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Adsorption–solution structure relationships of PET/POET polymeric surfactants in aqueous solutions

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Polyethylene terephthalate/polyoxyethylene terephthalate (PET/POET) water-soluble polymers are effective surface modifiers of polyester-containing textiles and exhibit surface activity in aqueous solutions. Adsorption of a PET/POET polymer on fabric was studied using ultraviolet–visible (u.v.–vis) and fluorescence spectroscopy. Aqueous PET/POET solutions exhibit two distinct fluorescent emission bands, 334 nm and 386 nm, and the latter band is assigned to an intramolecular excimer of terephthalate groups. The ratio of the fluorescence intensities of these two bands (I_{386}/I_{334}) decreases upon adsorption of the polymer onto fabrics, indicating that one of the solution structures is preferentially adsorbed. Addition of anionic surfactant such as sodium dodecylsulfate (SDS) inhibits the formation of excimers whereas nonionic surfactant does not. Effects of nonionic, anionic surfactants, as well as salt effects (Na^+, Ca^{2+}) on the formation of excimers and on the adsorption behaviour were investigated using both u.v. absorption and fluorescent emission bands, cloud point, and surface techniques. Polymer–surfactant interactions were observed predominantly at surfactant concentrations below the critical micelle concentration (*cmc*). The apparent *cmc* of SDS increased with increasing polymer concentration, and SDS interactions with the polymer can be explained by models previously used to describe interaction between polyethylene oxide and SDS. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyethylene terephthalate; polyoxyethylene terephthalate; surfactants; fluorescence; adsorption)

INTRODUCTION

Hydrophilically modified polyethylene terephthalate/polyoxyethylene terephthalate (PET/POET) polymers are widely used to enhance wettability of textiles, as fabric modifiers, and in detergents to improve oily soil release from polyester-containing fibres[1–3]. The structure of these polymers is shown in *Figure 1*. Surface modification is achieved in these applications by adsorption of the PET/POET polymer from solution onto the hydrophobic surface. The adsorbed state involves direct contact of the lipophilic PET groups with the polyester fabric such that the hydrophilic POET groups provide increased hydrophilicity and improved water-wettability of the modified surface.

Although numerous patents have been filed for the use of PET/POET polymers in textile and detergent industries, the surface activity of these polymers[4] and the effect of solution structure on subsequent adsorption are not well understood. The solution structure is a complex function of the molecular structure of the block copolymer (i.e. the parameters *m*, *n*, and *x* in *Figure 1*) and various solution properties, including temperature, concentration, ionic strength, and pH. As noted, the PET groups are lipophilic and act as the 'sticker' during adsorption on hydrophobic surfaces, whereas the polyethylene glycol chains in the POET groups are hydrophilic and act as flexible extenders. Due to the presence of both lipophilic and hydrophilic moieties in a single molecule, PET/POET polymers are surfactants. As expected, interaction of these polymers in solution with other surfactants are important and in many cases may drastically affect the adsorption behaviour.

Fluorescence spectroscopy is an excellent tool for probing effects of solution environment and can be used to monitor changes in the structure adopted by PET/POET polymers at various points in an adsorption isotherm. Mattice and others used terephthalate groups connected by a flexible extender as model compounds for polyester-type polymers and have calculated the most probable conformations for excimer formation of each model compound[5–10]. Fluorescence spectra of these compounds indicate that the length of the extender is critical: excimer formation is most favourable for $n = 3$ with $-(CH_2)_n-$ as an extender, and for $n = 2$ with $-(CH_2-CH_2-O)_n-$. The intramolecular excimer is a complex between 'sandwiched' aromatic rings, one in an excited state and the other in ground state, separated

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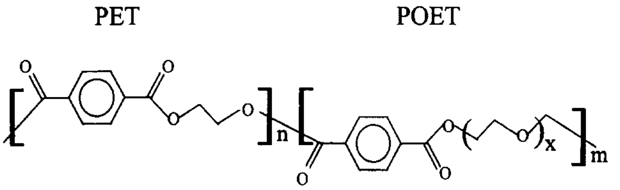


Figure 1 Structure of PET/POET polymer

by 3–5 Å. Excimer formation between terephthalate groups can occur for PET/POET polymers if two aromatic rings are already in a conformation that gives such a sandwich configuration.

