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Polymer 42 (2001) 3657–3664

polymer

www.elsevier.nl/locate/polymer

Association of hydrophobically modified positively charged *N*-isopropylacrylamide copolymers with the nonionic surfactant Triton X-100

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Received 14 August 2000; accepted 30 August 2000

Abstract

The association in dilute aqueous solution of the nonionic surfactant *t*-octylphenoxy polyoxyethanol (Triton X-100) with hydrophobically modified copolymers based on an *N*-isopropylacrylamide (NIPAM) backbone is presented. The NIPAM-based copolymers contain also *N*,*N*-[(dimethylamino)propyl] methacrylamide (MADAP), the content *x* of MADAP varying from 0 up to 25 mol%, completely alkylated with dodecylbromide or octadecylbromide. The highly hydrophobic copolymers are characterised by a compact conformation in aqueous solution, due to the formation of intrachain hydrophobic aggregates. Association with Triton X-100 leads to the destruction of these intrachain aggregates and to their replacement by mixed alkyl/surfactant ones, revealed macroscopically by a gradual viscosity increase upon addition of surfactant. Fluorescence probing studies and dialysis equilibrium experiments confirmed that polymer/surfactant association starts in the vicinity of the critical micelle concentration (CMC) of Triton X-100.

Keywords: Hydrophobically modified polymers; *N*-isopropylacrylamide; Triton X-100

1. Introduction

The hydrophobically modified water-soluble polymers (HMWSP) are based on a hydrophilic backbone, like polyacrylamide [1–5] or poly(sodium acrylate) [6,7], on to which alkyl chains have been randomly introduced by copolymerisation or grafting methods. The great interest in these polymers is mainly due to their striking thickening efficiency in aqueous solution, as the alkyl tails form interchain hydrophobic aggregates above a threshold polymer concentration (C^0), leading to the development of a transient network. Another important property of HMWSP is their ability to associate with surfactants, as the side alkyl groups form mixed aggregates with surfactant molecules [8]. Most studies concern hydrophobically modified poly(sodium acrylate) [7,9–11] or hydrophobically modified cellulose derivatives [12–17], and they are focused on the rheology and phase separation effects upon addition of charged or nonionic surfactants. Bell-shaped curves are usually obtained as a function of the surfactant concentration: in the first stages of association, the addition of surfactant reinforces the interchain transient network, resulting in a pronounced viscosity enhancement. Nevertheless, further increase of the surfactant concentration favours the formation of isolated alkyl/surfactant aggregates and viscosity decreases. Phase separation occurs mainly in mixtures of HMWSP with oppositely charged surfactants, and it is due to the decrease of the net charge of the polymer/surfactant structure formed.

Recently, we reported on the phase behaviour and shear induced thickening properties of new hydrophobically modified positively charged polymers based on an *N*-isopropylacrylamide (NIPAM) backbone [18]. These polymers, denoted as PNIPAMxCn (Scheme 1), are synthesised by copolymerisation of NIPAM with an amine-containing comonomer, the *N*,*N*-[(dimethylamino)propyl] methacrylamide (MADAP), the molar content *x* of the latter varying from 0 up to 25 mol%. The alkyl groups of length *n*, such as dodecyl or octadecyl ones, are introduced by full alkylation of the MADAP units with the corresponding alkylbromide in an organic solvent. In aqueous solution, the derivatives characterised by high *x* or *n* adopt very compact conformations even at very low concentrations, due to intrachain hydrophobic aggregation. At higher concentrations, interchain aggregates are formed under shear, resulting in a strong shear induced thickening behaviour.

The association of these polymers with surfactants is

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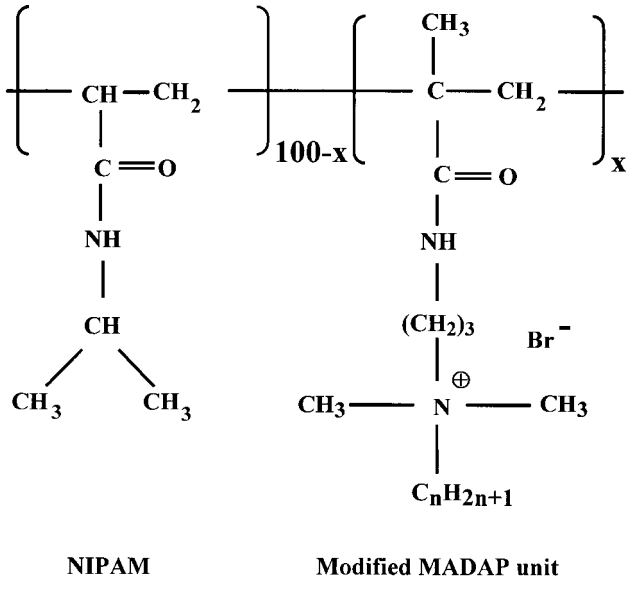
0032-3861/01/$ - see front matter
PII: S0032-3861(00)00650-9



