spectrometry, and gel permeation chromatography. IGC will be widely applicable to the studies of multicomponent polymer systems.

Registry No. PMMA-PEO-PMMA, 52864-39-8; PMMA-PTMO-PMMA, 83560-33-2.

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Dynamics and Hydrophobic Binding of Quaternized Laurylpoly(ethylenimine) in Aqueous Solution

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ABSTRACT: A spin-label method was used to investigate the dynamics of quaternized laurylpoly(ethylenimines) (LQPEI) in aqueous solution. The nitroxide radical was covalently attached to the polymer in two different ways; in the first, the radicals were coupled at primary amino groups of LQPEI, whereas in the second a small amount of the radical was attached at cross-linking positions. The ESR spectra of these spin-labeled polymers in aqueous solution consisted of two components having different rotational relaxation times. The fraction of the lower mobility component increased with increase in the lauryl content of the LQPEI. It was concluded that the polymer consists of two types of domains, one a hydrophobic cluster of lower mobility and the other a peripheral region of higher mobility. The hydrophobic binding ability of the polymeric cluster was quantitatively evaluated from static and dynamic fluorescence measurements of the excimer of pyrenebutyric acid bound to LQPEI, and the results were compared with those for micelles of low molecular weight cationic detergents, cetyltrimethylammonium chloride (CTAC), and lauryltrimethylammonium chloride (LTAC). The LQPEI cluster binds the hydrophobic molecule effectively at concentrations one to several orders of magnitude lower than required for similar binding by CTAC or LTAC micelles.

Introduction

Quaternized poly(ethylenimine) with lauryl adducts (LQPEI) has been utilized as an effective catalyst for ester hydrolysis and as a favorable environment for other reactions and interactions.[1,2] The efficacy of this polymer has been attributed to the formation of micelle-like clusters within the polymer framework. The micellar effects observed with the LQPEI were often much more pronounced than those of the low molecular weight cationic detergents. Such behavior may be a result of higher local densities of the hydrophobic groups and the positive charges along the highly branched poly(ethylenimine) chain than are present in conventional detergent micelles.

In this study the static and dynamic structures of LQPEI were investigated by a spin-labeled technique.[3] Since the ESR line shape of a nitroxide radical is very sensitive to its mobility in solution, this label attached to the modified PEI can detect a small change in the mobility of its environment. The technique has been applied to micellar aggregates of low molecular weight detergents.[4] Because the spin-label method provides dynamic information for the polymer cluster, it reflects more directly the environmental differences in this domain than do the static data obtained by ^{19}F NMR[5] and by stationary fluorometry.[6]

The application of the spin-label technique to modified PEI's may be perturbed by the presence of two types of amino groups, primary (about 25%) and secondary (about 50%). These may possess different mobilities, yet react equally with spin-labeling reagents for amino groups. In this study two approaches were attempted to eliminate the complexity. One used regenerated primary amino groups[7] which had been protected during the attachment of lauryl moieties and the subsequent quaternization. After the protecting groups had been removed, a spin-labeling reagent was added. In this way one can attach the spin probe exclusively to primary amino groups of the modified PEI. The second type of approach placed the spin probe at a bridged position in a slightly cross-linked polymer. The latter polymer was prepared by reaction of PEI with a diester derivative of the nitroxide radical, which was used as a cross-linking reagent for the PEI. With the cross-linked polymer, information on skeletal motions of PEI could be obtained.

Excimer formation of aromatic hydrocarbons in micelles

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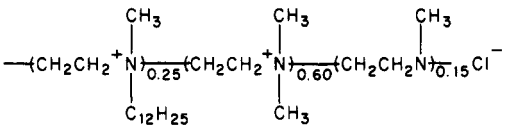
has been investigated extensively,[8] and the kinetics of the decay of monomer fluorescence and of the rise and decay of excimer fluorescence have been analyzed quantitatively by pulse fluorometry.[9] These studies indicate that the fluorescence probe is a sensitive tool to evaluate binding ability of various micelles, especially at very low concentrations of micelle. In the second part of this report, dynamic and stationary fluorometries were examined in aqueous solutions of pyrenebutyric acid in the presence of LQPEI and of other low molecular weight cationic detergents. Poly(ethylenimines) and peracetylated poly(ethylenimines), to which pyrenyl fluorophores are covalently attached, have also been prepared, and the excimer intensity of these was analyzed statistically to evaluate the extent of the interaction between fluorophores.[6]

Experimental Section

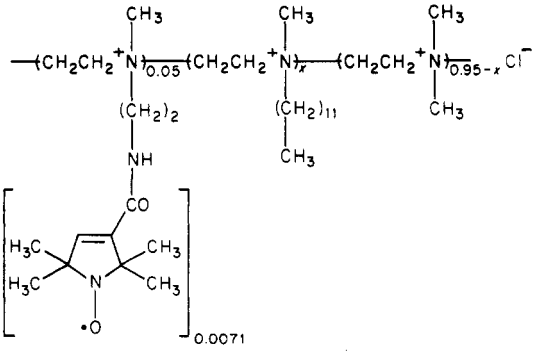
Synthesis and Characterization of Polymer Samples. Quaternized Laurylpoly(ethylenimine) ($L_{0.25}$QPEI) (I). The