Interactions of polymers such as polyethylene oxide (PEO), polyvinyl pyrrolidone, polyvinyl alcohol, and ethyl(hydroxyethyl)cellulose with surfactants such as sodium dodecylsulfate (SDS) have been studied extensively[11-14]. Addition of these polymers to aqueous SDS solutions changes the apparent critical micelle concentration (*cmc*) of the SDS. Aggregate sizes smaller than those of normal micelles have been estimated from surface tension and potentiometric measurements, and SDS head-group interaction with the PEO chain has been suggested[15,16]. Based on these studies and small angle neutron scattering (SANS) experiments[17], a micelle-bound polymer model is now generally accepted. Fluorescence of a probe such as pyrene in polymer/surfactant solutions has been used to investigate solution structures of aggregates formed as a result of polymer–surfactant interactions[18,19]. Addition of a probe molecule in this manner is challenging because the probe itself may significantly affect the formation and structure of the aggregate. Investigations related to SDS interactions have largely focused on polymers that do not contain separate hydrophobic/hydrophilic blocks, except in the cases of PEO/polypropylene oxide or styrene/ethylene oxide block copolymers[20-22]. In the case of PET/POET, the terephthalate moiety provides a convenient internal fluorescence probe to elucidate the interaction between surfactants and the polyethylene glycol (PEG) chain of the POET block at much lower concentrations than conventional methods. By combining analysis of how surfactants affect both the solution structure and adsorption behaviour of PET/POET polymers, a model is proposed to explain surfactant interaction and adsorption mechanism. This understanding can lead to the identification of PET/POET polymers that provide improved surface modification characteristics.

EXPERIMENTAL

Materials

Commercially available PET/POET from Du Pont was used as supplied throughout this study. Neodol 25-9 was obtained from Shell Development Company, and sodium dodecylsulfate was purchased from Aldrich. All surfactants were used as received.

Polymer characterization

^{13}C Fourier Transform nuclear magnetic resonance (*FT*n.m.r.) spectra were collected on a Brucker AM-500 (11.75 T) operated at 125 MHz using deuterated chloroform as solvent. For quantitative structural calculations inverse gated decoupling experiments were performed with 90° pulse and 10 s recycle time. Molecular weight determination by gel permeation chromatography (g.p.c.) was performed on a Waters 745 with a refractive index detector using various PEO standards for calibration at 30°C. Tetrahydrofuran (THF) was used as the eluent at flow rate 1.0 ml min^{-1}.

Adsorption and surface tension measurements

Fluorescence emission and excitation spectra were collected on a Perkin Elmer LS-5 spectrofluorimeter. Ultraviolet (u.v.) absorption spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Surface tension measurements were performed on a SensDyne 6000 Bubble Tensiometer using nitrogen gas at bubble frequency 0.5–1.2 s^{-1}. Deionized double-distilled water and h.p.l.c. grade methanol were used to calibrate the tensiometer. Adsorption studies were conducted at 25°C and fabric loading was 1.0 g per 50 ml solution in all experiments.

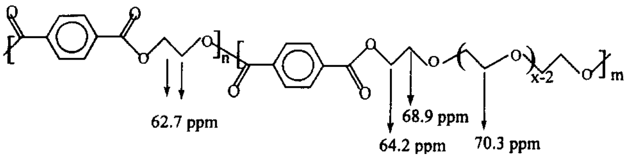
RESULTS AND DISCUSSION

Intramolecular excimer formation of PET/POET in water

Parameters used to characterize the structural features of PET/POET polymers include the number of PET units (*n*), number of polyoxyethylene terephthalate units (*m*), length of EO chain (*x*), overall ratio of aromatic to EO groups, and ratio of ethylene glycol to PEG end groups. Commercial PET/POET polymers typically contain a range of polymers varying in molecular weight, composition, and blockiness. In addition to conventional g.p.c. for molecular weight determination, n.m.r. analyses of ^{13}C and ^{1}H have been used to characterize these polymers[23-25]. Structural features were determined from the inverse gated decoupled ^{13}C n.m.r. data as shown in *Table 1*. The average values of the m/n ratio and x for the PET/POET were calculated to be 1.3 and 22, respectively. A rough estimate of the molecular weight distributions can be also calculated from the ^{13}C n.m.r. spectral analysis as shown in *Table 1*. Molecular weight determined by g.p.c. ($M_n = 4374$) using PEO as a standard did not agree with the calculated value of 2700. However, the spectral analysis is very sensitive to uncertainties in the ratios of the integrated n.m.r. signals. G.p.c. can also be inaccurate since it relies on calibration using PEO.

