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M. J. Tiera
V. Ap. de Oliveira Tiera
E. C. de Toledo
G. L. de Sena

Aggregation behaviour of hydrophobically modified poly(allylammonium) chloride

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M. J. Tiera (✉) · V. Ap. de Oliveira Tiera · E. C. de Toledo
Instituto de Biociências Letras e Ciências Exatas, Departamento de Química e Geociências, UNESP
São José do Rio Preto, Brazil
e-mail: mjt@qeg.ibilce.unesp.br
Tel.: +55-17-2212359
Fax: +55-17-2212356

G. L. de Sena
Universidade Federal do Espirito Santo
Departamento de Química, UFES
Espirito Santo, Brazil

Abstract The behaviour of hydrophobically modified poly(allylammonium) chloride having octyl, decyl, dodecyl and hexadecyl side chains has been studied in aqueous solution using fluorescence emission techniques. Micropolarity studies using the I_1/I_3 ratio of the vibronic bands of pyrene show that the formation of hydrophobic microdomains depends on both the length of the side chain and the polymer concentration. The I_1/I_3 ratio of the polymers with low hydrophobe content (less than 5% mol) changes substantially when reaching a certain concentration. These changes are assigned to aggregation originating from interchain interactions. This behaviour is also confirmed by the behaviour of the monomer/excimer emission intensities of pyrene-dodecanoic acid used as a probe. For polymers having dodecyl side chains and hydrophobe contents higher than 10%, aggregates are formed independently of the polymer concentration. Anisotropy measurements show that microdomains resulting from the inter- and/or intramolecular interactions are similar to those observed for cationic surfactants. Viscosity measurements show that the coil dimensions are substantially decreased for the polymers having high hydrophobe contents, indicating intramolecular associations.

Key words Cationic amphiphilic polymers · Aggregation · Pyrene fluorescence spectroscopy · Hydrophobic microdomains

Introduction

Polyelectrolytes bearing hydrophobic substituents bound to the main chain have been the subject of many investigations because of their ability to associate in aqueous solutions forming aggregates, which have potential applications in pharmaceutical, paint and cosmetics industries [1].

The association in aqueous solutions is due to intra- and/or intermolecular interactions and is related to polymer architecture. An entropic gain has been observed as a consequence of the modification of polyelectrolytes by introducing hydrophobic groups. This behaviour, known as hydrophobic interaction, leads to a reorganization of the polymer conformation to form hydrophobic microdomains. Conversely, the electrostatic repulsion between the fixed charges on the polymer chain plays an important role in the overall process, hindering the coil contraction. For copolymers having carboxylic groups, like ethyl methacrylate – acrylic acid copolymers [2], methacrylic acid – methyl methacrylate [3] and others [4], the "intramolecular aggregates" are progressively destroyed when the charge density on the polymer chain is increased by ionization of the carboxylic groups. However, with copolymers having a higher hydrophobic character, the hydrophobic microdomain is not disrupted and chains self-organize forming an aggregate with hydrophobic and hydrophilic domains (charged interfaces) [5]. Similar systems have been constructed with hydrophobically modified polysulfonates by controlling their hydrophobic content [6, 7].

Besides the formation of intramolecular aggregates, intermolecular interactions can also assist the formation of microdomains resulting from interchain associations. It has been shown recently that cationic copolymers with different alkyl groups on the chain associate to form intermolecular aggregates [8].

The tendency to associate depends on both the hydrophobe content and the flexibility of the macromolecule, which in turn determines their properties. Hydrophobically modified poly(allylamine) in nonprotonated and partially protonated states has been the subject of recent studies aiming to evaluate its self-organization in aqueous solutions and its capability to bind small molecules [9, 10].

Knowledge of the contribution of the polymer structure to the interactions may provide further insight into the importance of the effects of hydrophobic and electrostatic interactions on the aggregates properties. This idea led a number of workers to study hydrophobically modified polyelectrolytes in order to obtain more information about the aggregation process [11].

The present work examines the association behaviour of hydrophobically modified poly(allylammonium) chloride (PALA) in aqueous solutions using several fluorescent probes. Hydrophobically modified PALA polymers containing octyl, decyl, dodecyl and hexadecyl side chains have been studied in aqueous solution. The formation of aggregates by self-association was investigated using pyrene, pyrene-3-carboxaldehyde (PyC), pyrenedodecanoic acid (PyDod) and *trans*, *trans*, *trans*-1-[4-(3-carboxypropyl)phenyl]-6-(4-butylphenyl)-1,3,5-hexatriene (4H4A), which was used in fluorescence depolarization measurements to obtain information on the aggregates. The chemical structures of the probes and polymers used in this work are shown in Fig. 1.

Experimental

Materials M_w = weight average molecular weight

The PALA used in this work was supplied by Polysciences (M_w = 60,000) and purified by double precipitation in methanol. PyDod was purchased from Molecular Probes and was used without further purification. Pyrene was recrystallized twice from ethanol. The 4H4A probe was prepared as reported previously [12].