I

modified polymer was prepared[7] from a commercial poly(ethylenimine) (PEI-600, average molecular weight 60 000, $\bar{DP}$ = 1400). A sample was treated with lauryl bromide in ethanol and subsequently quaternized. To increase the extent of quaternization, the methylation was carried out twice, first with methyl iodide and then with dimethyl sulfate. The modified polymer was ultrafiltered first against 0.01 M NaCl solution, to exchange the counteranion with chloride ion, and then against distilled water. Elemental analysis at each stage indicated that the attachment of the lauryl group was quantitative (25%) but the degree of methylation was incomplete (160%, compared with the theoretical value of 175%). Hence about 15% of tertiary amino groups remains unreacted in modified-polymer I.

Quaternized Laurylpoly(ethylenimines) with Nitroxide Radicals Attached to Regenerated Primary Amino Groups ($L_xA_{0.05}N^*_{0.007}$QPEI) (II). LQPEI's with 5% regenerated primary amino groups and various contents of lauryl groups were prepared by the procedure described previously.[7] To attach a nitroxide radical to the regenerated primary amino groups, 0.0071 mol of 2,2,5,5-tetramethyl-1-oxy-3-pyrroline-3-carboxylic acid *N*-hydroxysuccinimide ester (Tempyo ester, Eastman) was mixed with 1 monomer residue mol of the modified PEI in absolute ethanol containing about 0.07 mol of triethylamine. After standing for 2 days at room temperature the ethanol solution was poured into water, and the mixture was ultrafiltered first against 0.01 M NaCl and then against water. The content of nitroxide radicals was so small that spin–spin exchange interaction can be neglected. The amounts of lauryl and methyl groups on the polymers were determined by elemental analysis and are listed in Table I. The stoichiometric composition of these polymers is represented by II and will also be designated by the notation $L_xA_{0.05}N^*_{0.007}$QPEI,



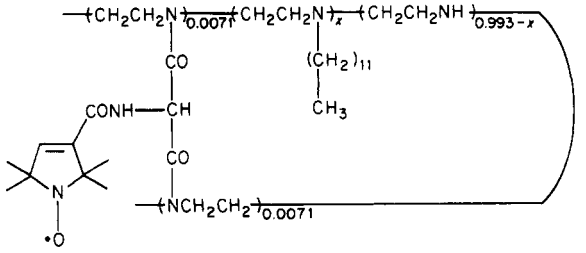
II

where L_x denotes the lauryl groups, $A_{0.05}$ the regenerated primary amines, $N^*_{0.007}$ the nitroxide spin label, and QPEI the quaternized macromolecule. Each subscript denotes the mole ratio of that moiety per mole of monomer residue.

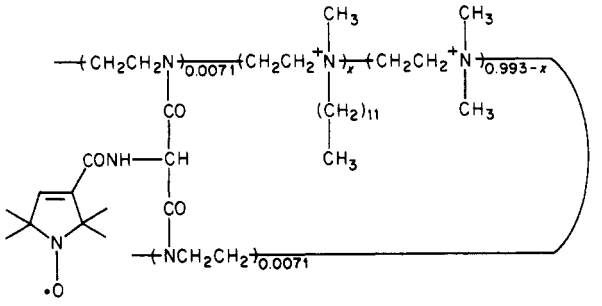
Table I
Constitution of Polymer Samples

polymer	% lauryl groups	% methyl groups
$L_0A_{0.05}N^*$QPEI	0	192
$L_{0.06}A_{0.05}N^*$QPEI	6	128
$L_{0.16}A_{0.05}N^*$QPEI	16	100
$L_{0.22}A_{0.05}N^*$QPEI	22	125
$L_{0.30}A_{0.05}N^*$QPEI	30	123
$L_{0.35}A_{0.05}N^*$QPEI	35	74
$L_{0.43}A_{0.05}N^*$QPEI	43	115
L_0*N*QPEI	0	183
$L_{0.05}$*N*QPEI	5	147
$L_{0.11}$*N*QPEI	11	147
$L_{0.20}$*N*QPEI	20	152
$L_{0.29}$*N*QPEI	29	169
$L_{0.38}$*N*QPEI	38	145
$L_{0.48}$*N*QPEI	48	104

Laurylpoly(ethylenimines) and Quaternized Laurylpoly(ethylenimines) with Nitroxide Radicals at the Bridge Positions of Cross-Links, L_x*N*$_{0.007}$PEI (III) and L_x*N*$_{0.007}$QPEI (IV), Respectively. L- and LQPEI's containing spin labels at cross-linked positions were synthesized as follows. A diethyl ester derivative of the nitroxide radical, 2,2,5,5-tetramethyl-1-oxy-3-pyrroline-3-carboxylic acid *N*-(bis(ethoxycarbonyl)methyl)amide (Tempyo ME; see structures III and IV)



III



IV

(0.0071 mol), was mixed with PEI-600 (1 monomer residue mol) in ethanol, and the solution was refluxed for 2 days. The infrared spectrum showed a complete disappearance of ester groups and the appearance of a very intense amide peak. The labeled polymer was dissolved in water and ultrafiltered against water. Alkylation of the latter polymer with lauryl bromide afforded the L_x*N*PEI series, where *N* designates the bridging nitroxide spin label. These polymers were subsequently quaternized to yield L_x*N*QPEI derivatives. The stoichiometric constitutions of these polymers are shown in III and IV.