U.v.-vis. absorption and fluorescence spectroscopic techniques were employed to quantitatively determine adsorption of polymer from solution onto fabric, and to study the solution structure of these polymers. For PET/POET polymers in aqueous solution, the terephthalate chromophore exhibits $\pi \rightarrow \pi^*$ transitions at 244 nm

Table 1 Characterization of PET/POET based on ^{13}C n.m.r. spectra



PET/POET	m	n	m/n	x	M_n
original	2.1	1.6	1.3	21.9	2700
extract	0.9	1.1	0.8	13.4	1000

(K-band) and 295 nm (B-band). The location of the K-band observed in the absorption spectra was the same in water, methanol, and in water/glycerol mixture. However, as shown in *Figure 2*, the fluorescence emission spectra were much more sensitive to solvent properties. In aqueous solutions, two distinct emission bands are observed, at 334 nm and 386 nm, for excitation at 244 nm. The fluorescence spectrum in methanol is very similar to that in water except that the two peaks are not as clearly defined and are shifted to slightly lower wavelengths. In water/glycerol the maximum emission intensity is observed at 312 nm and the relative intensity of the second peak at higher wavelength is greatly reduced. The emission spectrum for dimethylterephthalate (DMT) in water is also shown in *Figure 2*; DMT is only slightly water-soluble and exhibits a single band at 330 nm. As shown in *Figure 3*, the emission intensity ratio of the two bands, I_{386}/I_{334}, is independent of polymer concentration. Based on these observations, the emission band for PET/POET polymers at 386 nm was assigned as an intramolecular excimer resulting from the complexing of the phenyl rings of two terephthalate groups within the same chain. This assignment is consistent with previous work by other researchers[6,7]. The effect of glycerol noted in *Figure 2* may be attributed to the increased solution viscosity, which reduces the flexibility of the polymer backbone, thereby decreasing excimer formation.

Terephthalate groups separated by a single ethylene oxide group (as in the case of adjacent PET–PET or PET–POET blocks) in a good solvent most likely do not form intrachain excimers due to the lack of a sufficiently long extender; in other words, excimer formation is not energetically favourable due to the strain that such a structure would impose on the backbone. Terephthalate groups separated by a long PEG moiety are also unlikely to form intrachain excimers since the probability of bringing the two rings into proximity in solution decreases as the extender becomes too long as shown in Mattice's work[8]. Solvent polarity and solubility of polymers in a solvent are also important factors in fluorescent spectra. For example, intermolecular excimer formation of PET has been reported with hexafluoro-2-propanol as a solvent[26]. Intramolecular excimer formation observed in this work is most likely due to the fact that water is a poor solvent for PET blocks so that, by adopting a sandwich conformation of the aromatic rings, the exposure of the hydrophobic terephthalate groups to water is minimized.

Adsorption of PET/POET from aqueous solution

Adsorption of PET/POET from dilute aqueous solutions (concentrations less than 100 ppm) onto polyester fabric was monitored by u.v. absorption and fluorescence emission spectra. The isotherm for adsorption of PET/POET from water onto polyester adsorbent is shown in *Figure 4* (curve with no surfactant). The adsorption isotherm can be described using a Langmuir model[27]; the equilibrium constant for adsorption in water was estimated to be $2.3 \times 10^5\,\mathrm{l\,mol^{-1}}$ and the observed saturation amount was $0.53\,\mathrm{mg\,g^{-1}}$ adsorbent.

Figure 5 shows the post-adsorption fluorescence spectra of aqueous PET/POET solutions. Comparing *Figure 5* with the original solution spectra in *Figure 3*, the intensity of the excimer band at 386 nm decreases

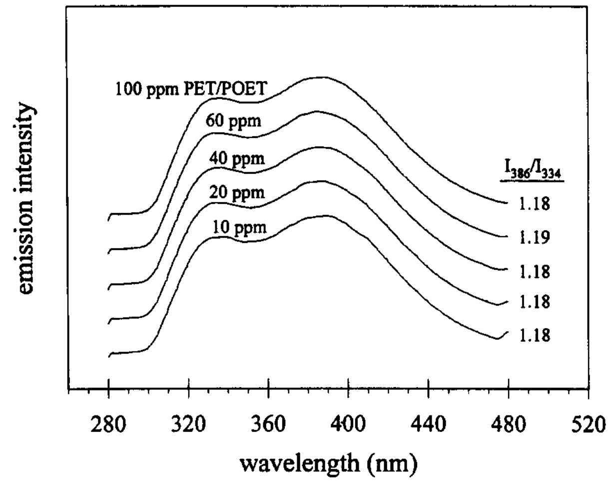


Figure 3 Effect of polymer concentration on fluorescence spectra of PET/POET in water. The intensity ratio I_{386}/I_{334} is proportional to the degree of excimer formation