Synthesis of polymers

PALA derivatives having alkyl side chains were prepared by reaction of the nonprotonated polymer with *n*-bromoalkanes. Typically, PALA was dissolved in a KOH/methanolic solution under stirring. The resulting solution was cooled to 5 °C and the KCl formed was separated by centrifugation. *n*-Bromododecane was added to the solution and was left to react for 48 h at 50 °C. The methanolic solution containing the polymer was acidified with

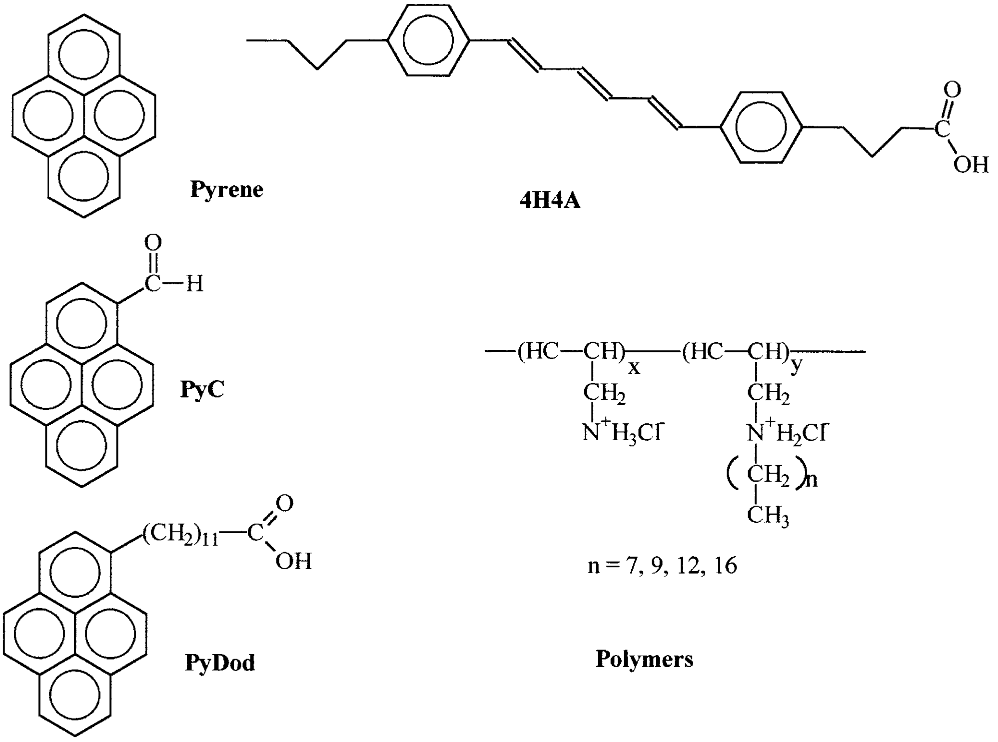

Fig. 1 Chemical structures of the probes and polymers used in this work: pyrene-3-carboxaldehyde (*PyC*), pyrenedodecanoic acid (*PyDod*), *trans*, *trans*, *trans*-1-[4-(3-carboxypropyl)phenyl]-6-(4-butylphenyl)-1,3,5-hexatriene (*4H4A*)

HCl (pH = 3.0) to recover the chloride salt of the polymer. The remaining bromide counter-ion was replaced by chloride after dissolving the polymer solution in an aqueous solution containing freshly prepared AgCl. The solution was stirred for 5 h, maintained at 5 °C for 24 h and centrifuged to separate the AgBr/AgCl. The polymer solution was dialysed in HCl (10^{-3} M) and purified by double precipitation in methanol/ethyl ether (40:60).

NMR measurements

All NMR spectra were recorded on a Brucker AC200 MHz spectrometer, using 1%wt solutions in D_2O at room temperature. For the relaxation time measurements the inversion-recovery technique (180°-τ-90° pulse sequence) was used.

Fluorescence spectroscopy

All measurements were performed at 25 ± 0.1 °C on a Hitachi 4500 fluorescence spectrometer. The temperature of the water-jacketed cell holder was controlled with a circulating bath. The ratio between the fluorescence intensities of peaks 1 (373 nm) and 3 (384 nm) of the emission spectrum of pyrene (1×10^{-6} M), (I_1/I_3), was used to evaluate the polarity of the local environment [13]. PyC (1×10^{-5} M) and PyDod (5×10^{-7} M) were excited at 356 nm and 4H4A (5×10^{-6} M) was excited at 357 nm and its fluorescence monitored at 435 nm.

Anisotropy

Fluorescence depolarization measurements using 4H4A were made on the Hitachi 4500 spectrofluorimeter equipped with a polarization accessory (right-angle geometry). The degrees of polarization were calculated using the relationship

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} ,$$

where $G = I_{HV}/I_{HH}$ is an instrumental factor (polarization characteristic of photometric system) and I_{VV}, I_{VH}, I_{HV} and I_{HH} refer to the resultant emission intensities polarized in the vertical or horizontal detection planes after excitation with vertically or horizontally polarized light, respectively.