Other Reagents. The diethyl ester derivative of the nitroxide radical 2,2,5,5-tetramethyl-1-oxy-3-pyrroline-3-carboxylic acid *N*-(bis(ethoxycarbonyl)methyl)amide (Tempyo ME) was prepared from the Tempyo ester (1 mol), purchased from Eastman, and diethyl 1-aminomalonate hydrochloride (1 mol) in the presence of triethylamine in ethanol.

Commercial 4-(1-pyrene)butyric acid (PBA) was recrystallized twice from benzene. Cetyltrimethylammonium chloride (CTAC)

Table II
Rotational Correlation Times

polymer	$10^{10}\tau_c$, s
Tempyo ME (in 2% ethanol)	1.0
Tempyo ME + $L_{0.25}$QPEI (7×10^{-3} residue M) (in 2% ethanol)	0.99
$L_0A_{0.05}$N*QPEI	3.1
$L_{0.06}A_{0.05}$N*QPEI	3.6
$L_{0.16}A_{0.05}$N*QPEI	4.6
L_0*N*PEI	3.5
$L_{0.05}$*N*PEI	6.7
$L_{0.11}$*N*PEI	6.8
L_0*N*QPEI	4.9
$L_{0.05}$*N*QPEI	6.6
$L_{0.11}$*N*QPEI	7.9

and lauryltrimethylammonium chloride (LTAC) were recrystallized from methanol.

Spectroscopic Measurements. ESR Spectra and Calculation of the Rotational Correlation Time. Polymer samples were dissolved in 0.05 M Tris buffer at pH 7.4. The radical concentration was 5×10^{-5} M. ESR measurements were carried out with a Varian E-4 instrument using a standard cuvette at room temperature. The rotational correlation time, τ_c, was calculated by the method of Stone et al.,[10] using the quadratic term in M (nitrogen nuclear spin quantum number).

Fluorescence Spectra. Fluorescence spectra were recorded on a Hitachi MPF-4 instrument. The fluorescence rise and decay curves were measured with a Hitachi time-resolved spectrometer unit, which relies on a sampling technique using a gated photomultiplier. A combination of solution filters (saturated solutions of $NiSO_4$, $CoSO_4$, and $NaNO_2$) and some glass filters were used to select the excitation and the fluorescence wavelengths. The rise and decay curves were repeatedly deconvoluted to obtain the best least-squares fit to the computed curve.[11] Before each measurement, N_2 was bubbled for 20 min through the sample solution in a cuvette with a stopcock.

Results and Discussion

Spin-Label Studies. Effect of Fixation of the Nitroxide Radical onto PEI. Rotational correlation times for Tempyo ME and for spin-labeled PEI's are listed in Table II. Free Tempyo ME in water containing 2% ethanol shows a rotational correlational time typical for low molecular weight nitroxide radicals.[3] The τ_c of the Tempyo methyl ester did not change on addition of $L_{0.25}$QPEI. If almost all Tempyo ME is bound to the hydrophobic region of the polymer cluster under the present conditions, the above result indicates that the radicals are moving freely within this domain. On the other hand, the rotational correlation times became longer when the radicals were covalently attached to the modified PEI's (Table II).

Effect of the Content of Lauryl Group. As is evident from Table II, an increase of lauryl content increased the rotational correlation time of the spin label in any series of related polymers. Figures 1 and 2 illustrate ESR spectra of $L_xA_{0.05}$N*QPEI and L_x*N*QPEI, respectively. As is apparent from these two figures, the modified PEI's with higher lauryl contents show ESR spectra consisting of dual components with different τ_c values. The shorter τ_c values are in the range $(3–6) \times 10^{-10}$ s and approximately the same as those of nonlaurylated PEI samples (i.e., $L_0A_{0.05}$N*QPEI, L_0*N*PEI, and L_0*N*QPEI). The longer τ_c, evaluated roughly from the $L_{0.48}$*N*QPEI spectrum, was about 10^{-9} s.[3a,12] The latter time is much longer than those reported for local segmental rotational motion of polymer chains (ca. $(1–6) \times 10^{-10}$ s)[3b] but shorter than that for an overall rotation of a protein molecule (ca. 10^{-8} s).[13]

A reasonable interpretation for the two-component spectra is that there are two distinguishable regions in laurylated poly(ethylenimines) (Figure 3). In the inner region, a cluster of hydrocarbon chains is tightly packed so that segmental motions are highly restricted. In the region near the periphery of this domain, however, segmental motions are active. The biphasic structure of the modified PEI's can also explain the increased presence of the component with slower motion in polymers having higher lauryl contents. Furthermore, it can account for the observation that quaternization reduced the slow motional component (see below), for repulsive forces between positive charges on the framework swell the polymer and tend to open up the tight structure of the inner cluster.