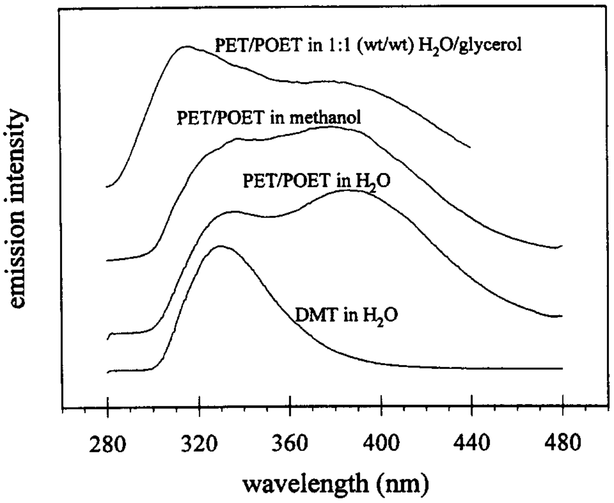


Figure 2 Fluorescence spectra of PET/POET in various solvents and for DMT in water. All fluorescence spectra were obtained at 25°C with excitation at 244 nm

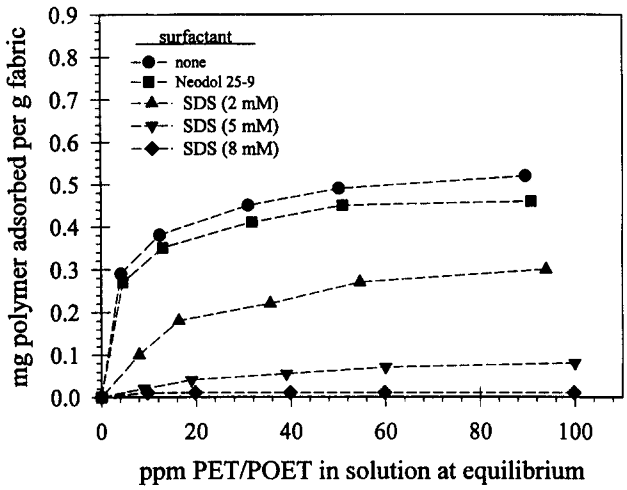


Figure 4 Adsorption isotherms at 25°C for adsorption of PET/POET from aqueous solution onto polyester fabric

relative to the monomer band; i.e. the I_{386}/I_{334} ratio decreases as polymer is adsorbed from solution.

After adsorption, fabric swatches were removed from solution, wrung and pressed to eliminate excess solution, air dried, and immersed in acetone to extract adsorbed polymer. The acetone was decanted and evaporated, and the residue was then dissolved in water. The fluorescence spectrum of one such solution of extracted polymer is shown in *Figure 6*. The I_{386}/I_{334} ratio for the solution containing extracted polymer is significantly higher than the value of 1.18 observed for the original solution, clearly demonstrating that the polymer fraction capable of adopting the intramolecular excimer conformation in solution is also preferentially adsorbed when the solution is in contact with polyester fabric.

The inverse gated decoupled ^{13}C n.m.r. spectrum of the extract confirms the structural differences in the polymer distribution. As shown in *Table 1*, the average values of the m/n ratio and x for extracted polymer are 0.8 and 13, respectively; in comparison to the original polymer, the m/n ratio and x are both lower for the extracted material. Polymer structures with shorter EO chain length seem to favour intramolecular excimer formation. The more hydrophobic structures, those having higher than average number of PET groups and shorter EO chains in POET, adsorb preferentially from solution onto polyester fabric. These results suggest that modification of polyester textile surfaces by adsorption of PET/POET polymers from solution can be significantly improved by synthesizing polymers with structural characteristics similar to those listed in *Table 1* for the polymer extract. The PET/POET polymer studied here, for example, contains significant amounts of polymers that are quite hydrophilic (high m/n ratio and x) which do not adsorb appreciably; this polymer fraction does not contribute to the observed adsorption and surface modification.