Viscosity measurements

Viscosities were determined by using a Ubbelohde capillary viscometer. The viscosimeter was immersed in a thermostatic bath at 298.15 ± 0.05 °C and the samples were allowed to equilibrate for 10 min in the bath before measurements. Measurements at each concentration were repeated and the reproducibility was better than ±0.01 s. The results of the viscosity measurements are presented as reduced viscosity values calculated from

$$\eta_r = \frac{(t - t_o)/t_o}{c} ,$$

where t is the measured efflux time of the polymer solution, t_o is the efflux time of the pure solvent and c is the polymer concentration.

Results and discussion

The incorporation of hydrophobic side chains on the backbone of PALA was determined by ^{1}H NMR spectroscopy. A representative ^{1}H NMR spectrum of PALA with a hydrocarbon side chain is shown in Fig. 2. This figure shows the ^{1}H NMR spectra of hydrophobized polymer with an *n*-decyl chain in D_2O solution at 9 g l^{-1}. A comparison with the ^{1}H NMR spectra of unmodified PALA shows that the signal at 0.92 ppm corresponds to the terminal methyl of the incorporated hydrocarbon chain. The methylene protons of the incorporated hydrocarbon chain are observed at 1.3 ppm and the intensity of the signal depends on the size of the *n*-alkyl group. The other peaks are the same as observed in the spectra of pre-formed PALA. The signals of the methylene and methine protons on the main chain are observed at 1.6 and 2.1 ppm, respectively. The methylene protons in the position α to the quaternized nitrogen are observed at 3.1 ppm.

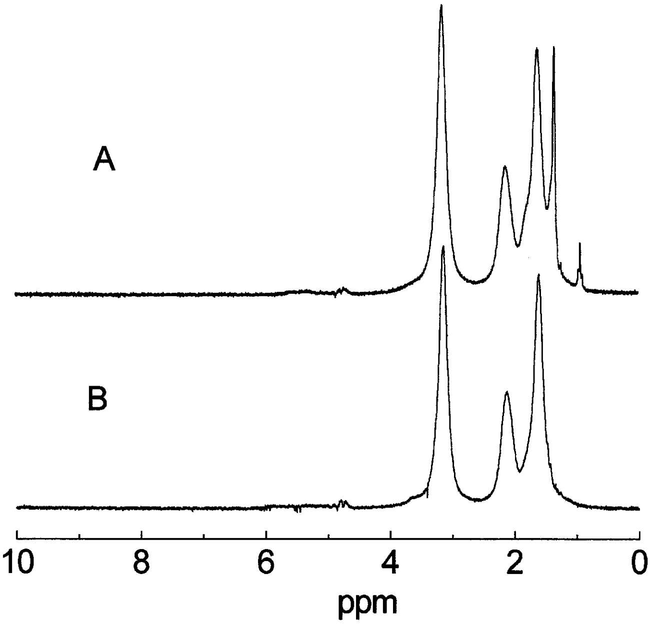

Fig. 2 ^{1}H NMR spectra of hydrophobized poly(allylammonium chloride)(*PALA*) PALA10 (*A*) and PALA (*B*) in D_2O solution at 9 g l^{-1}

The number of *n*-alkyl groups incorporated into the polymer may be determined using the conventional method of compositional analysis by NMR. The molar fraction of the alkyl side chains is given by

$$F_{AC} = (I_{AC}/n_{AC})/(I_{AC}/n_{AC} + I_{PALA}/n_{PALA}) , \qquad (1)$$

where F_{AC} is the mole fraction of the alkyl side chain and I_{AC} and I_{PALA} are the total integrated signals assigned to the alkyl side chain and PALA protons, respectively. n_{AC} and n_{PALA} are the total number of protons of the alkyl side chain and PALA, respectively. I_{AC} and I_{PALA} were calculated from

$$I_{PALA} = I_\alpha + (I_\alpha/1.4609) \qquad (2)$$

and

$$I_{AC} = I_T - I_{PALA} \ , \qquad (3)$$

where I_α is the integration of the signals from alkyl protons (3.1 ppm) and I_T is the total integration for the hydrophobized PALA. This method is an adaptation of that used in a previous article [14]. To distinguish between the protons of the aliphatic chains and those of the polymeric chain appearing at the same field (0.9–2.2 ppm), the total integration is corrected by the factor 1.4609. This factor was obtained from the ratio between the areas of the signals centred at 2.1 and 1.6 ppm with the signal centred at 3.1 ppm. The values obtained for the amount of hydrophobe incorporated are between 3.5 and 4.0 mol%. This agrees with the amount of reagent used in the feed, taking into account the error (±10%). These results confirm the total incorporation of the *n*-alkyl reactant used in the feed and are collected in Table 1.

The spin-lattice relaxation times (T_1) of protons were measured to estimate qualitatively the rigidity of the modified PALA micelles as a function of the length of the incorporated alkyl side chain. The results are shown in Table 2 and the protons were labelled as in Fig. 3.

