino^{6a} or thiol^{6b} groups) by incorporating a protected group into a comonomer followed by deprotection; these functions exhibit dramatic increases in reactivity against small molecular weight substrates.^{5,6} Stereochemical selectivity of optically active functionalised microgels has been demonstrated.⁷ Functionalised microgels also bind or complex substrates⁷ and exhibit a molecular exclusion effect due to the size of the substrates.⁵ Little other work has been reported on the reactivity of functionalised microgels although these species have been used as phase-transfer catalysts in the reactions of cyanide ion with halides,⁸ as carriers of enzymes,⁹ and as markers in immunological studies.⁴

Cross-linked resins and linear synthetic polymers are known to absorb small molecules.^{10,11} For example Amberlite XAD cross-linked beaded polymers are used extensively in reversibly absorbing organic molecules from water solution.¹² There have been many studies of the 'swelling' by monomer of latex particles, formed by emulsion polymerisation with non-cross-linking monomer units;¹³ classical theory of emulsion polymerisation holds that 'swelling' of the latex particle by the monomer is required to enable the particle to grow.¹⁴ It was not surprising that control experiments, where non-reactive microgels were added to an ester solution instead of the reactive polymer, showed a decrease in the background rate of hydrolysis of the substrate. We ascribe this decrease in reactivity to binding of the substrate within the microgel bulk which protects it from reaction with buffer or lyate species present in the solution [equations (1)] to give a reduced rate constant.



The purpose of this study was to examine the binding of substrates and microgels in more detail than was attempted earlier, to determine the effect of monomer feed compositions on binding potential. We have investigated polymers with no reactive groups in order to separate the problem of binding from that of reaction of a functional group. Binding was monitored by observing the reaction of hydroxide ion with the esters in the presence of increasing amounts of polymer. We chose to study the hydrolysis of a neutral ester [4-nitrophenyl acetate (1)] and a positively charged ester [4-nitrophenyl 4-trimethylammonio-benzoate iodide (2)] to monitor the type of binding forces between ester and polymer.

Experimental

Materials.—Monomers were obtained from either Aldrich or Fluka and were redistilled under reduced pressure to remove free-radical traps. 4-Nitrophenyl acetate was prepared by the method of Chattaway,¹⁵ recrystallisation from toluene gave material, m.p. 79–80 °C (lit.,¹⁵ 79.5–80 °C). 4-Nitrophenyl 4-trimethylammonio-benzoate iodide was prepared from the acid and phenol with dicyclohexylcarbodi-imide in ethyl acetate solvent as described previously.¹⁶ The material had m.p. 185–187 °C (lit.,¹⁶ 185–187 °C).

Buffer and other reagents were of analytical reagent grade; water doubly distilled from glass was used throughout the investigation.

Table 1. Molar percentage monomer^a composition of the polymerisation feeds

| | Polymer | | | | | | | | |
|-----------------------|---------|-----|-----|-----|------|----|----|----|----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| MA | 68 | 68 | 68 | 68 | MMA | 63 | 57 | 40 | 35 |
| HEA | 30 | 25 | 15 | 5 | HEMA | 30 | 30 | 30 | 30 |
| EDM | 2 | 2 | 2 | 2 | EDM | 2 | 8 | 25 | 30 |
| AA | 0 | 5 | 15 | 25 | MAA | 5 | 5 | 5 | 5 |
| Diam. ^b | 120 | 126 | 156 | 215 | | | | | |
| Diam. ^c | 74 | 64 | 81 | 70 | | | | | |
| Mol. wt. ^d | 127 | 83 | 167 | 108 | | | | | |
| Area ^e | 81 | 94 | 74 | 42 | | | | | |

^a Abbreviations: AA, acrylic acid; MA, methyl acrylate; HEA, 2-hydroxyethyl acrylate; EDM, ethylene glycol dimethacrylate; MAA, methacrylic acid; MMA, methyl methacrylate; HEMA, 2-hydroxyethyl methacrylate. ^b Measured with a Coulter Nanosizer instrument at pH 10.23; units nm. Figures refer to the 'wet' diameter. ^c 'Dry' diameter (units nm) measured from photographs from electron microscopy. ^d Molecular weight ($\times 10^{-6}$) determined from the dry diameter assuming a density of 1 g ml^{-1} ; the polymers, as judged from the electron micrographs, are essentially monodisperse. ^e Surface area of the microgel particles in $\text{m}^2 \text{ g}^{-1}$ (wet).