NIPAM Modified MADAP unit

Scheme 1.

expected to influence drastically the shear induced thickening properties of the polymer solutions. A systematic study of such association in dilute and semidilute solutions is now under way. Depending on the nature of the surfactant, several polymer/surfactant interactions, including charge interactions and association of the surfactant not only with the pendant alkyl groups but also with the thermosensitive NIPAM backbone [19,20], are expected to complicate considerably the association mechanism. The simplest case to study is the interaction of the PNIPAMxCn derivatives with a nonionic surfactant, where only the association of the surfactant with the alkyl groups of the hydrophobically modified polymer is plausible. *t*-Octylphenoxypolyoxyethanol (Triton X-100, denoted as Triton) is chosen, offering the advantage of the easy determination of its concentration in dialysis equilibrium studies by exploiting its absorption spectrum in the 200–300 nm region.

Here, the study of the PNIPAMxCn/Triton association in dilute aqueous solution is presented. Viscometry, static fluorescence probing and dialysis equilibrium experiments are employed, in order to clarify the basic

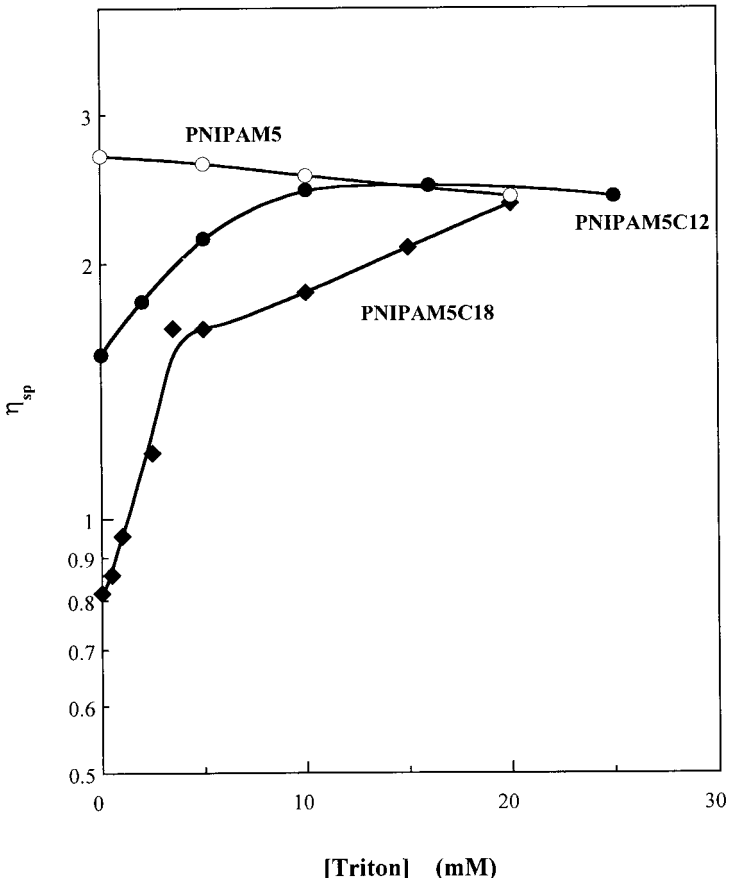


Fig. 1. The variation of the specific viscosity of PNIPAM5Cn/Triton mixtures with the surfactant concentration. The polymer concentration is 2.5×10^{-3} g cm^{-3}. (○) PNIPAM5; (●) PNIPAM5C12; (◆) PNIPAM5C18. $T = 25$°C.

