Photophysical Studies of a Copolymer of Acrylic Acid and 1-Pyreneacrylic Acid adsorbed on Calcium Carbonate

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The emission spectrum, polarisation of fluorescence measurements, and transient fluorescence decay characteristics of pyrene in an adsorbed copolymer of acrylic acid and 1-pyreneacrylic acid yield information on the location of the pyrene with respect to the surface; this is related to the configuration of the adsorbed polyanions as revealed by e.s.r. spectroscopy.

The adsorption of polymers onto surfaces and their effect on the properties of particulate dispersions has received considerable attention in recent years. Attempts to elucidate their mechanism of action has led to the development of a number of techniques to establish the configuration of the adsorbed polymer molecules. These include i.r.,[1] n.m.r.,[2] e.s.r.,[3] small angle neutron scattering,[4] and photon correlation spectroscopy.[5] Although photophysical studies of adsorbed molecules have been reported,[6,7] as far as we are aware no attempt has been made to relate luminescence properties to the configuration of the adsorbed macromolecules. The aim of the present work, therefore, is to compare the fluorescence behaviour of pyrene when covalently bound to sodium polyacrylate with the configuration of the polyanion, when adsorbed on $CaCO_3$, as revealed by e.s.r. spectroscopy.

$CaCO_3$ was prepared by bubbling carbon dioxide through a solution of $Ca(OH)_2$. The surface area was 80 m^2g^{-1} (nitrogen adsorption); e.s.c.a. showed no measureable surface impurities. A copolymer of 1-pyreneacrylic acid and acrylic acid was kindly provided by Deh-Ying Chu, University of Notre Dame,

Indiana. The mole ratio of pyrene to monomer was 1 in 1 780 and the molecular weight was 7×10^5. Photon correlation spectroscopy gave a polydispersity index (Pusey Q factor) of 0.83. For e.s.r. studies sodium polyacrylate (molecular mass 90 000; Aldrich) was spin-labelled with 4-amino-2,2,6,6-tetramethylpiperidine N-oxyl,which was covalently attached through the polymer carboxy groups by the method previously described.[3] The copolymer was adsorbed on $CaCO_3$ from water and from 0.5 mol dm^{-3} NaCl, both at pH 9. The absorbance of the pyrene label at 345 nm was used to obtain adsorption isotherms by the depletion from solution method. The isotherms were of the high affinity type with adsorption capacities of 16.0 and 50.5 mg g^{-1} from water and NaCl respectively. For both e.s.r. and fluorescence studies the $CaCO_3$ and adsorbate were washed five times, using identical solvent to that used for adsorption, by repeated centrifugation and decantation to ensure there was no free polymer present. For fluorescence measurements 0.05% dispersions were used.

E.s.r. measurements were carried out with a Jeol JES ME 1X spectrometer. Steady state fluorescence spectra were obtained using a Perkin Elmer MPF44B spectrofluorimeter. The degree of polarization was obtained by measuring the intensity of fluorescence at crossed ($I_{v,h}I_{h,v}$) and parallel ($I_{v,v}I_{h,h}$) positions of polarising filters. The degree of polarisation is given by equation (1).[8] Fluorescence lifetimes were measured using a standard pulsed technique following excitation with a Lamda Physik EMG 100 nitrogen laser with a 6 nano-second pulse.[6]

$$P = \frac{I_{v,v} - I_{v,h}\,(I_{h,v}/I_{h,h})}{I_{v,v} + I_{v,h}\,(I_{h,v}/I_{h,h})} \qquad (1)$$