Polymers were prepared by emulsion polymerisation under the following standard conditions. Water (100 ml) was deaerated and placed in a thick-walled screw-capped glass beverage bottle with a polythene cap-liner. The bottle was placed in a trigol bath set at $60\text{--}70^\circ\text{C}$. The required amounts of monomer feed components (total weight 5 g) were added together with sodium dodecyl sulphate (100 mg). The contents of the bottle were purged with a stream of nitrogen; ammonium persulphate (50 mg) was added to initiate polymerisation and the bottle was sealed. The polymerisation mixture was kept at $60\text{--}70^\circ\text{C}$ for about 1–1.5 h, during which time it was stirred magnetically. The cloudiness of the emulsion rapidly disappeared, and a delicate blue-tinged clear colloidal solution remained. Hydroquinone (50 mg) was added before the solution became opaque and started to deposit massive polymer. The solution was cooled and the pH adjusted to 7; it was then treated with Amberlite A-26 macroreticular strong base ion-exchange resin (10 g in the chloride form) to remove emulsifier. Passage of the polymer in batches through a column of Sephadex G-25 removed traces of emulsifier, unused monomer, and the stopping agent. The polymer solution was then subjected to ultrafiltration (Amicon PM 30 membrane, exclusion limit mol. wt. 30 000), which concentrated the polymer and purged it of any final traces of monomer or emulsifier. The polymer was tested with BaCl_2 to check the absence of emulsifier; passage through an analytical G-25 column usually gave an excellent 'Gaussian' peak indicating a monodisperse solution.

The concentration of polymer was determined by evaporating a known volume of the purified latex (buffer salts were removed by ultrafiltration) and weighing the residue. The yield of the polymerisation was obtained by precipitation of a sample of the 'raw' polymer sol with dilute hydrochloric acid, and washing and weighing the dried precipitate. The compositions of the monomer feeds for each polymer are given in Table 1. The yields, based on monomer feed, were between 60 and 70%.

Methods.—The hydrolysis of the 4-nitrophenyl esters in buffer solution was followed by observing the release of 4-nitrophenol with a u.v.-visible spectrophotometer (Pye-Unicam SP800). The substrate (10λ ; stock solution in

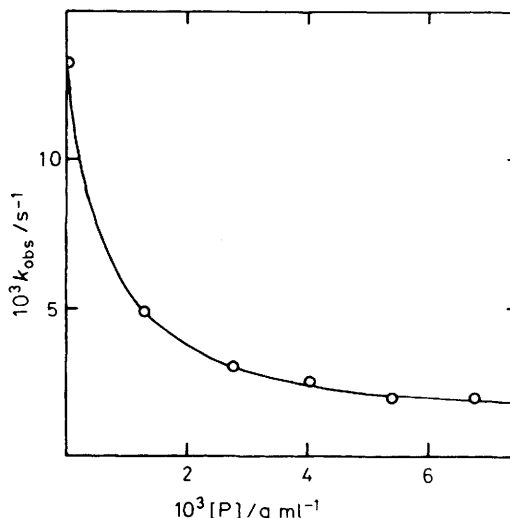


Figure 1. Hydrolysis of 4-nitrophenyl 4-trimethylammonioibenzoate iodide (2) in the presence of increasing amounts of polymer 6; conditions as shown in Table 4; the line is calculated from equation (2) with parameters from Table 4.

acetonitrile) was added to solution (2.5 ml) containing buffer at a fixed pH and polymer. The absorbance at 400 nm was recorded as a function of time and pseudo-first-order rate constants were obtained from semi-logarithmic plots of $A_t - A_\infty$ versus time. The pH of the solution was measured with a Radiometer PHM 62 digital pH meter calibrated with E.I.L. standard buffers to ± 0.02 pH units. A run without the added polymer but with the same pH and buffer gave the background hydrolysis rate of the ester. The polymer concentrations were not high enough to cause reflectance problems due to light scattering. Low ionic strengths were necessary to prevent opacity of the solutions under investigation.