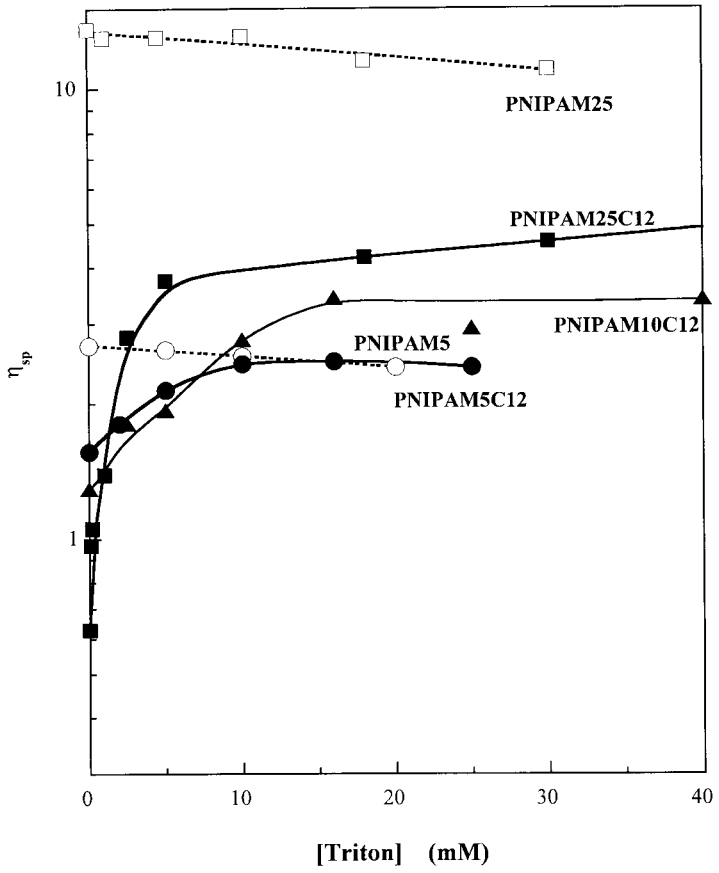


Fig. 2. The variation of the specific viscosity of PNIPAMxC12/Triton mixtures with the surfactant concentration at 25°C. The polymer concentration is 2.5×10^{-3} g cm^{-3}. (○) PNIPAM5; (●) PNIPAM5C12; (◇) PNIPAM10C12; (□) PNIPAM25; (■) PNIPAM25C12.

characteristics of the association mechanism. This comprehension will be an indispensable guide for the investigation of the PNIPAMxCn/Triton mixtures in more concentrated solutions.

2. Experimental

2.1. Materials

Triton X-100 is a product of Aldrich and it was used with no further purification.

Details on the synthesis and characterisation of the PNIPAMxCn samples are given elsewhere [21]. The mean-weight molar mass of the polymers is estimated to be $1–1.5 \times 10^6$.

2.2. Methods

Viscometry measurements were carried out with an automated viscosity measuring system AVS 300 (Schott-Geräte), equipped with a micro-Ostwald type viscometer. Temperature was controlled at 25 ± 0.02°C.

Steady state fluorescence spectra were recorded on a Perkin Elmer LS50B luminescence spectrometer. Pyrene (py) was used as a fluorescence probe at a concentration 6×10^{-7} mol l^{-1}. The excitation wavelength was 334 nm and the intensities at 373 and 384 nm were used to calculate the first to the third peak intensity ratio (I_1:I_3).

For the dialysis equilibrium experiments, 5 ml of the polymer solution were put in a semipermeable dialysis bag (Sigma, cut-off: 12,000 Da). The dialysis bag was then dipped in a sealed tube containing 20 ml of Triton solution of the desired concentration and the system was left to equilibrate under gentle stirring. The Triton concentration in the outer solution was determined from its absorption at 223 or 275 nm, depending on its concentration. A UV-visible spectrophotometer U 2001 (Hitachi) was used for this purpose.

2.3. Sample preparation

First, concentrated polymer and Triton stock solutions were prepared. Polymer/surfactant solutions were prepared by mixing the appropriate volumes of the stock solutions and diluting with water to obtain the desired concentration. Mixtures were let under gentle stirring for 24 h before performing the measurements. Water used for the preparation of the various solutions was purified with a Seralpur