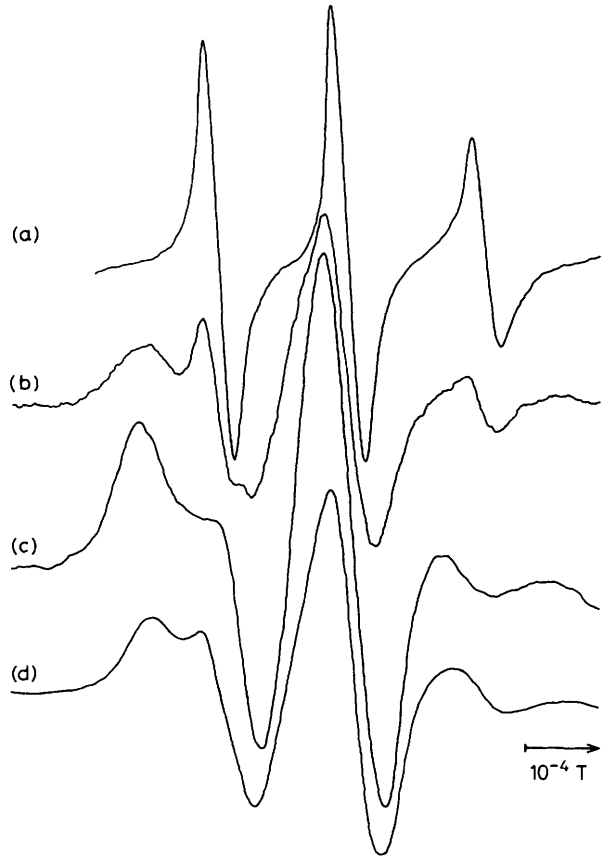

Figure 1. E.s.r. spectra of sodium polyacrylate (a) in aqueous solution, (b) in 80% glycerol, (c) adsorbed on $CaCO_3$ from H_2O and (d) adsorbed on $CaCO_3$ from 0.5 mol dm^{-3} NaCl.

Figure 1 shows the e.s.r. spectra of spin-labelled sodium polyacrylate in aqueous solution (a), in 80% glycerol (b), adsorbed onto $CaCO_3$ from water (c), and adsorbed from 0.5 mol dm^{-3} NaCl (d). In aqueous solution the spectrum appears as three sharp peaks indicating that there is a high degree of mobility. When the viscosity of the solution is increased, *i.e.* in 80% glycerol, the mobility of the spin label is reduced and this is reflected in a broadening of the peaks. When the polymer is adsorbed onto a surface, if the polymer segments distribute themselves in the form of loops and tails extending away from the surface into solution then a mobile-type spectrum would be expected, whereas, if the polymer segments are close to the surface in trains then the rotation of the spin-label would be restricted, giving an immobile-type spectrum. A more detailed description of the interpretation has been given elsewhere.[3] For sodium polyacrylate adsorption onto $CaCO_3$, therefore, it is concluded that in water alone, since the spectrum is of the immobile type, the polymer segments are very close to the particle surface in trains, whereas, in 0.5 mol dm^{-3} NaCl, where the spectrum shows increased mobility, some of the segments are now present in loops and tails protruding into solution.

Figure 2 shows the time resolved fluorescence of a deareated colloidal dispersion of the pyrene in the copolymer when adsorbed on $CaCO_3$ from 0.5 mol dm^{-3} NaCl. The decay can be fitted to a double exponential function, equation (2), which is the sum of two first-order decay functions. Each first-order decay has an observed rate constant, k_1 or k_2 respectively and each is weighted by a factor α or $1-\alpha$ respectively. Figure 2 shows good agreement between experimental and calculated data; k_1 is 9×10^7 s^{-1} and k_2 is 9×10^6 s^{-1} with α equal to 0.21. In solution the fit is adequately described by a single exponential with a corresponding rate constant of 9×10^6 s^{-1}. This suggests that the pyrene exists mainly in two different environments in the adsorbed state, one that is similar to that in solution (k_2). The higher rate (k_1) may be due to pyrene groups that are close to and are quenched by the surface. For dispersions in water, the time resolved fluorescence data also fit a double exponential, in which k_1 and k_2 have similar values to those in the electrolyte environment; however α is now much higher (0.38), suggesting that the fraction of pyrene groups near to the surface is much greater in an aqueous medium, in broad agreement with the e.s.r. data.

$$I(t) = I(t = 0)\,\{\alpha \exp(-k_1 t) + (1 - \alpha)\exp(-k_2 t)\} \qquad (2)$$

The first excited singlet state of pyrene is quenched by many solute molecules.[7] The rate of quenching depends on the rate

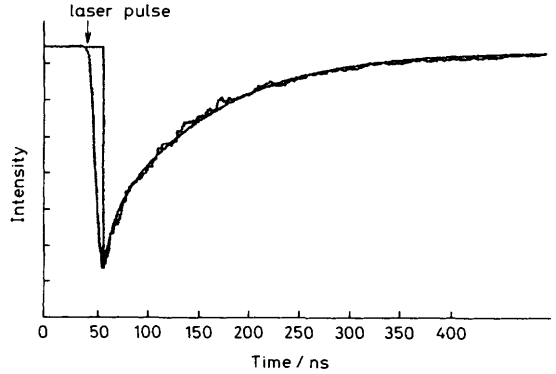

Figure 2. Double exponential fit of the transient emission of pyrene (in sodium polyacrylate copolymer) adsorbed on $CaCO_3$ from 0.5 mol dm^{-3} NaCl.