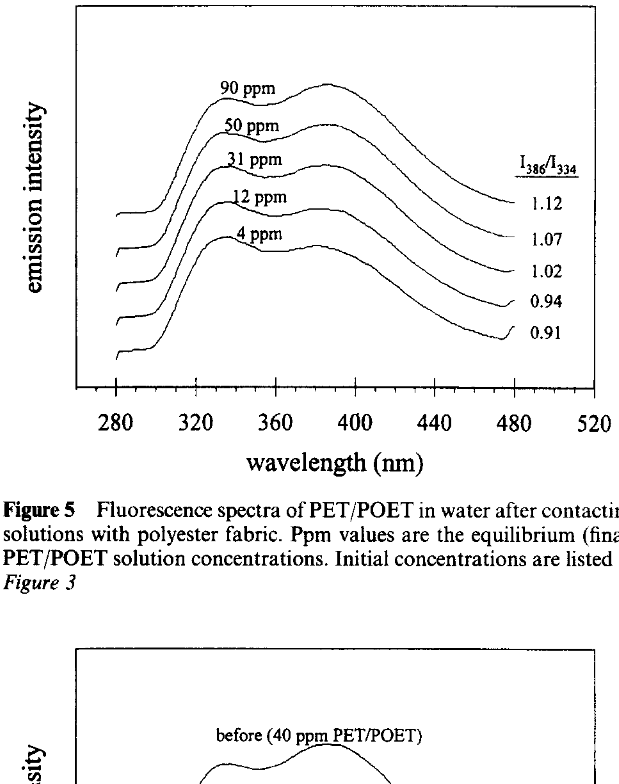


Figure 5 Fluorescence spectra of PET/POET in water after contacting solutions with polyester fabric. Ppm values are the equilibrium (final) PET/POET solution concentrations. Initial concentrations are listed in *Figure 3*

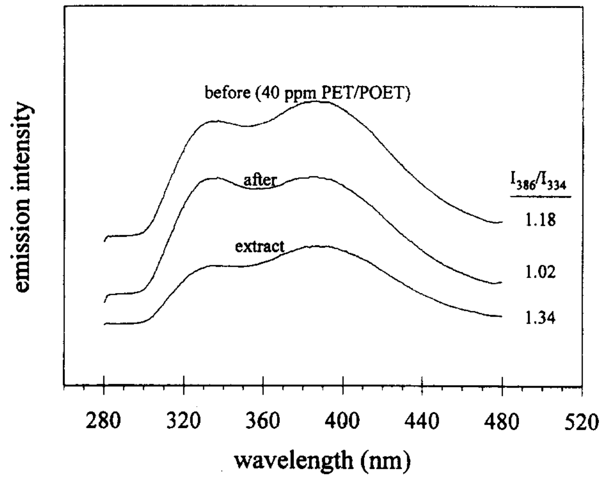


Figure 6 Comparison of fluorescence spectra before and after adsorption of PET/POET from solutions containing only PET/POET and water. Also shown is the spectrum for aqueous solution of PET/POET extracted from fabric after adsorption

Polymer structures with adjacent PET blocks seem to be the cause of intramolecular excimer formation. The same structural feature may allow more favourable interactions of the polymer with the polyester surface during the adsorption process, which in turn facilitates a preferential adsorption. The PEG moiety of the POET block may form a loop at the adsorbent surface. Assuming a fully extended model of PET/POET on the substrate surface, a molecular surface area of 1184 Å^2 (assuming the polymer structure corresponds to the extract listed in *Table 1*) was estimated using molecular mechanics force field available on HyperChem^{TM} and ChemPlus^{TM}. The surface area of the substrates were measured to be $0.125\,\mathrm{m^2\,g^{-1}}$ adsorbent from BET measurements. The saturation amount of adsorbate can then be calculated from the Langmuir model[27]

$$\left(\frac{n}{w}\right)_{\mathrm{sat}} = \left(\frac{A_{\mathrm{sp}}}{N_{\mathrm{A}}\sigma^{0}}\right)$$

where n is the number of moles of adsorbate, w is the mass of adsorbent, A_{sp} is the specific surface area of adsorbent, σ^0 is the molecular surface area of adsorbate and N_{A} is Avogadro's number. The calculated saturation amount is $0.02\,\mathrm{mg\,g^{-1}}$ adsorbent for the fully extended model. Comparing this value to the experimental value of $0.53 \pm 0.02\,\mathrm{mg\,g^{-1}}$ adsorbent suggests that the PEG of the POET is indeed looping out of the surface rather than fully extending on the surface.