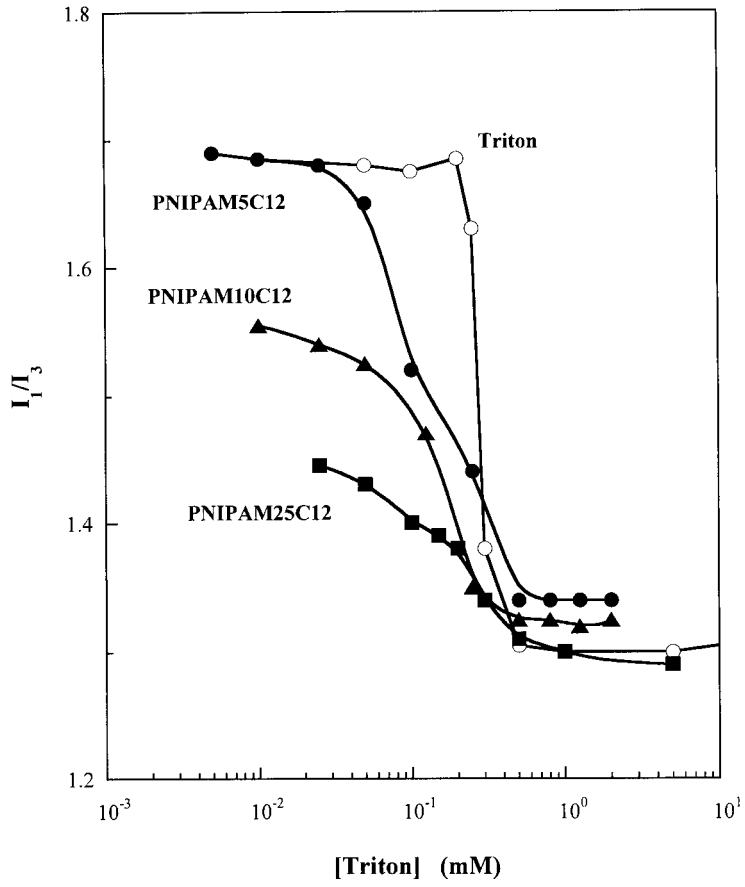


Fig. 3. The variation of the ratio I_1:I_3 of PNIPAMxC12/Triton mixtures with the surfactant concentration at 25°C. The polymer concentration is 5×10^{-5} g cm^{-3}. (○) no polymer; (●) PNIPAM5C12; (◆) PNIPAM10C12; (■) PNIPAM25C12.

water purification apparatus, combining inverse osmosis membrane and ion exchange resins.

3. Results and discussion

3.1. Viscosity

The specific viscosity η_{sp} of mixtures of Triton with the NIPAM-based derivatives containing 5 mol% alkyl groups, PNIPAM5Cn is plotted in Fig. 1 against the Triton concentration. The polymer concentration is 2.5×10^{-3} g cm^{-3} and the temperature is 25°C. To compare, we have also plotted the corresponding behaviour of the NIPAM–MADAP precursor, denoted as PNIPAM5, containing 5 mol% MADAP units neutralised with HCl. As expected, in the absence of surfactant, increasing the alkyl length n of the copolymer leads to a gradual decrease of its specific viscosity, revealing that the copolymer chain adopts more and more compact conformations as the alkyl groups become longer. Addition of Triton to the PNIPAM5 solution leads only to a smooth decrease of the specific viscosity of the mixture. This behaviour has been observed with the mixtures of Triton with the other two precursors (see also Fig. 2) and indicates that the polymer/surfactant interactions are not important in these cases. On the contrary, for the mixtures of Triton with PNIPAM5C12 and mainly with PNIPAM5C18, the specific viscosity of the mixtures increases considerably upon addition of surfactant. When the viscosity of the mixture reaches that of the precursor PNIPAM5 under the same conditions, the viscosity enhancement stops and, for further surfactant addition, seems to follow the corresponding PNIPAM5/Triton curve.

The influence of the alkyl content x on the viscosity of the mixtures of Triton with the copolymers PNIPAMxCn is presented in Fig. 2. These results concern the dodecyl derivatives at a constant polymer concentration of 2.5×10^{-3} g cm^{-3} at 25°C. The PNIPAM25 curve is displaced to higher values than the PNIPAM5 curve, due not only to the slightly higher molar mass of PNIPAM25 but mainly to the much higher charge density of PNIPAM25, that provokes a considerable expansion of the polymer chain. The curve for PNIPAM10 (not shown here) is placed within these two curves. Contrary to the precursors, the viscosity of the dodecyl modified samples decreases remarkably with increasing x, in the absence of surfactant.