Dry particle size of selected latices was measured with an electron microscope (A.E.I. 801A; 60 kV, without shadowing at magnifications from 16 000 to 25 000; we are grateful to Mr. R. J. Newsam for operating the machine).

Results

The release of 4-nitrophenol from the acetate and trimethylammonioibenzoate esters in buffers containing polymer followed pseudo-first-order kinetics over at least 90% of the reaction. The effect of the non-reactive polymers was to reduce the hydrolysis rates (Figure 1); the variation of rate constants with polymer concentration obeyed the rate law (equation (2))

$$1/(k_1 - k_{\text{obs}}) = 1/(k_1 - k_2) + K/(k_1 - k_2)[P] \quad (2)$$

which can be derived from the mechanism (1)¹⁷ where a single complex is formed between ester (E) and polymer (P). The rate constants k_1 and k_2 represent those for bimolecular attack of hydroxide ion on free and bound ester. The values of k_1 , k_2 , and K are given for various ester-polymer pairs in Tables 2–4. [Here K is equivalent to $1/K$ in equation (1) and ref. 17.] In all the cases k_2 is smaller than k_1 and close to or within the error limits (as given by the mean deviation) of the experimental method. It was not possible to measure the kinetics at the high concentration of polymer required to obtain k_2 accurately, owing to light-scattering problems.

Table 2. Hydrolysis of 4-nitrophenyl 4-trimethylammonio benzoate iodide (2) in the presence of polymers with varying acrylic acid monomer feed^a

| Polymer | 10 ⁴ × Concn. (g ml ⁻¹) | k ₂ /l mol ⁻¹ s ⁻¹ | 10 ³ K/g ml ⁻¹ | N ^b | pH ^d | % ^c |
|---------|------------------------------------------------|-----------------------------------------------------|--------------------------------------|----------------|-----------------|----------------|
| 1 | 2.4–24 | 28 ± 21 | 1.8 ± 0.06 | 7 | 10.63 | 0 |
| 2 | 5–56 | 16 ± 7 | 0.84 ± 0.01 | 4 | 10.64 | 5 |
| 3 | 4–49 | 7 ± 3 | 0.64 ± 0.04 | 4 | 10.63 | 15 |
| 4 | 4.5–47 | 8 ± 4 | 0.37 ± 0.01 | 4 | 10.64 | 25 |
| 2 | 5–40 | 0.5 ± 7 | 2.4 ± 0.2 | 5 | 10.33 | 5 |
| 3 | 5–25 | -13 ± 12 | 2.1 ± 0.2 | 5 | 10.32 | 15 |
| 4 | 4–24 | -5 ± 3 | 1.01 ± 0.01 | 5 | 10.33 | 25 |

^a Borate buffer 0.01M, 25 °C, ionic strength kept at 0.02 with KCl, 20% EtOH–water; k₁ = 92 l mol⁻¹ s⁻¹ (rate constant for reaction of hydroxide ion with 4-nitrophenyl 4-trimethylammonio benzoate iodide); substrate concentrations ca. μM. ^b Number of data points, not including duplicates. ^c Percentage feed composition of acrylic acid. ^d Average pH (kinetics with pH deviations greater than 0.02 units were excluded).

Table 3. Hydrolysis of 4-nitrophenyl acetate (1) in the presence of acrylate polymers with varying acrylic acid monomer feed^a

| Polymer | 10 ⁴ × Concn. (g ml ⁻¹) | k ₂ /l mol ⁻¹ s ⁻¹ | 10 ³ K/g ml ⁻¹ | N ^b | pH ^d | % ^c |
|---------|------------------------------------------------|-----------------------------------------------------|--------------------------------------|----------------|-----------------|----------------|
| 1 | 4–25 | 1.8 ± 2.7 | 3.0 ± 0.2 | 6 | 10.52 | 0 |
| 2 | 5–56 | 1.5 ± 1.2 | 1.2 ± 0.1 | 5 | 10.52 | 5 |
| 3 | 4–25 | 3.5 ± 1.0 | 0.96 ± 0.01 | 4 | 10.51 | 15 |
| 4 | 4.5–33 | 2.1 ± 0.8 | 0.6 ± 0.1 | 5 | 10.52 | 25 |