The relaxation time measurements show that the protons localized closer to the main chain are in a more rigid environment (lower T_1) than the methylene and methyl protons localized in the microdomain. The different values of T_1 obtained for the protons of the hydrocarbon chain of PALA suggest the formation of a microphase, since in homogeneous systems the same values of T_1 are usually obtained for all protons, owing to the spin-transfer process [15]. The value of T_1 for the terminal CH_3 on PALA16 is 24% lower than on PALA10. This difference is large and can be ascribed to the larger micelles formed by PALA16.

Fluorescence spectroscopy

The I_1/I_3 ratio of the fluorescence spectra of pyrene was used to obtain information on the aggregation process in the hydrophobically modified polymers and reflects the polarity of the microenvironments where the probe is solubilized. Typical pyrene spectra in PALA12 solutions are shown in Fig. 4. The relative intensity of peak 3 in the fluorescence spectra and that of the excimer emission are substantially altered when the polymer concentration is increased. Values for the I_1/I_3 ratio for aqueous solutions of polymers containing pyrene are given in Fig. 5 as a function of polymer concentration. As the polymer concentration is increased, the I_1/I_3 ratio decreases in a different way depending on both the hydrophobe content and the size of the *n*-alkyl side chain. For polymers with low hydrophobe content (3.5 mol%), the variation of the I_1/I_3 ratio is due mainly to the size of the incorporated *n*-alkyl side chain. Above a certain concentration, the I_1/I_3 ratio for PALA08, PALA10, PALA12 and PALA16 solutions decreases suddenly, indicating that intermolecular interactions are taking place at those concentrations. The intercept observed in the figures can be interpreted as a critical aggregation concentration, which decreases as the length of the *n*-alkyl chain increases. For the polymers with

Table 1 Molar percentage of hydrophobe incorporated in hydrophobically modified poly(allylammonium) chloride (*PALA*)

Polymer	PALA	PALA08	PALA10	PALA12	PALA16	PALA12 10%	PALA12 20%
%Hydrophobe		3.5	3.5	3.5	3.5	9.8	18.5

Table 2 Spin-lattice relaxation times (T_1) for the protons of PALA, critical aggregation concentrations (*cac*) and anisotropy of *trans*, *trans*, *trans*-1-[4-(3-carboxpropyl)phenyl]-6-(4-butylphenyl)-1,3,5-hexatriene (*4H4A*) in the presence of polymers

Polymer of surfactant	T_1 for protons of PALA (s)					cac (g/l)	Fluorescence anisotropy of 4H4A	
	a	b	c	d	e		1.0 g/l	5.0 g/l
PALA	0.199	0.175	0.207	–	–	–	0.16	0.16
PALA08						0.92	0.21	0.23
PALA10	0.201	0.179	0.204	0.578	1.597	0.55	0.20	0.21
PALA12	0.202	0.178	0.206	0.507	1.309	0.43	0.35	0.35
PALA16	0.201	0.179	0.204	0.555	1.203	0.28	0.35	0.35
PALA12–10%							0.32	0.32
PALA12–20%							0.35	0.35
Dodecyltrimethylammonium bromide							0.28	
Cetyltrimethylammonium bromide							0.28	

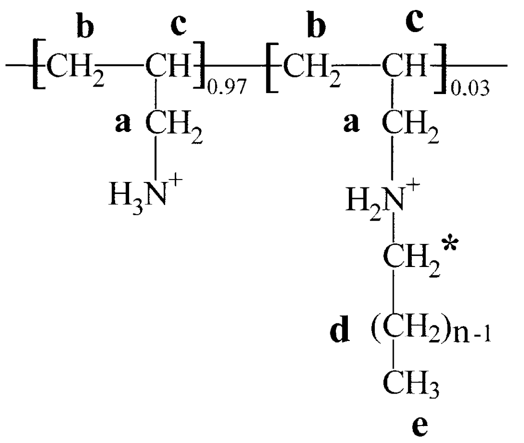

Fig. 3 Labelling of protons for the relaxation times

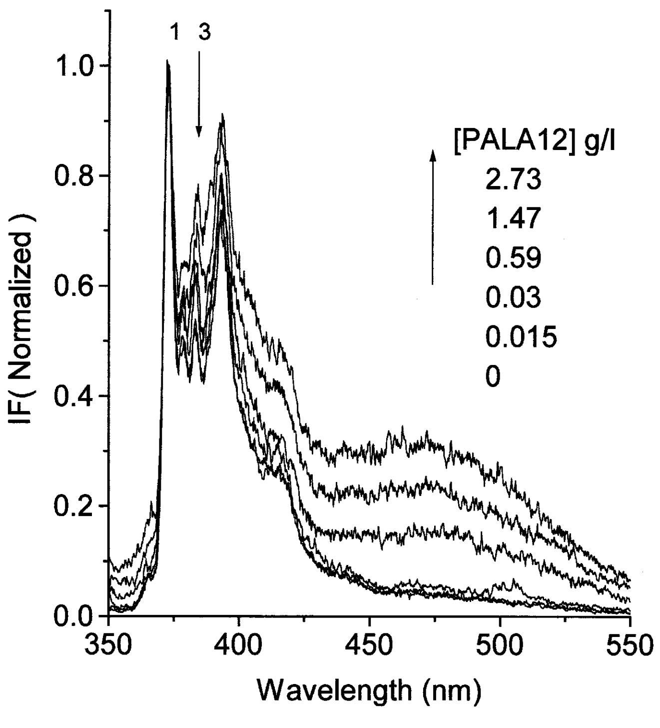

Fig. 4 Normalized steady-state fluorescence spectra of pyrene (1×10^{-6} M) as a function of PALA12 concentration