On the other hand, an alternative interpretation for the two-component spectra must also be considered. Tempyo ME can react either with primary or with secondary amino

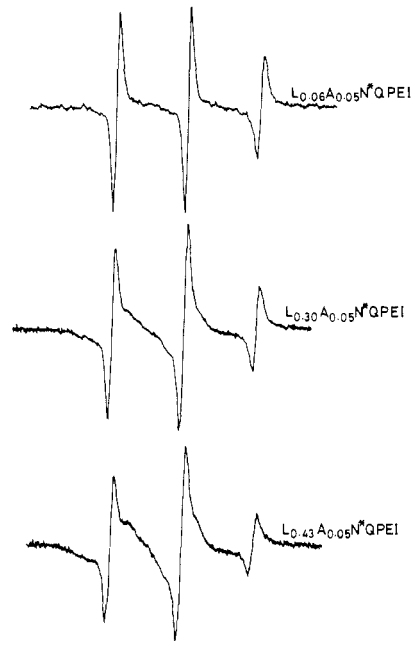


Figure 1. ESR spectra of spin-labeled, modified poly(ethylenimines), $L_xA_{0.05}$*N*QPEI, with different contents of lauryl group.

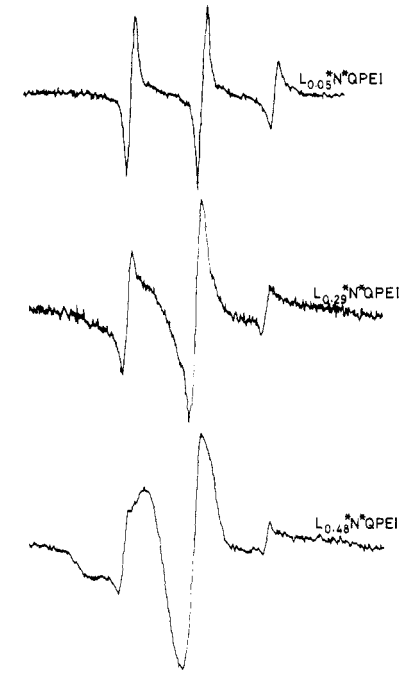


Figure 2. ESR spectra of cross-linking spin-labeled, modified poly(ethylenimines), L_x*N*QPEI, with different contents of lauryl group.

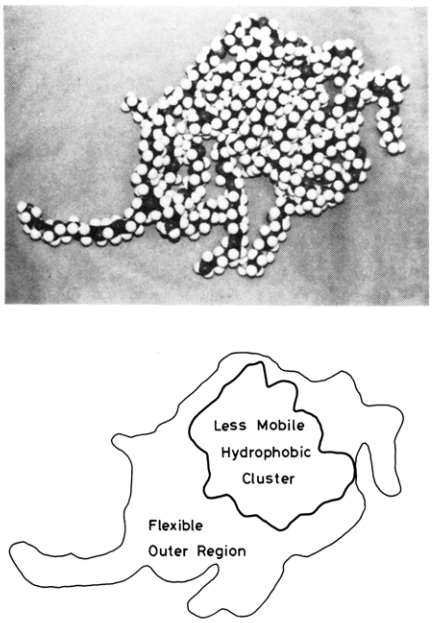


Figure 3. Photograph of space-filling molecular model of a segment of laurylated poly(ethylenimine) constituted of 100 ethylenimine residues and 10 lauryl groups. The sketch below outlines the inner apolar region with a relatively immobile hydrophobic cluster, in which $\tau_c \sim 3 \times 10^{-9}$ s. Flanking this region on all sides is the relatively flexible outer domain, constituted of nonlaurylated ethylenimine residues of the polymer framework; in this region $\tau_c \sim (3\text{–}6) \times 10^{-10}$ s.

groups of poly(ethylenimine). The spin labels attached to primary amino groups should show shorter τ_c values and those attached to secondary amino groups should show longer ones. However, this interpretation cannot account for the two-component spectra observed for quaternized polymer derivatives with regenerated primary amines, $L_xA_{0.05}N^*QPEI$, which had only primary amines. Moreover, it is inconsistent with the absence of multiple components in the polymers containing both primary and secondary amines but no lauryl groups, i.e., $L_0{}^*N^*PEI$ and $L_0{}^*N^*QPEI$.

The fraction of the slow motional component, f_s, was evaluated from the equation

$$f_s = 1 - \frac{3 \times (\text{area of the sharp peak in } M = 1 \text{ band})}{\text{total area}} \quad (1)$$

Although the f_s values obtained by this method are not of quantitative significance, they are adequate for the qualitative discussion which follows.

Figure 4 shows the dependence of f_s on the extent of laurylation in each of three series of modified PEI's. This fraction increases with the lauryl content, and the increase is more marked in the $L_x{}^*N^*PEI$ and $L_x{}^*N^*QPEI$ series than in the $L_xA_{0.05}N^*QPEI$ polymers. The dependence on lauryl content does not show any discontinuity; evidently the formation of the inner hydrocarbon cluster is not a cooperative process.