^a Average pH 10.52, 25 °C, 20% v/v EtOH–water, ionic strength kept at 0.02 with KCl, borate buffer at 0.01M total concentration; substrate concentration 8.34 × 10⁻³M; k₁ = 151 l mol⁻¹ s⁻¹. The value for the reaction of hydroxide ion with 4-nitrophenyl acetate agrees well with that measured previously (W. P. Jencks and J. Garriolo, *J. Am. Chem. Soc.*, 1960, **82**, 1778). ^b Number of data points not including duplicates. ^c Percentage feed composition of acrylic acid. ^d Average pH (kinetics where pH changed by more than 0.02 units of pH were excluded).

Table 4. Hydrolysis of 4-nitrophenyl 4-trimethylammonio benzoate iodide (2) in the presence of polymer of varying cross-linking monomer content^a

| Polymer | 10 ⁴ × Concn. (g ml ⁻¹) | k ₂ /l mol ⁻¹ s ⁻¹ | 10 ³ K/g ml ⁻¹ | N ^b | pH ^c | % ^d |
|---------|------------------------------------------------|-----------------------------------------------------|--------------------------------------|----------------|-----------------|----------------|
| 5 | 2–13 | 1.7 ± 1.2 | 0.71 ± 0.02 | 9 | 10.17 | 2 |
| 6 | 13–70 | 3.7 ± 1.5 | 0.69 ± 0.04 | 6 | 10.19 | 8 |
| 7 | 1.6–8.0 | 8.4 ± 4.2 | 0.52 ± 0.11 | 4 | 10.14 | 25 |
| 8 | 2–15 | 9.1 ± 4.9 | 0.46 ± 0.01 | 8 | 10.32 | 30 |

^a Borate buffer at 0.01M, 25 °C, ionic strength maintained at 0.033M with KCl; k₁ = 92 l mol⁻¹ s⁻¹, ester concn. 4.00 × 10⁻⁵M. ^b Number of data points, not including duplicates. ^c Average pH (kinetics with pH variation outside the range ± 0.02 were discarded). ^d Percentage feed composition of ethylene glycol dimethacrylate cross-linking monomer.

We express the value of *K* in g mol⁻¹ because it is not appropriate to employ a molarity term for the polymer concentration. The binding of the ester is not at a single site in the polymer so that the ester–polymer complex should be strictly considered as E_n·P where *n* is at present an indeterminate but large number. The data obey the simple equation (2) over the range of concentrations of polymer and ester employed; this is assumed to be because the [ester]:[polymer] ratio is never such that ester–ester interactions occur in the complex E_n·P.

Polymers 2 and 6 have similar polymer feed compositions and also have similar *K* values, indicating reasonable reproducibility in the polymer preparations. The slight differences in parameters may be due to solvent differences and the use of methacrylate in polymer 6 as opposed to acrylate monomers in polymer 2. Control experiments involving added sodium dodecyl sulphate in the hydrolysis of the 4-nitrophenyl esters in the presence of polymers indicate that this detergent had no effect on the rate constants (from 2.54 × 10⁻⁴ to 2.29 × 10⁻³ mol l⁻¹ in sodium dodecyl sulphate). We therefore conclude that, even though sodium dodecyl sulphate has been removed from the polymer prior to kinetic study, the presence of residual amounts of detergent is not responsible for any kinetic irregularities.

Measurements of particle diameter for some of the microgels are reported in Table 1 for the dry polymer (electron microscopy) and for the solvated polymer (Coulter Nanosizer).

The dry particle diameter is smaller than that of the solvated species. Assuming a density of 1 g ml⁻¹ for the dry particles, we estimate the 'molecular weights' of the particles which are recorded in Table 1 with the surface area.

The variation in 'wet' particle diameter as a function of pH shows a plateau in the pH 8–11 range with more rapid changes at lower and higher pH values (Figure 2).