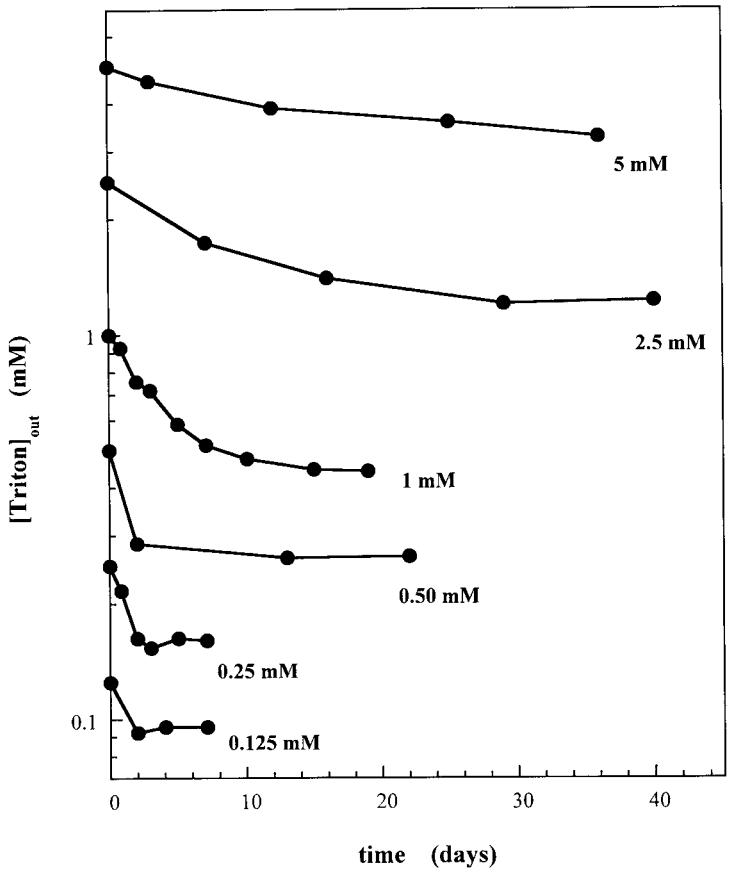


Fig. 4. Kinetics of the dialysis equilibrium experiments for the PNIPAM25C12/Triton system at 25°C. The polymer concentration is 1×10^{-3} g cm^{-3}. The concentration noted next to each curve is the initial Triton concentration in the outer solution.

Obviously, the attractive hydrophobic interactions between the pendent dodecyl groups prevail against the repulsive Coulomb interactions within each chain, so that the modified derivatives become more and more compact with increasing x. This is in agreement with the phase behaviour of these samples observed in more concentrated solutions [18]. Furthermore, upon addition of Triton, the specific viscosity of the mixtures increases considerably for all the dodecyl modified samples. This viscosity enhancement is more pronounced for the PNIPAM25C12/Triton mixtures, where the viscosity gain is about one order of magnitude. Nevertheless, contrary to the PNIPAM5C12/Triton system, the plateau viscosity of the PNIPAM25C12/Triton systems is substantially lower than the viscosity of the corresponding mixtures of Triton with the precursor PNIPAM25.

It should be noted that the specific viscosity of pure Triton solutions in the surfactant concentration range presented in Figs. 1 and 2 is very low (less than 0.2 when the Triton concentration is 50 mM), compared with the viscosity enhancement observed for the PNIPAMxCn/Triton mixtures. Therefore, the observed viscosity changes should be attributed to the interaction of Triton with the pendent alkyl groups of the hydrophobically modified derivatives and the consequent formation of mixed alkyl/surfactant aggregates. Although not negligible, the possibility of these mixed aggregates to cross-link several polymer chains is low, as the polymer solutions are rather dilute. Thus, the viscosity enhancement reflects mainly the unfolding of the polymer chains upon addition of Triton. In the absence of surfactant, the chain conformation of hydrophobically modified samples (mainly PNIPAM5C18 and PNIPAM25C12) is compact due to the formation of intrachain hydrophobic aggregates. This is reflected to the low specific viscosities of these samples and also to the quite low I_1:I_3 in much more dilute solutions, as it will be discussed in the following section. Upon addition of surfactant, the intrachain hydrophobic aggregates are disrupted and replaced by mixed dodecyl/surfactant aggregates, containing a lower number of dodecyl groups per aggregate compared to the initial intrachain aggregates. This number decreases gradually as the Triton concentration increases and the polymer chain tends to the conformation of the unmodified analogue.