higher hydrophobe contents (PALA12–10% and PALA12–20%), the formation of hydrophobic microenvironments occurs at concentrations below 0.3 g/l (Fig. 5). This behaviour can be explained by assuming the existence of pre-formed microphases resulting from intramolecular interactions. The I_1/I_3 values obtained for these polymers are very similar to those observed in cationic surfactants such as cetyl trimethylammonium chloride (CTAC) (I_1/I_3 = 1.35) and cetyl trimethylammonium bromide (CTAB) (I_1/I_3 = 1.30) [16]. For the more hydrophobic polymer (PALA12–20%), the I_1/I_3 ratio is still smaller and is close to the value observed for Sodium dodecyl sulfate micelles [17].

PyDod was also used to obtain information on the aggregation process. Owing to its high hydrophobic character this probe exhibits a large excimer emission in aqueous solution, which may be a good tool to investigate intermolecular interactions. Typical fluorescence spectra obtained in the presence of copolymers are shown in Fig. 6. In the presence of PALA the emission spectra is almost exclusively due to the excimer emission, while for the hydrophobically modified polymers the excimer emission disappears progressively as the length of the *n*-alkyl chain of the hydrophobe is increased. Whereas for PALA the ratio of the excimer-to-monomer emissions (I_{mon}/I_{exc}) remains constant, independent of the polymer concentration, for PALA08 and PALA10 the I_{mon}/I_{exc} ratio increases substantially above certain concentrations, which are coincident with the values obtained using pyrene as a micropolarity probe (Fig. 7). For PALA12 and PALA16 the I_{mon}/I_{exc} ratio increases without any apparent break in the plot, probably because the probe interacts more strongly with the side chains, promoting a more efficient redistribution of the PyDod probe molecules.

PyC shows large spectral shifts with increasing polarity and has been used to monitor polarity changes [18]. Owing to the polar carbonyl group, PyC is preferentially solubilized near the micelle–water interface and the spectral shifts can be interpreted in terms of the polarity at the micelle–water interface [19]. Figure 8 shows that the emission maximum is shifted towards longer wavelengths with increasing concentrations of PALA12–10%. This tendency was also observed for PALA16–3.5%, PALA12–3.5% and PALA12–20%. In the presence of these polymers the maximum wavelength is shifted from 472 nm to about 502 nm (Fig. 9). The addition of small amounts of polymer to the PyC solution results in an initial decrease in the fluorescence quantum yield (Φ_f). Further addition of polymer leads to an increase in the Φ_f until a plateau is reached. The initial decrease is probably related to the migration and distribution of the probe between the aggregates, leading to microenvironments containing two or more probes and promoting bimolecular self-quenching of the emitting excited state. The shift observed as well as the fluorescence quantum yield changes can be related to the binding of the probe to the polymer. The maximum wavelength at 502 nm indicates that the probe is localized in a microenvironment of high dielectric constant. The effect of dielectric constant (ε) on the maximum wavelength (λ_{max}) of PyC has been studied by Kalyanasundaran and Thomas [19]. These workers found a relationship between λ_{max} and ε ($\lambda_{max} = 0.52\varepsilon + 431.5$). This relation leads to $\varepsilon = 79$ (dielectric constant of water) for $\lambda_{max} = 472$ nm. On the other hand, when the probe is solubilized in solutions of the