Preferential adsorption of PET/POET polymers capable of forming the intramolecular excimer is important for a number of reasons. First, the correlation between excimer formation and adsorption suggests that fluorescence spectroscopy offers a fast, simple method of screening different PET/POET polymers to identify those that exhibit the desired adsorption behaviour. As described in the next section, fluorescence can also be used to study the effect of other components in the solution on excimer formation and these effects are observed to have similar impact on adsorption. Secondly, understanding the factors that influence excimer formation should allow for synthesis of PET/POET polymers with improved efficacy as surface modifiers.

Effect of surfactants on solution structure and adsorption of PET/POET

Successful use of PET/POET polymers for surface modification in various applications depends on understanding the interactions in solution between the polymer and other components. As noted previously, one common use of these polymers is in detergents, where PET/POET polymers aid in the removal of oily soils from polyester-containing fabrics, prevention of soil redeposition during the wash cycle, and imparting soil release properties to the laundered fabric. Given the complex composition of a typical detergent matrix and the low concentrations of PET/POET employed (use-levels generally less than 40 ppm), understanding the effect of the major constituents of the detergent on polymer adsorption is obviously important.

The effects of a nonionic surfactant (Neodol 25-9) and an anionic surfactant (SDS) on adsorption of PET/POET on polyester are shown in *Figure 4*. Neodol 25-9 is an alkyl polyethoxylated alcohol surfactant having 12–15 methylene groups in the alkyl chain and an average of 9 EO groups. The *cmc* of Neodol 25-9 in water is 0.065 mM. Adsorption of PET/POET was slightly decreased in the presence of Neodol 25-9 at 0.76 mM: effects at Neodol 25-9 concentrations less than 0.2 mM were negligible. SDS on the other hand was observed to have a significant influence; polymer adsorption gradually decreased with increasing SDS concentration and was completely prevented at surfactant concentrations $\geq$8 mM. At 2 mM SDS, the equilibrium constant for the Langmuir adsorption of PET/POET was decreased to $5.9 \times 10^4 \, \mathrm{l\,mol^{-1}}$ adsorbate and the saturation amount was $0.30 \, \mathrm{mg\,g^{-1}}$ adsorbent, indicating that SDS shifts the surface equilibrium toward the polymer in bulk solution rather than on the surface compared to adsorption from pure water.

The effect of SDS on the fluorescence spectra of PET/POET solutions is illustrated in *Figure 7*. Excimer formation, which is proportional to the I_{386}/I_{334} ratio, decreases rapidly with increasing SDS concentration below the *cmc*; above the *cmc*, increasing surfactant concentration has relatively little effect on the polymer structure. The fluorescence spectra of SDS and PET/POET solutions before and after contact with polyester fabric, and for polymer extracted from fabric after adsorption are presented in *Figures 8*, *9* and *10*, respectively. Comparing these results with polymer-only solutions (*Figures 3*, *5* and *6*), it is apparent that addition of SDS results in a significant decrease in the I_{386}/I_{334} ratio indicating that SDS inhibits excimer formation. As before, I_{386}/I_{334} for these solutions decreases after adsorption, but the decrease was much less in the presence of SDS because the total amount of polymer adsorbed from solution was also much less. Binding of SDS on the PEG moiety of the POET blocks apparently causes conformational changes in the PET blocks such that excimer formation is prevented. A possible explanation for this marked reduction in adsorption efficiency of the polymer is that the polymer with adsorbed (bound) SDS is more soluble. Further evidence is that concentrated PET/POET solutions (>400 ppm) are cloudy at room temperature, but become clear as SDS is added. This change occurs near the apparent *cmc* of the SDS/polymer solution and turbidity measurements follow the same pattern as the surface tension behaviour. The interaction between SDS and PET/POET thus acts to make the polymer more soluble and reduces its tendency to adsorb.