Effect of the Position of Nitroxide Radicals. In the $L_xA_{0.05}N^*QPEI$ series, the spin labels are attached covalently to regenerated primary amino groups, which should be in the most flexible or most mobile position of the modified polymers. In contrast, the $L_x{}^*N^*PEI$ and $L_x{}^*N^*QPEI$ derivatives possess the spin labels at cross-linking positions, where the rotational freedom is highly restricted. Consequently, it is reasonable that $L_0A_{0.05}N^*QPEI$ shows a shorter τ_c than either of the other two classes of polymer with no lauryl groups.

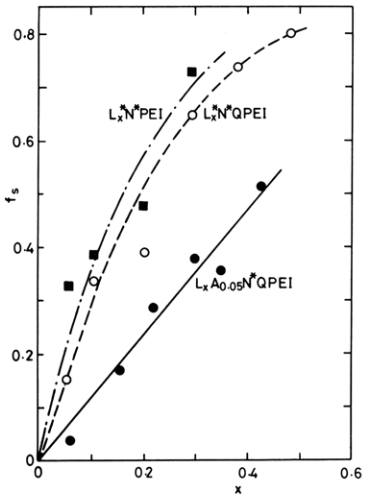


Figure 4. Fraction (f_s) of slow motional component in ESR spectra of $L_xA_{0.05}N^*QPEI$ (-●-), L_xN^*PEI (--■--), and L_xN^*QPEI (--○--) plotted against x, the fraction of monomer residues alkylated with lauryl groups. A relative error of about 10% may be inherent in values of f_s.

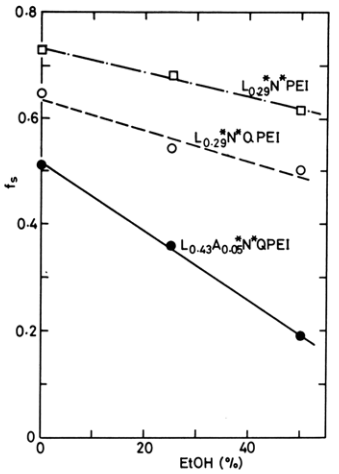


Figure 5. Fraction of slow motional component in ESR spectra of $L_{0.43}A_{0.05}N^*QPEI$ (-●-), $L_{0.29}{}^*N^*PEI$ (--□--), and $L_{0.29}{}^*N^*QPEI$ (--○--) plotted against the ethanol content in the solvent. A relative error of about 10% may be inherent in values of f_s.

The fraction of slow motional component is always larger in the series of $L_x{}^*N^*PEI$ and $L_x{}^*N^*QPEI$ than in $L_xA_{0.05}N^*PEI$ (Figure 4). This distinction may reflect differences in the shapes of the PEI's. Cross-links in $L_x{}^*N^*PEI$ and in $L_x{}^*N^*QPEI$ polymers could constrain their conformations in a more compact form and hence restrain the motion of the spin label.

Effect of Quaternization. As is evident from a comparison of the $L_x{}^*N^*PEI$ series with the $L_x{}^*N^*QPEI$ (Figure 4), quaternization reduces slightly the contribution of the slow motional component. This trend can be interpreted as a consequence of the repulsive forces between positive charges on the polymer framework, which partially loosen the inner hydrophobic cluster.

Effect of Ethanol. If the slow motional component reflects the presence of a hydrophobic core in the polymer, a perturbant of hydrophobic interactions, such as ethanol, should loosen the cluster. In the range 0–50% ethanol, in which the concentration of dissolved oxygen is almost constant,[14] the fraction of the slow motional component decreases monotonically with the increase of alcohol content (Figure 5). The result is consistent with the assumption that the spin label is restrained by hydrophobic

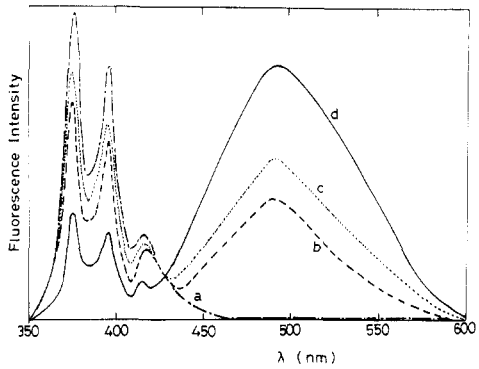


Figure 6. Fluorescence spectra of aqueous solution of pyrenebutyric acid (1×10^{-5} M) in the presence of $L_{0.25}$QPEI. Concentration of lauryl group: a, 4×10^{-5} M; b, 7×10^{-5} M; c, 2×10^{-4} M; d, 3×10^{-4} M.

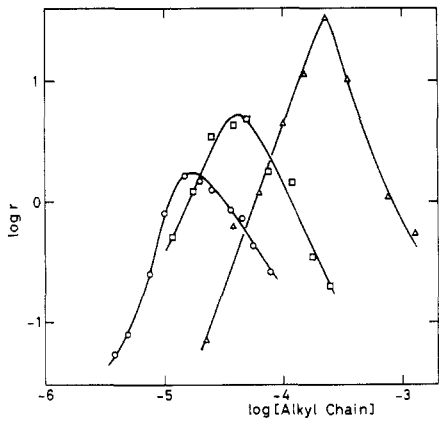


Figure 7. Excimer/monomer intensity ratios observed in the fluorescence spectra of 1×10^{-6} M (○), 1×10^{-5} M (□), and 1×10^{-4} M (△) pyrenebutyric acid in the presence of $L_{0.25}$QPEI.

interactions with the cluster of lauryl groups. The decrease is less pronounced in the $L_{0.29}$*N*PEI and $L_{0.29}$*N*QPEI derivatives than in $L_{0.43}A_{0.05}$N*QPEI; clearly the cross-links contribute to the stability of the inner core cluster of the polymers. Thus the spin probe results fit well with the model of poly(ethylenimines) illustrated in Figure 3.