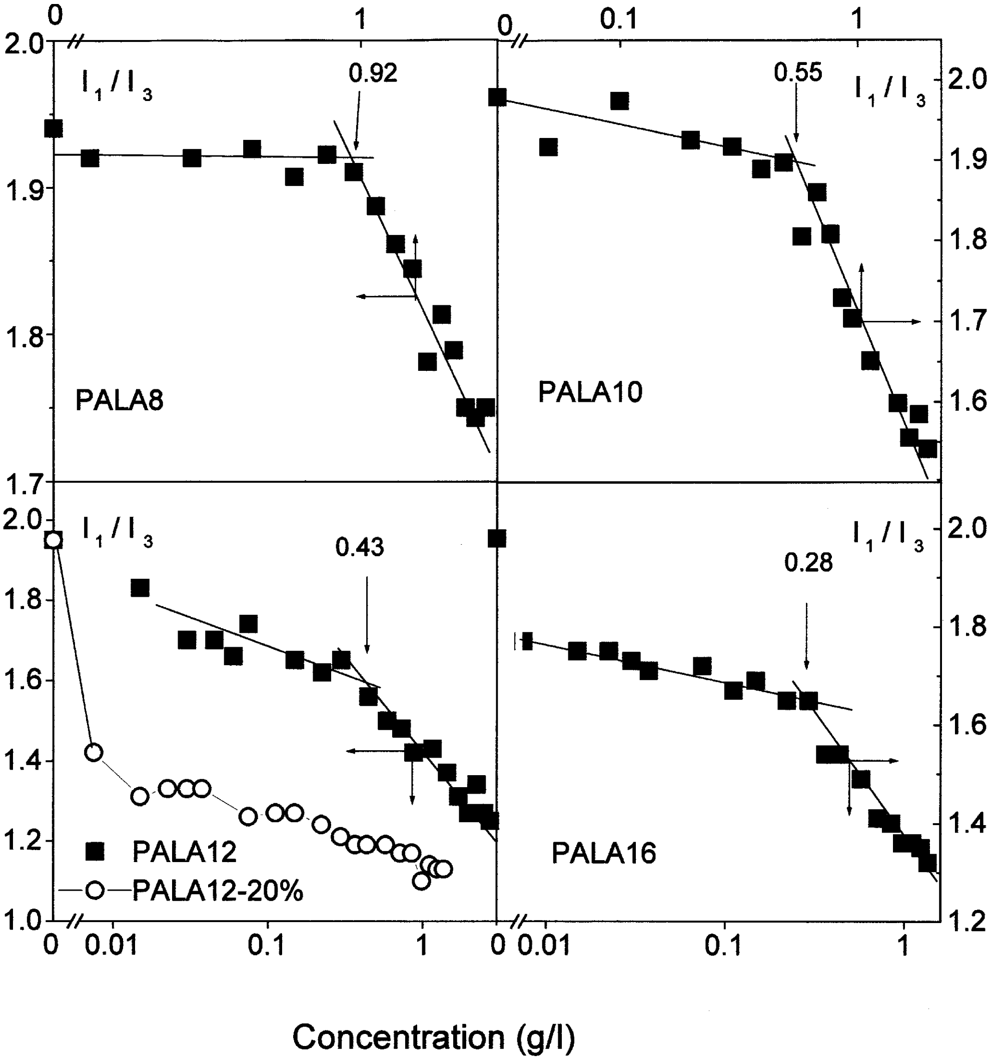

Fig. 5 I_1/I_3 ratio of the vibronic band intensities of pyrene (1×10^{-6} M) as a function of PALA concentration

more hydrophobic polymers, the dielectric constant can be estimated as 135, which is too high to be interpreted as a mere solvent effect. This value is probably due to the localization of the probe near the charged interface, where it might form a Schiff's base with free $-NH_2$ groups [19]. The fluorescence spectra of PyC in the presence of PALA12–10% (1.4 g/l) in water/methanol (60:40 v/v) showed a maximum at 460 nm, indicating that some of the intramolecular interactions are eliminated in the presence of the alcohol (Fig. 8).

For the polymers with octyl, decyl and dodecyl side chains, PALA08, PALA10 and PALA 12, $\lambda_{\max}$ is maintained around 473–475 nm. This behaviour leads to the conclusion that for these polymers the probe is solubilized in smaller aggregates which have more open structures. In order to investigate the properties of the aggregates and the relation with the hydrophobe content, fluorescence anisotropy (r) measurements were performed employing the probe 4H4A. This probe has been used to investigate the "gel"-to-liquid crystal phase transition of dioctadecyl dimethylammonium bromide (DODAB) vesicles obtained using different preparation protocols [20]. Its fluorescence is very sensitive to the local organization of the microenvironment and was used to compare the different polymers and determines whether the aggregates are more or less organized than those of simple CTAC or dodecyltrimethyl ammonium bromide (DTAB) micelles.

The fluorescence anisotropy of 4H4A solubilized in different copolymers corroborates the fluorescence results obtained with pyrene and PyC. The addition of 4H4A to aqueous solutions containing the polymers results in an increase in the fluorescence quantum yield with little spectral shifts. The r values obtained for all polymer and surfactant micelles are collected in Table 2. For the more hydrophobic polymers the anisotropy values are very close to those obtained for DTAB and CTAB micelles ($r \sim 0.3$), indicating that the probe

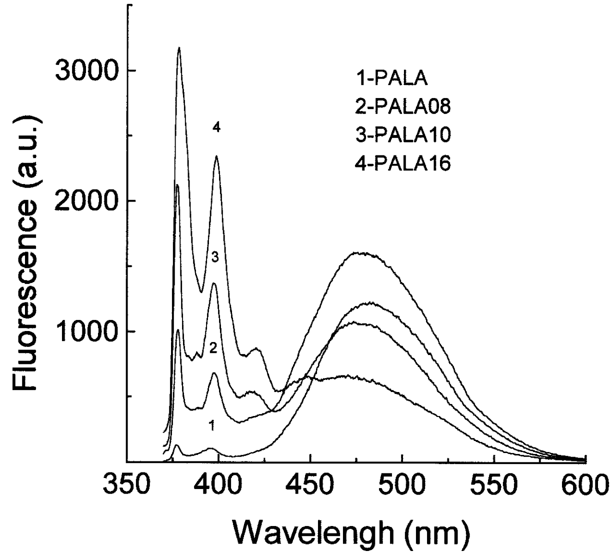

Fig. 6 Fluorescence spectra of PyDod (5 × 10^{-7} M) in the presence of PALA, PALA08, PALA10 and PALA16 at 1.4 g/l