Surface tension values for aqueous solutions of SDS and PET/POET are presented in *Figure 11*. At low SDS concentrations, the surface tension decreases with

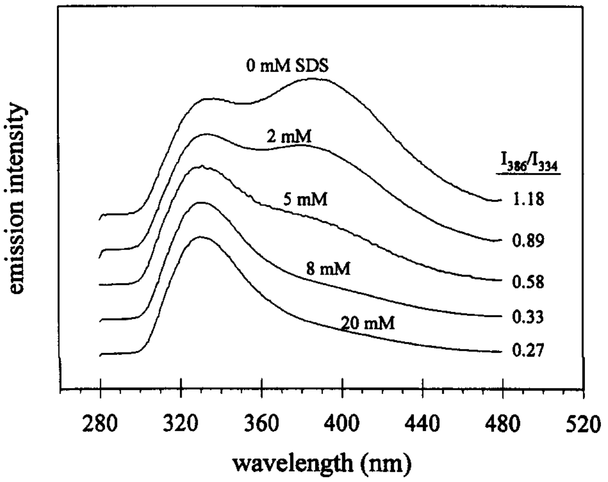


Figure 7 Effect of SDS concentration on fluorescence spectra of aqueous solutions containing 40 ppm PET/POET

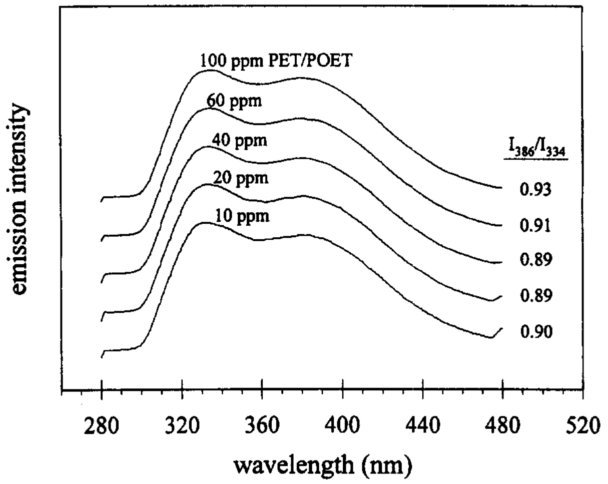


Figure 8 Effect of polymer concentration on fluorescence spectra of PET/POET in aqueous 2 mM SDS

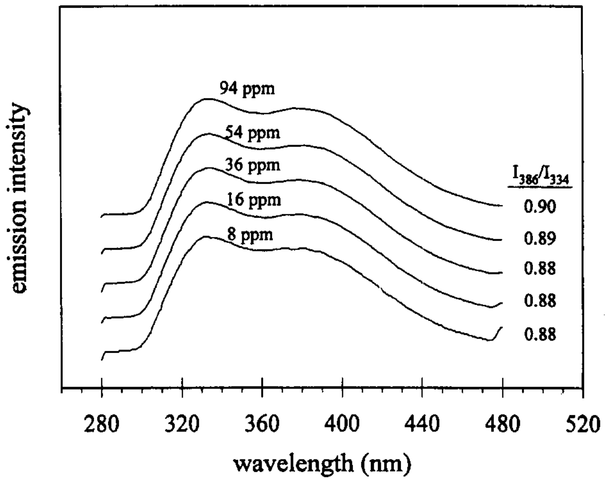


Figure 9 Effect of surfactant on fluorescence spectra of PET/POET after contacting solutions with polyester fabric at various initial polymer concentrations. All solutions contained 2 mM SDS. Ppm values are the equilibrium (final) PET/POET solution concentrations. Initial concentrations are listed in *Figure 9*

increasing polymer concentration due to the fact that PET/POET polymers are themselves surface-active. The *cmc* was determined from the break in the surface tension plot; for SDS/polymer solutions, the apparent *cmc* of SDS increases from 8 to 20 mM as polymer is varied from 10 to 1000 ppm. A common assumption made for surfactant/polymer solutions is that the surfactant monomer concentration at the *cmc* is unaffected by polymer, i.e. for SDS with no added electrolyte, micelle formation begins in all cases when the SDS monomer concentration reaches 8 mM. According to this viewpoint, the polymer affects the apparent *cmc* by complexing some of the surfactant so that below the *cmc* the total and monomeric surfactant concentrations are not equal. Although a number of thermodynamic arguments can be made against this assumption, it has been found to be a good approximation for many systems at low polymer concentrations for estimating the number of surfactant monomers associated per polymer molecule:

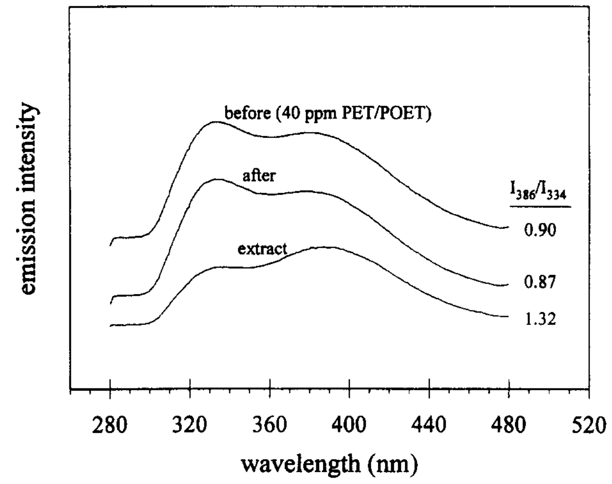


Figure 10 Comparison of fluorescence spectra before and after adsorption of PET/POET from aqueous solutions containing PET/POET and 2 mM SDS. Also shown is the spectrum for aqueous solution of PET/POET extracted from fabric after adsorption

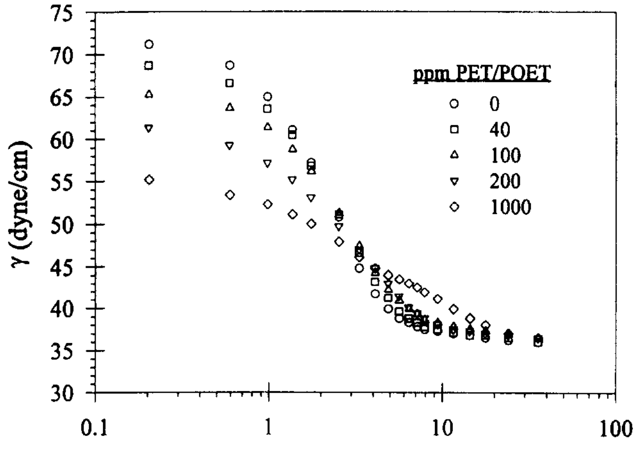


Figure 11 Effect of PET/POET on surface tension of aqueous solutions of SDS at 25°C

$$n_{\text{bound}} = n_{\text{total}} - n_{\text{free}}$$
$$n_{\text{total}} = \textit{cmc} \text{ of SDS and PET/POET mixture}$$
$$n_{\text{free}} = \textit{cmc} \text{ of SDS alone}$$

Calculations using the data in *Figure 11* and the polymer structure analysis in *Table 1* result in 0.7 SDS monomers per EO group, a value that agrees very well with the literature[28], over a polymer concentration range from 40 to 1000 ppm. The indicated number of monomers per polymer chain suggests formation of polymer-bound surfactant aggregates below the *cmc*. If the polymer is viewed as a substrate upon which surfactant adsorbs, these aggregates can be considered admicelles. The aggregation number of the admicelles is considerably lower than for normal SDS micelles (whose aggregation number ranges from 80 to 90); admicelles formation is thermodynamically 'easier' than micelle formation due in part to the fact that interaction between anionic sulfate groups of SDS and polymer EO groups significantly reduces the electrostatic repulsion between surfactant head groups. The interaction of PET/POET with SDS most likely occurs primarily through PEG moieties of the POET block since PEG 1000 exhibits very similar behaviour.

Addition of a monovalent electrolyte such as NaCl had negligible effect on aqueous solutions containing only PET/POET, but significant effect when SDS was present. At a given SDS concentration below the *cmc*, excimer formation as monitored by the I_{386}/I_{334} ratio decreased with increasing NaCl concentration. The fact that electrolytes lower the *cmc* of ionic surfactants is well known and these results indicate that added NaCl also effectively lowers the concentration at which polymer-bound surfactant aggregates form. Interestingly, the opposite effect was observed for the addition of $CaCl_2$ to aqueous solutions of PET/POET and SDS. The interaction between Ca^{2+} and dodecylsulfate anions is apparently much stronger than SDS/polymer interactions, so that the divalent cations tie-up a fraction of the surfactant; this in turn reduces the SDS binding on the polymer so that excimer formation occurs at much higher SDS concentrations than seen in the absence of Ca^{2+}. As with NaCl, addition of $CaCl_2$ to PET/POET solutions with no surfactant present had no significant effect on excimer formation or adsorption.

CONCLUSION

In conclusion, intramolecular excimer formation in PET/POET solutions is primarily due to the polymer fraction with higher PET/POET ratio and shorter EO length in the POET block. Polymers capable of adopting the excimer conformation also adsorb preferentially when the solution is contacted with polyester fabric. Addition of anionic surfactant, SDS, inhibits excimer formation and reduces polymer adsorption. SDS/polymer interaction follows the SDS–PEO interaction model; surfactant binding of approximately 0.7 SDS per EO chain was observed.

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