Discussion

The inhibitory effect of the polymers on the alkaline hydrolysis of esters (1) and (2) is interpreted in terms of binding of the polymer with the ester to give a less reactive ester. The major factor causing changes in binding constant (*K*) is the acid monomer content of the polymer feed (Figure 3). The more open structure of the microgel caused by the extra carboxy functions should allow more ready access of the ester to the microgel network, and hence provide a greater binding potential. Table 1 indicates that the size of the solvated microgel increases with increasing carboxy content while the 'dry' polymers have approximately the same diameters. This is consistent with the proposed more open structure of the microgels with high carboxy content. The solvated particle size changes with pH (Figure 2), with a plateau between pH 8 and 11; in this region it is probable that the majority of the carboxy groups are ionised.^{5b,c} As the pH increases above 11, the solvated particle diameter increases more rapidly.

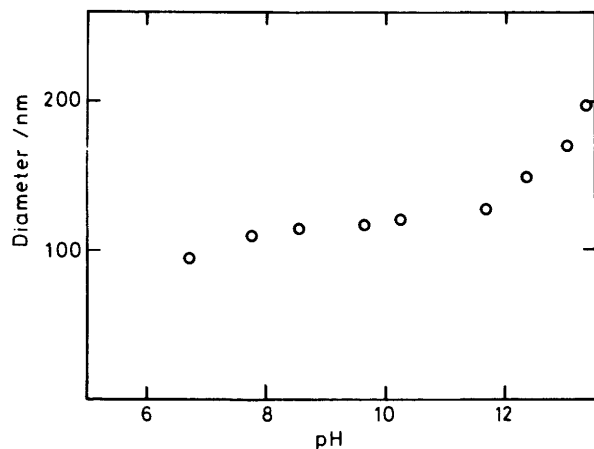


Figure 2. Dependence on pH of the 'wet' diameter of polymer 1. Buffers employed were: phosphate (pH 6–8), tris(hydroxymethylamino)methane (pH 8–10), borate (pH 10), hydroxide ion (pH 11–13.5). The ionic strength was kept at 0.03M at pH values below 11; buffer concentrations, except hydroxide, were at 0.01M total. Above pH 11 the ionic strength was equivalent to the added NaOH.

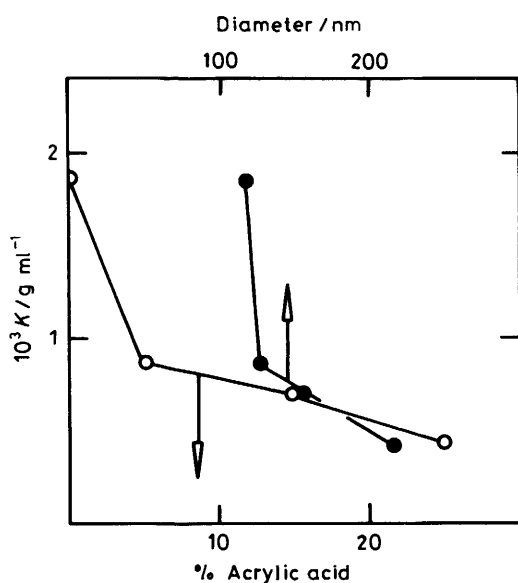


Figure 3. Dependence of binding constant (K) on the percentage acrylic acid comonomer and on the 'wet' diameter for the interaction of 4-nitrophenyl 4-trimethylammonio-benzoate iodide (2) with polymers 1–4; data from Tables 1 and 2

Although the microgels are to a large extent completely ionised under the pH conditions employed in this work, there is little advantage gained by using positively charged esters (Tables 2 and 3); Figure 4 shows that the binding behaviours of neutral and charged esters are almost identical. The electrostatic component of the binding is thus minimal; we ascribe this to tight solvation of the charged groups on the polymer by counterions. We rule out the possibility of the ester binding mainly at the surface of the microgel because it is unlikely that hydrophobic or network entrapment effects could act at the interface. Our results do not allow us to decide between hydrophobic forces and network entrapment as the major binding force.