Excimer Kinetics of 4-(1-Pyrene)butyric Acid Bound to LQPEI Clusters. Efficiency of Excimer Formation in the Photostationary State. Figure 6 shows fluorescence spectra of 4-(1-pyrene)butyric acid (PBA) (1.0×10^{-5} M) in the presence of $L_{0.25}$QPEI. At concentrations less than 4×10^{-5} M lauryl group of $L_{0.25}$QPEI, no excimer formation is evident; the fluorescence spectrum (Figure 6) is that of the small amount of pyrenebutyric acid that is soluble in water in the nonbound state. The excimer fluorescence, centered at 502 nm, reached maximum intensity at 3×10^{-4} M lauryl group of $L_{0.25}$QPEI, at which concentration the local effective concentration of bound pyrenebutyric acid in the hydrophobic cluster must be maximal. With further additions of the polymer, the pyrenebutyric acid was partitioned between separated clusters. As a result the probability of excimer formation was decreased and the intensity of the 502-nm band dropped. In Figure 7, the intensity ratio, r, of the excimer fluorescence peak (502 nm) to that of the monomer peak (376 nm) is plotted against the concentration of lauryl groups of $L_{0.25}$QPEI at each of three different concentrations of pyrenebutyric acid, 10^{-6}, 10^{-5}, and 10^{-4} M, respectively. For comparison, the same plot was made for the low molecular weight cationic detergents, CTAC and LTAC (Figure 8). Comparison of $L_{0.25}$QPEI and LTAC at the same alkyl group concentration in solution clearly shows that the hydrophobic cluster of the polymer binds

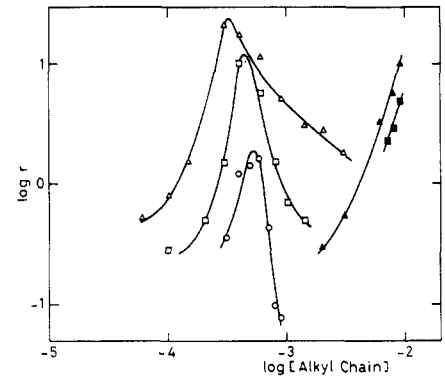


Figure 8. Excimer/monomer intensity ratios observed in the fluorescence spectra of 1×10^{-6} M (○), 1×10^{-5} M (□, ■), and 1×10^{-4} M (△, ▲) pyrenebutyric acid in the presence of cetyltrimethylammonium chloride, CTAC (○, □, △), and of lauryltrimethylammonium chloride, LTAC (■, ▲).

pyrenebutyric acid molecules at concentrations of lauryl group 2 or more orders of magnitude lower than those required with the corresponding low molecular weight detergent. The efficiency of this polymer domain is apparent also in a comparison (Figures 7 and 8) of its binding ability with that of the low molecular weight detergent having longer alkyl chains, i.e., CTAC.

Another interesting feature of the interactions with pyrenebutyric acid is that with the polymer the smaller the substrate concentration, the lower the concentration of alkyl group required to attain the maximum excimer concentration. In contrast, with CTAC an increase in concentration of pyrenebutyric acid is paralleled by a shift in optimum detergent concentration to the lower side. This behavior is probably a consequence of the following structural features. In the polymer, positive charges and lauryl groups are covalently linked to the macromolecular framework, so the polymer cluster assumes the same size and conformation irrespective of concentration of PEI in bulk solution. Thus for smaller numbers of pyrenebutyric acid molecules, smaller numbers of polymer clusters are enough to assimilate the substrate. In contrast, the size of CTAC aggregates depends strongly on the detergent concentration. Actually the critical micelle concentration of CTAC is around 4×10^{-3} M,[15] substantially higher than the concentrations for maximal excimer importance in concentrating the aromatic substrate. Such a structure for CTAC evidently begins to form at a concentration as low as 5×10^{-4} M, and its growth is facilitated by the presence of the aromatic substrate.

Kinetic Analysis of Monomer Fluorescence Decay Curves at Low Detergent Concentrations. In dilute solutions of the polymer or of the low molecular weight detergent, where the number of alkyl chains is comparable to or smaller than that of pyrenebutyric acid molecules, only a portion of the aromatic substrate is bound to the cluster of aggregate. Therefore, two states of pyrenebutyric acid molecules should be considered in the decay kinetics of the monomer fluorescence. For the nonbound, free substrates in solution, monomer fluorescence decays with a lifetime of about 120 ns. For bound substrates, which form excimers almost instantaneously, the monomer fluorescence lifetime is reduced to less than 10 ns. The resolution of the two-phase decay curve thus provides a measure of the fraction, f_m, of bound substrate. Typical observed decay curves and their fitting in terms of contributions from two states are shown in Figure 9. The calculated fractions of the bound substrate are plotted in Figure 10 against the concentration of alkyl groups of the polymer and detergent, respectively.