It is worthy to note that for all systems the viscosity increase starts at Triton concentrations much higher than ~0.2–0.3 mM, the critical micelle concentration (CMC) of this surfactant [22–24]. To determine precisely the onset of the PNIPAMxCn/Triton association, static

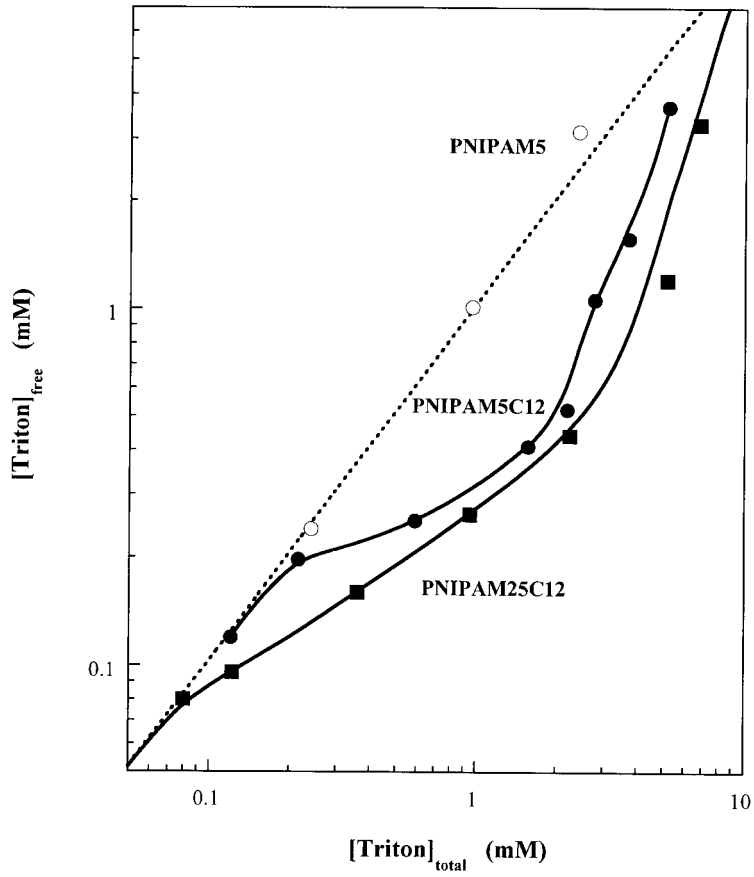


Fig. 5. The free (not bound) Triton concentration as a function of the total Triton concentration at equilibrium for the systems: (○) PNIPAM5/Triton; (●) PNIPAM5C12/Triton; and (■) PNIPAM25C12/Triton at 25°C. The polymer concentration is 1×10^{-3} g cm^{-3}. The diagonal dotted line corresponds to the case of no polymer/surfactant association.

fluorescence probing studies and dialysis equilibrium experiments were carried out.

3.2. Fluorescence probing study

For the fluorescence probing studies the ratio I_1:I_3 of the py emission spectrum was used as it is sensitive to the polarity of the microenvironment that py experiences [25]. Fig. 3 presents the variation of the ratio I_1:I_3 with the Triton concentration for pure surfactant solutions and for the mixtures of Triton with the dodecyl NIPAM-based derivatives. The polymer concentration for these experiments is set at 5×10^{-5} g cm^{-3}. The curve obtained for the pure Triton solution follows the typical pattern for surfactant solutions: at low Triton concentrations, the ratio I_1:I_3 is constant at a value of around 1.7, indicating an aqueous polar microenvironment, and decreases sharply within a narrow surfactant concentration region to much lower values of about 1.3, indicating that now py experiences the lower polarity microenvironment of Triton micelles. The inflection point of the curve, used for the determination of the CMC of the surfactant, is at a Triton concentration of 0.27 mM, within the values reported in the literature [22–24].