There have been many studies of the interaction of small charged molecules with linear or branched polymers of opposite

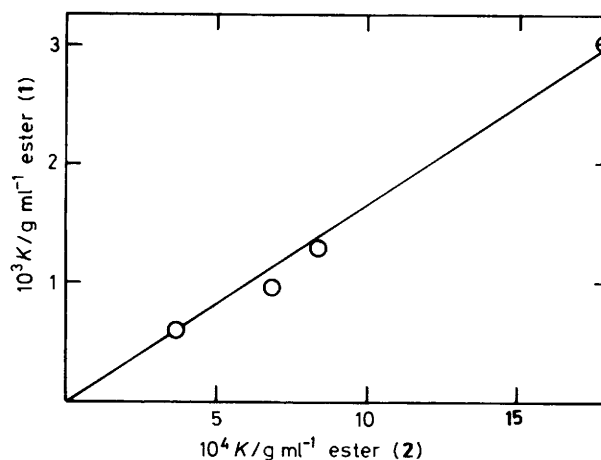


Figure 4. Correlation between the binding constants (K) for 4-nitrophenyl acetate (1) and 4-nitrophenyl 4-trimethylammonio-benzoate iodide (2) with polymers 1–4; data from Tables 2 and 3

charge. The interaction in these cases has been assumed to be largely electrostatic.¹⁸ There are cases where the electrostatic effect is probably minimal, for example the interaction of 4-nitrophenyl indolylacetate with linear copolymers of *N*-benzyl-4-vinylpyridinium bromide and *N*-acetyl-4-vinylpyridinium bromide.¹⁹ The interaction in the present example is probably of the charge-transfer type,¹⁹ but linear polymethacrylic acids almost certainly bind esters by a hydrophobic process.^{11b,20}

Reference to Table 4 indicates that the cationic ester (2) is bound slightly more tightly to microgels with higher cross-linking percentages than to those with little cross-linking. This result is a little surprising, as access to the polymer network should become more difficult as the cross-linking increases; the observed changes in K are close to the errors in measuring K . Previous work has indicated a size-exclusion phenomenon^{5c} in the reaction of functionalised microgels with esters of different sizes. An excellent probe of accessibility of the bound ester would be the ratio of k_1 to k_2 if it were possible to measure k_2 accurately. Although there is a trend in the k_2 data shown in Table 4 the values are very close to their individual errors and cannot therefore be relied upon.

The low value of k_2 relative to k_1 could be due to exclusion of a highly polar species from an essentially hydrophobic network constituting the core of the microgel. The existence of a low k_2 value for microgels with zero acid in their monomer feeds might be taken to confirm this. However, the exclusion could be electrostatic in origin because microgels formed with anionic emulsifiers and persulphate initiators almost always have adventitious negatively charged functions, even if there is no monomer acid in the feed.

The absorption of substrates by polymers is well known. The binding of small molecules to microgels is not well documented although swelling of non-internally cross-linked latex particles has been studied. Absorption of small foreign molecules into micelles is well known and the concentration effect caused by the absorption of reactant and reagent is probably involved in catalysis by such species.²¹ The dramatic enhancements in rate constant observed for attack of microgel hydroxamate ion on esters,⁵ microgel amino function on esters and pyridine sulphonate,^{6a} and microgel thiolate anion on esters^{6b} could be caused in part by the absorption of the ester into the microgel causing a large local increase of concentration of the ester. For example polymer 6 at 5 mg ml⁻¹ will absorb ester (2) from a 4×10^{-5} M-solution to leave 0.5×10^{-5} M ester in the bulk solution. The volume occupied by the microgel is approximately 200 times smaller than that occupied by the bulk solution, so

that the concentration of the ester has effectively increased to 7mM (in the microgel) which is 175 times larger than in the bulk solution. The effect of such an increased concentration will only be observed catalytically if the functional reactive groups are located within the bulk of the particle. There is good evidence that the surface functional groups are much less reactive than the 'buried' ones in microgels with hydroxamic acid groups.⁵

The decrease in reactivity against ester is correlated with a decrease in diameter of amino-functionalised microgels,^{6a} consistent with greater resistance to penetration of substrate into the bulk of the particle.

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