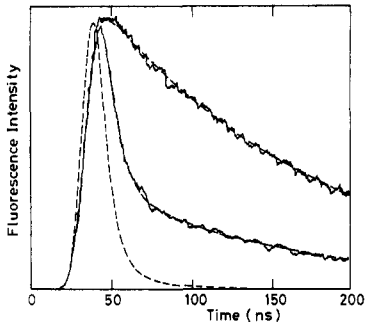


Figure 9. Fluorescence decay curves of the monomer emission of 1×10^{-5} M pyrenebutyric acid in the presence of 5×10^{-5} M (lower curve) and of 1.8×10^{-4} M (upper curve) cetyl group of cetyltrimethylammonium chloride, CTAC. The dashed line is the excitation pulse. The broken curves superimposed on the observed decay curves show values calculated by least-squares curve fitting, taking the width of the excitation pulse into account.

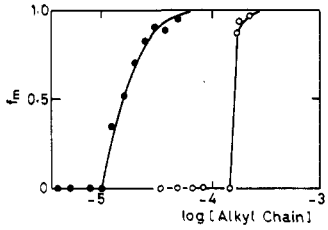


Figure 10. Fraction of pyrenebutyric acid bound to micelle domains of $L_{0.25}$QPEI (●) and of cetyltrimethylammonium chloride (○).

The uptake of pyrenebutyric acid by $L_{0.25}$QPEI begins at the concentration where the number of alkyl chains is exactly equal to the number of substrate molecules. Binding is complete when the number of alkyl chains per substrate molecule has reached five. Thus small numbers of alkyl chains in the polymer clusters can bind aromatic substrates effectively.

In contrast, with detergent aggregates, about 20 CTAC and even more LTAC molecules are necessary to bind one pyrenebutyric acid molecule. These numbers, however, are determined not by the alkyl chain/substrate ratio but by the concentration at which the detergents begin to form premicellar structures.

Kinetic Analysis of Excimer Fluorescence Rise and Decay Curves at High Detergent Concentrations. At concentrations where all pyrenebutyric acid molecules are bound in the detergent aggregate, the kinetics of the excimer formation and dissociation should follow the Birks mechanism.[16,17] In this representation an excited pyrenebutyric acid molecule associates reversibly with a ground-state PBA to form an excimer. The excited monomeric PBA and the excimer are deactivated radiatively or nonradiatively, at different rates. Kinetic analysis of a rise and decay curve of excimer fluorescence yields rate constants of the elemental steps of the Birks mechanism. The time evolution of the monomer and the excimer fluorescence intensities should follow eq 2 and 3[17]

$$I_m(t) = A \exp(-t/\tau_1) + B \exp(-t/\tau_2) \quad (2)$$

$$I_e(t) = C[\exp(-t/\tau_2) - \exp(-t/\tau_1)] \quad (3)$$

$$1/\tau_i = -(1/2)\{(1/\tau_m + k_1(\mathrm{PBA}) + 1/\tau_e + k_2) \pm [(1/\tau_m + k_1(\mathrm{PBA}) + 1/\tau_e + k_2)^2 + 4k_1k_2(\mathrm{PBA})]^{1/2}\} \quad i = 1, 2 \quad (4)$$

In these equations, τ_m and τ_e are the intrinsic lifetimes for the monomer and the excimer excited states, respectively, and k_1 and k_2 are the rate constants of the excimer formation and dissociation, respectively. It is apparent from

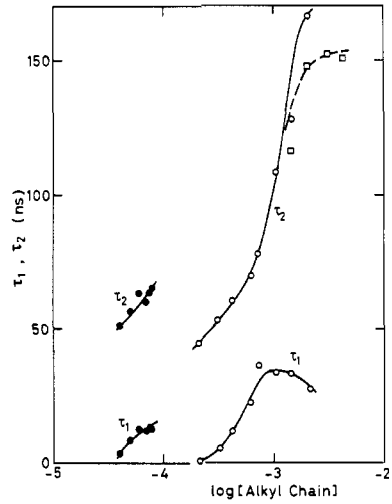


Figure 11. Time constants τ_1 and τ_2 for the excimer rise and decay, respectively, of pyrenebutyric acid in the presence of $L_{0.25}$QPEI (●) and of cetyltrimethylammonium chloride, CTAC (○). The τ_2 values obtained from the monomer decay curve in the presence of CTAC (□) are also shown.