When the mixtures contain the hydrophobically modified derivatives the behaviour is not as simple. With the exception of PNIPAM5C12, the ratio I_1:I_3 for the other two polymers is substantially lower than 1.7, even in the absence of surfactant. In fact, I_1:I_3 is around 1.6 for PNIPAM10C12 and only 1.45 for PNIPAM25C12. These values indicate that the polymers exhibit a hydrophobic behaviour (moderately or substantially hydrophobic, respectively) in the absence of surfactant, even at this very low polymer concentration used. Upon addition of surfactant, the ratio I_1:I_3 decreases more gradually than in the pure Triton solutions, after the initial plateau. This behaviour is clearly evidenced for the PNIPAM5C12/Triton mixtures. On the contrary, for the PNIPAM10C12/Triton and especially for the PNIPAM25C12/Triton mixtures, the onset of the I_1:I_3 decrease is not as well defined, probably due to complications arising from the low I_1:I_3 values exhibited by these two polymers. The inflection point of the curves, however, is placed at a Triton concentration of 0.1–0.2 mM, i.e. not far from the CMC of the pure Triton solution. This

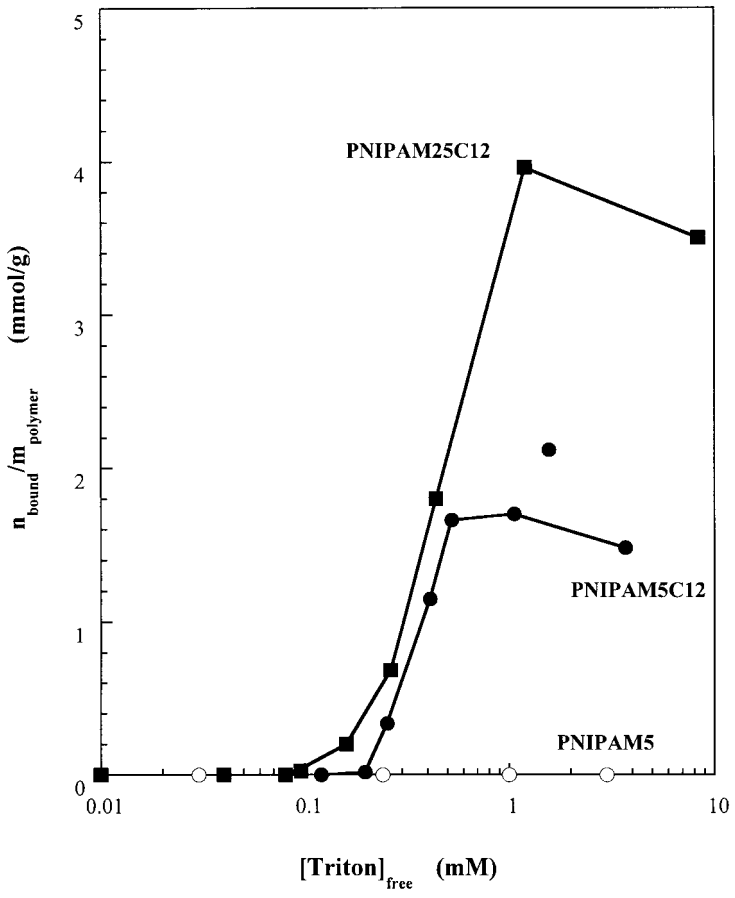


Fig. 6. Binding isotherms of Triton to: (○) PNIPAM5; (●) PNIPAM5C12; and (■) PNIPAM25C12. The polymer concentration is 1×10^{-3} g cm^{-3}. $T = 25$°C.

behaviour is indicative of a polymer–surfactant interaction starting close or just before the CMC region.

3.3. Dialysis equilibrium study

Fig. 4 presents the change with time of the concentration of Triton in the outer solution, for several initial surfactant concentrations ([Triton]$_0$), varying from 0.125 up to 5 mM. The inner solution contains PNIPAM25C12 at a concentration of 1×10^{-3} g cm^{-3}. Dialysis kinetics is observed to be slow: for [Triton]$_0 = 0.125$ mM two days are needed to reach equilibrium, while about 35 days are needed when [Triton]$_0 = 5$ mM. This slow rate is probably due to the fact that in most cases the Triton concentration is much higher than the CMC of this surfactant. Indeed, a similar observation is reported for dialysis equilibrium studies [26] of the PNIPAM/sodium dodecyl sulphate (SDS) system, i.e. kinetics is very slow when the surfactant concentration is higher than the CMC of SDS, while it is much faster for lower surfactant concentrations.