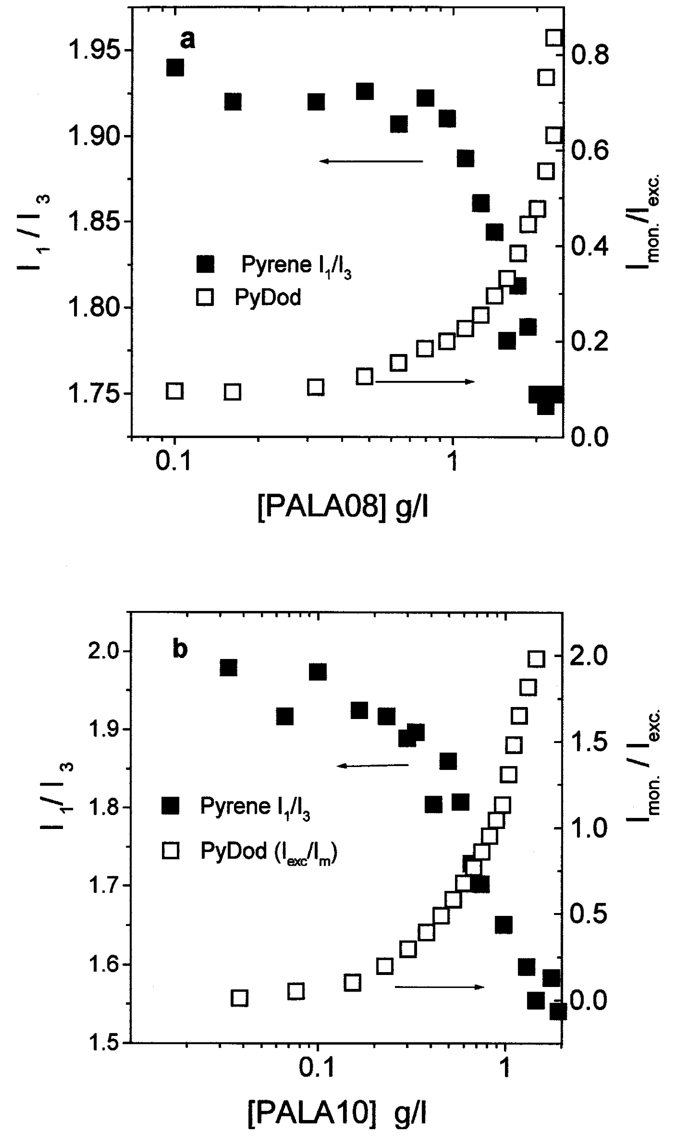

Fig. 7 Monomer/excimer (I_{mon}/I_{exc}) and I_1/I_3 vibronic band intensity ratios for PyDod and pyrene as a function of PALA08 and PALA10 concentration

senses a microenvironment similar to that of the cationic surfactants. On the other hand, when the probe is incorporated in PAL08 and PALA10 smaller anisotropy values are obtained, indicating, that these aggregates present looser structures according to the I_1/I_3 micropolarity studies.

Viscosity measurements

The addition of hydrophobic side chains to the polymeric backbone of a polyelectrolyte can produce profound changes in the molecular dimensions, which can be studied by viscosity measurements. A plot of reduced viscosity (η_r) versus polymer concentration for the series of PALA is shown in Fig. 10. Some of the polymers show a distinct increase in η_r when compared with the parent polymer (PALA); however, for the polymers with higher hydrophobe content (PALA12–10% and PALA12–20%) the reduced viscosity is lower than with PALA. In the case of PALA12–10%, the reduced viscosity decreases by about 4 times with respect to that of PALA (from 0.8 l/g for PALA to 0.2 l/g for PALA12–10%). Apparently the hydrophobic attractions of the side chains cause contraction in the molecular dimensions, leading to the formation of intramolecular aggregates. PALA12–20% displays similar behaviour but presents larger coil dimensions, as intermolecular interactions might be acting in some extension in polymers with higher hydrophobe content.

The copolymers PALA08 to PALA16 display the same behaviour with respect to that of the parent polymer, PALA. The reduced viscosity for these modified polymers is higher than that of the precursor PALA over the whole concentration range studied because of the formation of interchain aggregates. This behaviour has also been observed for hydrophobically modified poly(acrylic acid) [21] and pectin derivatives [22]. On the other hand, a substantial viscosity increase is found when the hydrocarbon chain is increased from 8 to 16 carbons, reflecting the higher hydrophobic interchain interaction for the more hydrophobic polymers.