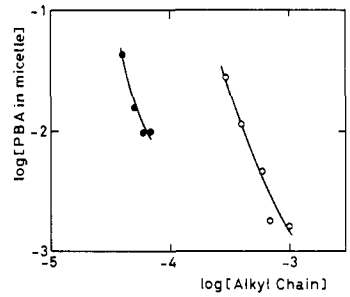


Figure 12. Effective concentration of pyrenebutyric acid (at bulk concentration = 1×10^{-5} M) in the micelle domains of $L_{0.25}$QPEI (●) and of cetyltrimethylammonium chloride, CTAC (○).

eq 2 and 3 that the lifetimes τ_1 and τ_2 are equally accessible from an analysis of monomer or excimer decay curves. However, since in our instrument it was difficult to follow the decay of monomer fluorescence because of interference from excimer fluorescence, especially when the latter is dominant, the following kinetic analysis was performed on data obtained from the rise and decay curve of the excimer. Calculated values for τ_1 and τ_2 in solutions of 1.0×10^{-5} M of PBA in the presence of $L_{0.25}$QPEI and of CTAC are plotted in Figure 11 against the concentration of alkyl group.

From eq 4, the following relation is obtainable:

$$k_1(\mathrm{PBA}) + k_2 = 1/\tau_1 + 1/\tau_2 - 1/\tau_m - 1/\tau_e \quad (5)$$

Since k_2 (ca. 0.006 ns^{-1})[17] is much smaller than k_1(PBA) (ca. 0.1–0.01), one can neglect the k_2 term in eq 5, and then the rate of excimer formation k_1(PBA) can be evaluated from the right-hand side of this equation. From the τ_2 found from monomer fluorescence at the lowest effective concentration of pyrenebutyric acid in the aggregate or at the highest detergent concentration, the intrinsic lifetime for monomer excited state, τ_m, was estimated to be 160 ns. From the τ_2 found from excimer fluorescence at the highest effective concentration of PBA in the aggregate or at the lowest detergent concentration where excimer fluorescence can be observed, the intrinsic lifetime for excimer, τ_e, was determined to be 44.2 ns.

Since in this kinetic treatment it is impossible to evaluate k_1 and PBA separately, the effective concentration of PBA in the aggregate was estimated by putting k_1 equal to the value obtained in a cyclohexane solution of pyrene

($6.7\ M^{-1}\ ns^{-1}$).[17] Such estimates of the effective concentration of PBA in the micellar environment are plotted in Figure 12 against the concentration of alkyl group in $L_{0.25}$QPEI and CTAC. At a concentration of PBA of 1×10^{-5} M in bulk solution, its concentration in the hydrophobic cluster of $L_{0.25}$QPEI at 4×10^{-5} M solution concentration of lauryl groups was raised to 3×10^{-2} M; in solutions of CTAC with 3×10^{-4} cetyl group, the corresponding PBA concentration in the aggregate was raised 3×10^{-2} M. These results demonstrate quantitatively that the polymer cluster is more powerful by an order of magnitude than are low molecular weight detergents in ability to sequester hydrophobic substrates from bulk aqueous solutions.

Thus both spin-label and fluorescence experiments can be understood in terms of the model illustrated in Figure 3, which attributes the special features of the behavior of modified poly(ethylenimines) to the presence of hydrophobic clusters at intervals within the polymer matrix.

Registry No. I, 88337-17-1; pyrenebutyric acid, 25338-56-1; Tempyo ester, 37558-29-5; Tempyo ME, 88337-16-0.

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Forces between Two Layers of Adsorbed Polystyrene Immersed in Cyclohexane below and above the Θ Temperature

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ABSTRACT: Forces between polystyrene layers absorbed on mica and immersed in cyclohexane have been measured. The measurements were made on two different molecular weights (6×10^5 and 9×10^5) in two different laboratories and therefore support the quantitative reliability of the results. We have reproduced previous results of this type of measurement below the Θ temperature and extended the force measurement to (a) adsorbed layers at lower surface coverage and (b) temperatures above the bulk polystyrene–cyclohexane Θ temperature. At a coverage of about 1.1 mg/m^2 of polystyrene, which is on the order of 20–30% of saturation, we found strongly attractive forces below T_Θ, detectable at separations of about 300 Å between the bare mica surfaces. The forces can be measured very accurately and precisely in this situation. The force reaches a minimum at 46 ± 2 Å and becomes strongly repulsive closer in. The long-range attractive portion of the force curve is very nearly exactly exponential, with a decay length of 45 ± 2 Å. For saturated surfaces with about 4.5 ± 1 mg/m^2 the force is detectably attractive at larger distances (600–1200 Å) both below (23 and 26 °C) and above (37 ± 2 °C) the Θ temperature (34.5 °C). For each molecular weight the positions of the minimum in the $F(D)$ curve and of the short-range repulsive barrier are at smaller separations at $T > T_\Theta$. The magnitudes of the minima are smaller at $T > T_\Theta$ as well. Both of these new results suggest strongly that the forces, especially the attractive components, between the polymer surfaces are influenced by effects in addition to the usual segment–segment interactions which determine bulk thermodynamic properties.

Introduction

Forces between polymer surfaces, mediated by solvent, are the essence of the physics of adhesion,[1,2] steric stabilization of colloids,[3] tack in rubbers,[4] and other polymer particle aggregation and coalescence problems. We are most interested here in cases where two adsorbed polymer layers, covering other surfaces, interact. In this case the forces due to the polymer layers can be either attractive or repulsive, depending (a) on the polymer segment interactions, which in turn depend on solvent and temperature, and (b) on whether or not desorption occurs or

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