At equilibrium conditions the concentration of not bound (free) Triton equals the surfactant concentration in the outer solution, while the concentration of Triton bound to polymer can be calculated from Eq. (1):

$$[\text{Triton}]_{\text{bound}} = (V_{\text{out}}[\text{Triton}]_0 - V_{\text{tot}}[\text{Triton}]_{\text{free}})/V_{\text{tot}}, \quad (1)$$

where V_{out} is the volume of the outer solution and V_{tot} the sum of the volumes of the outer and inner solutions. Thus, the total Triton concentration in the inner solution ([Triton]$_{\text{tot}}$) is given by

$$[\text{Triton}]_{\text{tot}} = [\text{Triton}]_{\text{free}} + [\text{Triton}]_{\text{bound}}. \quad (2)$$

The free Triton concentration [Triton]$_{\text{free}}$ is plotted in Fig. 5 against the total Triton concentration [Triton]$_{\text{tot}}$ for dialysis equilibrium experiments with the non-modified copolymer PNIPAM5 and the dodecyl-modified derivatives PNIPAM5C12 and PNIPAM25C12, at a polymer concentration of 1×10^{-3} g cm^{-3}. The diagonal dotted line represents the absence of any association between the surfactant and the polymer. In fact, this is the case for the solutions of PNIPAM5, confirming the viscometric and fluorescence probing results. On the contrary, PNIPAM5C12 and PNIPAM25C12 form mixed aggregates with Triton, and the corresponding experimental curves in Fig. 5 deviate from the diagonal. The deviation starts at a concentration [Triton]$_{\text{tot}}$ of about 0.2 mM for PNIPAM5C12 and at about 0.1 mM for PNIPAM25C12. These values,

taken as the critical aggregation concentrations (CAC) for the formation of mixed alkyl/surfactant aggregates, confirm that polymer/surfactant association occurs in the vicinity of the CMC of pure Triton solutions. Such a behaviour seems to be a more general trend for the interactions of HMWSP with nonionic surfactants, as it has also been observed in other similar systems [11,17].

The corresponding binding isotherms of Triton are presented in Fig. 6. At CAC, Triton starts to bind to PNIPAM5C12 and PNIPAM25C12. The quantity of surfactant bound to the polymers increases rather sharply with $[\text{Triton}]_{\text{free}}$, and finally a plateau seems to be reached at high surfactant concentration. In this region, about 1.8 or 4 mmol of Triton are found to be bound to 1 g of PNIPAM5C12 or PNIPAM25C12, respectively. From these values, we can find that one dodecyl group of PNIPAM5C12 or PNIPAM25C12 corresponds to four or two molecules of bound surfactant, respectively. We have no direct evidence whether all the alkyl groups of the copolymers are involved in mixed surfactant aggregates or not. Therefore, we have to assume that either these aggregates contain much more dodecyl groups in the case of PNIPAM25C12, or a large quantity of dodecyl groups still form intrachain aggregates (as in the absence of surfactant) and do not participate in mixed alkyl/surfactant aggregates. The low I_1:I_3 ratio observed in Fig. 3 for PNIPAM25C12 at very low surfactant concentration (or in the absence of surfactant) seems to support the latter assumption. Moreover, the remaining intrachain hydrophobic aggregates could explain why the expansion of PNIPAM25C12 chain is not complete with addition of Triton, contrary to the PNIPAM5C12 chain, as revealed by the viscometry results in Fig. 2.

4. Conclusions

The static fluorescence probing studies and, especially, the dialysis equilibrium experiments demonstrated that the nonionic surfactant Triton X-100 can form mixed hydrophobic aggregates with the alkyl groups of hydrophobically modified NIPAM-based polymers when the surfactant concentration is in the vicinity of or higher from the CMC of the pure Triton solution. The formation of mixed alkyl/surfactant aggregates and the consequent disruption of the initial intrachain hydrophobic aggregates upon addition of surfactant leads to the gradual unfolding of the initially contracted polymer chains. This is revealed by an important increase of the specific viscosity of the PNIPAMxCn/Triton mixtures, that tends towards the specific viscosity of the Triton mixtures with the corresponding unmodified analogue. This is clearly achieved only for the PNIPAM5C12/Triton system whereas, for the copolymers characterised by higher x, the unfolding of the polymer chains is incomplete, even at high surfactant concentration.

Acknowledgements

This work was supported by the European Union under the contract ERBFMBICT983240. Financial support by the Greek General Secretariat for Research and Technology (ΠΕΝΕΔ 99ΕΔ98) is also acknowledged. The author wishes also to thank Prof. G. Staikos for very helpful suggestions.

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