Conclusions

Hydrophobically modified PALA in aqueous solution can aggregate in different ways, depending on both the

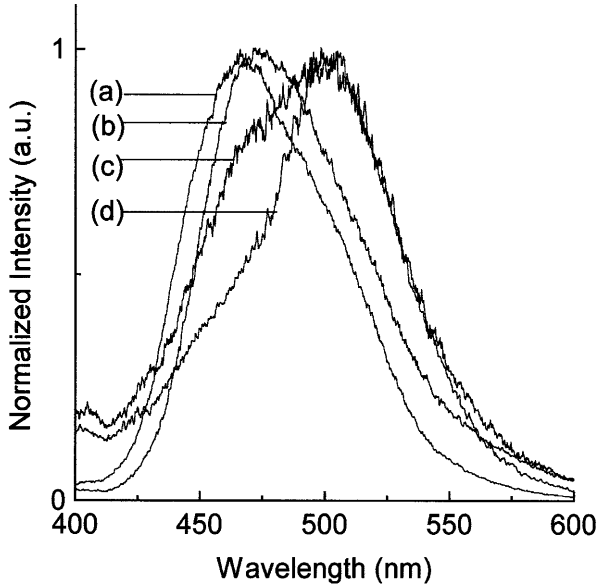

Fig. 8 Fluorescence spectra of PyC (1.0×10^{-5} M) in the presence of increasing concentrations of PALA12–10%. *a* 1.4 g/l in water/methanol (60:40 v/v); *b* no PALA; *c* 0.30 g/l; *d* 1.4 g/l in water

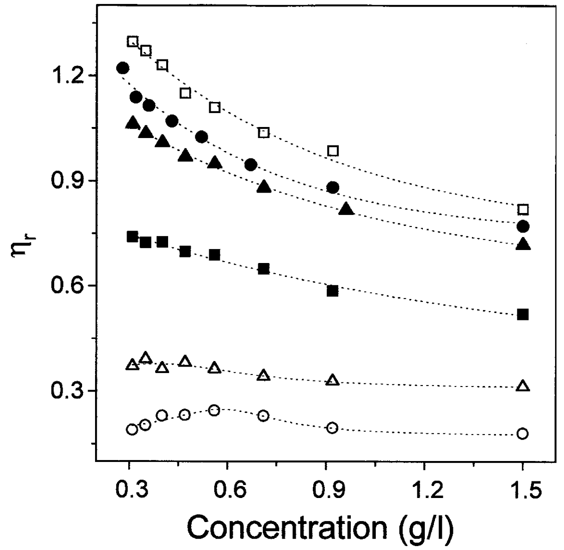

Fig. 10 Reduced viscosity (η_r) as a function of polymer concentration for the series of PALA: PALA (■); PALA10 (▲); PALA12 (●); PALA16 (□); PALA12–10% (○); PALA12–20% (△)

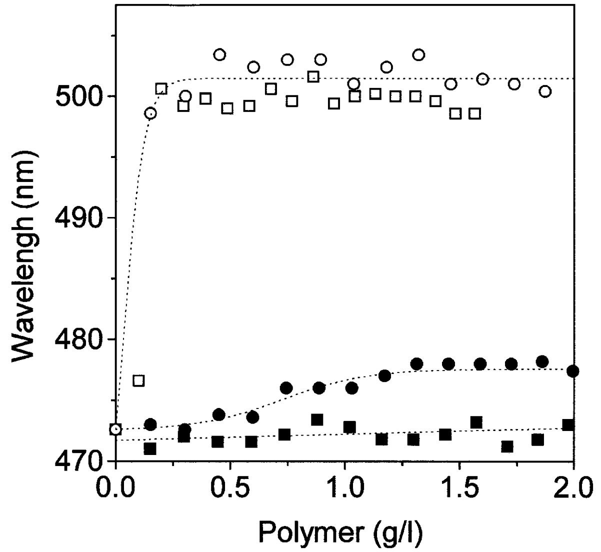

Fig. 9 Maximum fluorescence wavelength (λ_{max}) of PyC versus polymer concentration for PALA (■), PALA12 (●), PALA16 (□) and PALA12–10% (○)

hydrophobe content and the hydrocarbon chain length introduced into the parent polymer. For the polymers having low hydrophobe contents the fluorescence of pyrene showed that interchain interactions take place above certain concentrations, leading to intermolecular aggregate formation. The aggregation is more efficient when the hydrophobe length is increased. On the other hand, for polymers having increasing hydrophobe contents, intramolecular aggregates are formed owing to hydrophobic interactions of the side chains. Anisotropy measurements and micropolarity studies with 4H4A and pyrene, respectively, show that the polymers having longer chain lengths and/or higher hydrophobe contents form less polar and more structured aggregates. Viscosity measurements corroborate the fluorescence results, showing that for the polymers having high hydrophobe contents the coil dimensions are substantially reduced by intramolecular aggregation.

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