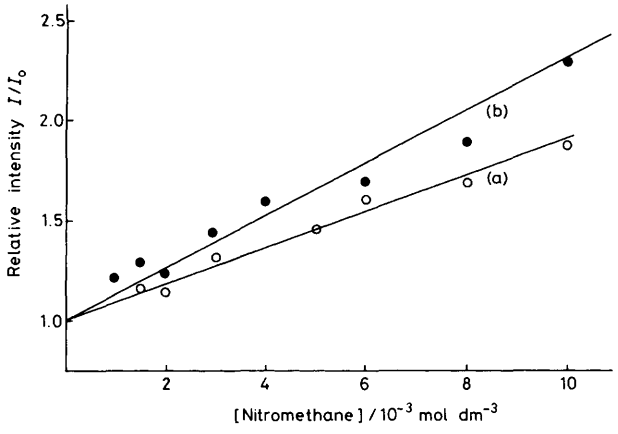

Figure 3. Nitromethane quenching of pyrene (in sodium polyacrylate copolymer) from steady state data, when adsorbed on $CaCO_3$ (a) from H_2O and (b) from 0.5 mol dm^{-3} NaCl.

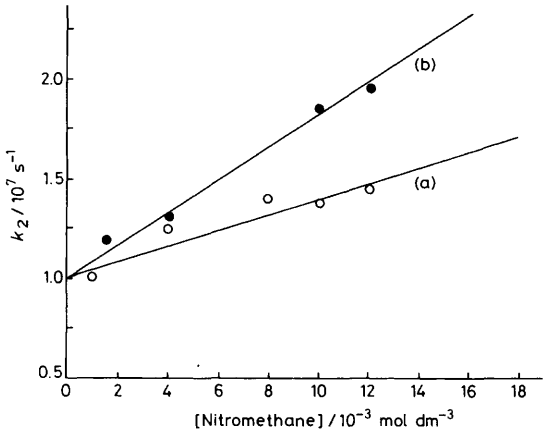

Figure 4. Variation of the decay constant k_2 with nitromethane concentration, when the copolymer is adsorbed on $CaCO_3$ (a) from H_2O and (b) from 0.5 mol dm^{-3} NaCl.

at which the quencher molecule can diffuse to the excited state pyrene. When in the adsorbed copolymer this will be related to the configuration of the polymer in the adsorbed state.

$$I_0/I = 1 + K_{sv}[Q] \quad (3)$$

Steady state and time resolved fluorescence data were obtained for quenching by nitromethane. The steady state results are shown in Figure 3 in the form of the Stern–Volmer equation, equation (3), where K_{sv} is related to the quenching rate, k_q, and the fluorescence lifetime, τ, ($K_{sv} = k_q\tau$). The time resolved fluorescence in the presence of nitromethane still fits the double exponential function. In an aqueous medium, α is independent of quencher concentration. The dependence of k_2 on the amount of quencher is shown in Figure 4. The value for k_q calculated from this data is 4×10^8 $s^{-1}mol^{-1}dm^3$. This value is less than that calculated from the Stern–Volmer data (8.5×10^8 $s^{-1}mol^{-1}dm^3$), which is similar in magnitude to k_q obtained from quenching pyrene in the copolymer in solution both from steady state and time resolved data.[9] This suggests that some static quenching occurs owing to some weak association betwen the nitromethane and the surface, although no permanent adsorption of nitromethane on $CaCO_3$ could be detected experimentally.

In 0.5 mol dm^{-3} NaCl the time resolved and steady state calculated values for k_q are 8×10^8 and 1.2×10^9 $s^{-1}mol^{-1}dm^3$ respectively; in addition α increases with increase in quencher concentration, although k_1 is not affected by the nitromethane in this concentration range. A possible explanation for this is that some excited state pyrene is shielded by the extended polymer coils, and as the nitromethane concentration is increased more molecules can reach these sites.

The degree of polarization, P, of the fluorescence of pyrene in the copolymer when adsorbed on $CaCO_3$ in water was 0.168, whereas when adsorbed from 0.5 mol dm^{-3} NaCl the value was 0.04. In solution both in water and NaCl the degree of polarization was zero. These results indicate that the polymer when adsorbed from NaCl has considerable freedom of motion, similar to that in solution, whereas when adsorbed from water the fairly large value for P is indicative that the pyrene groups are fairly rigidly confined with only a limited range of molecular motions available to them.

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