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ORIGINAL CONTRIBUTION

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Coil-to-globule transitions of interfacial copolymers in better than theta-solvents

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Abstract Experimental studies of the coil-to-globule transitions exhibited in better than θ-solvents by interfacial copolymers of *N*-isopropylacrylamide and acrylamide imply that a lower bound for the value of '*n*' in the *n*-clusters of poly(*N*-isopropylacrylamide) (PNIPAM) is 3. The corresponding upper bound is therefore likely to be 5 or 6. Statistical copolymers of PNIPAM containing upwards of 0.75 mole fraction of acrylamide (whose homopolymer does not itself display *n*-clustering) exhibited this transition, which disappeared at higher mole fractions of acrylamide. Interfacial homopolymers of *N*-ethylacrylamide and its statistical copolymers with *N*-isopropylacrylamide exhibited *n*-clustering at all compositions.

Key words Interfacial copolymers – coil-to-globule transitions – hydrophobically modified poly(acrylamides) – poly(*N*-isopropylacrylamide) – *n*-clusters

Introduction

A recent experimental study [1] of the coil-to-globule transition of poly(*N*-isopropylacrylamide) (PNIPAM) chains attached to the surfaces of latex particles dispersed in water revealed the existence of not one but two such transitions. Both transitions were broad relative to that observed in free solution. The first occurred under worse than θ-solvency conditions (i.e., at temperatures above 31 °C), whereas the second was observed in better than θ-solvents (i.e., below 31 °C). The former transition is analogous to that observed for PNIPAM chains in free solution so it may reasonably be assumed to be driven by the attractive binary segmental interactions that characterise worse than θ-solvency conditions. The second unexpected transition, by way of contrast, required for its explanation the invocation of the intramolecular *n*-clusters concept [2], which was first applied to interfacial polymers by de Gennes and co-workers [3] in this journal. According to this notion, the interactions of *n*-segments of a polymer can become attractive, even though the binary interactions remain repulsive. This occurs over a limited temperature range only. The value of '*n*' here signifies the number of monomeric repeat units ('mers') that participate in intramolecular cluster formation.

de Gennes [2] speculated that the value of '*n*' in *n*-clustering was likely to be relatively small (less than 10) for most polymers and so inferred that *n*-clusters could also be thought of as 'protomicelles'. This analogy with micelles is conceptually useful because it implies that for PNIPAM, the driving force for aggregation derives from the hydrophobic interactions between the isopropyl groups in an aqueous environment.

To-date there has been no experimental determination of the size of '*n*' for the intramolecular *n*-clusters of interfacial PNIPAM in water. In what follows, we show how to narrow the range of possible values for '*n*' and confirm its relatively small value. The strategy adopted was to copolymerize *N*-isopropylacrylamide (NIPAM) with increasing amounts of acrylamide (AM) until *n*-clustering could no longer be detected. Acrylamide was chosen as the comonomer in these experiments because its homopolymer does not display *n*-clustering phenomena, lacking as it does the hydrophobic isopropyl moiety. The sequence distribution for the composition of the statistical copolymers at which *n*-clustering just vanishes provides insights into the likely lower and upper bounds for '*n*'. Data are also presented for statistical copolymers of NIPAM with *N*-ethylacrylamide (NEAM) whose homopolymer, in contrast to polyacrylamide, also displays the *n*-clustering phenomenon.

Experimental

N-isopropylacrylamide (Monomer–Polymer) was purified by recrystallization from 65/35 mixture of hexane and benzene. Acrylamide (Merck) was recrystallized from benzene. *N*-ethylacrylamide (Datac Labs) was used as received. Styrene (Ajax) was purified by redistillation at 55 °C under reduced pressure. One component of the redox initiator, sodium metabisulphite (Merck), was used as received whereas the other, potassium persulfate (KPS), was recrystallized from water. All water used in the experiments was double distilled.

Full details of the method for preparing the latices have been published previously [1] except that it was found necessary for the copolymer systems to use a different redox initiator from that used previously. An excellent initiator was found to be KPS$(5\times10^{-4}\,\mathrm{M})/\mathrm{Na_2S_2O_5}$ $(2.5\times10^{-4}\,\mathrm{M})$.

In considering the composition of the copolymers formed relative to their comonomer feed compositions, it might be expected intuitively that the reactivity ratios of the comonomers, which are chemically very similar, would not depart significantly from unity. The results of Chiklis and Grasshoff [4] support this expectation, at least for the NIPAM/AM pair. They found that $r_1 = 0.50$ and $r_2 = 1.00$ (1 = NIPAM and 2 = AM) so that the respective mole fractions of monomers in the copolymers should not differ dramatically from that in the comonomer feed. These intuitive expectations were confirmed theoretically and by chemical analysis. The average compositions of the coating copolymers harvested prior to the introduction of any styrene was determined by both chemical microanalysis (C, H and N) and by ^{13}C and ^{1}H NMR of the copolymers in D_2O. Both methods were found to give results that were in good agreement (usually to about ± 5% in the mole fraction of AM present); moreover the results did not differ greatly from the monomer feed mole fractions used. The NMR composition results are reported below.

The measured intrinsic viscosities in water at 25 °C of the NIPAM/AM copolymers used to coat the latex particles all fell in the narrow range of $1.2 \pm 0.1\,\mathrm{dL\,g^{-1}}$, irrespective of their composition. Applying the Mark–Houwink equations for homopolymer PAM [5] and homopolymer PNIPAM [6] to this value implies viscosity average molecular weights of the copolymers somewhere in the range $(2\text{–}8)\times10^5$, with a likely value of order $(5 \pm 3)\times10^5$. This likely average is close to the actual viscosity average molecular weights measured for the homopolymer PNIPAM and PAM, which were 5×10^5 and 4×10^5 respectively. The general qualitative conclusion to be drawn is that all of the homopolymers and copolymers studied had comparable molecular weights.

Aqueous solutions of PNIPAM exhibit phase separation at temperatures close to the θ-point [7]. Usually, according to Fujishige [8], these temperatures are relatively insensitive to the volume fraction of polymer present in solution (which we have independently confirmed), as well as the polymer molecular weight. Such observations deviate from the predictions of the Flory–Huggins theory of polymer solution thermodynamics and appear to be associated with the coil-to-globule transition that accompanies phase separation. Only those copolymers with AM that contained at least 0.46 mole fraction of NIPAM exhibited phase separation in water at temperatures below 100 °C. Like homopolymer PNIPAM, the phase separation temperatures of these copolymers were found, within experimental error, to be insensitive to the copolymer concentration over the range 0.1–1 wt %. It should be noted that the application of the Flory concept of the θ-temperature to copolymers in general is not without its attendant difficulties but its use in the manner detailed above for statistical copolymers should not introduce major conceptual errors. Normally, an extrapolation procedure involving the polymer concentration is necessary to convert phase separation temperature data into a θ-temperature measurement [9–11] but the absence of a measurable concentration effect rendered this extrapolation unnecessary here. The interfacial coil-to-globule transitions were monitored by dynamic light scattering (DLS) of the latex particles using a Malvern 4700 SM particle size analyser, as described previously [1]. The core particle radius was determined by transmission electron microscopy.

Results and discussion

Coil-to-Globule transitions of copolymers of acrylamide and *N*-isopropylacrylamide

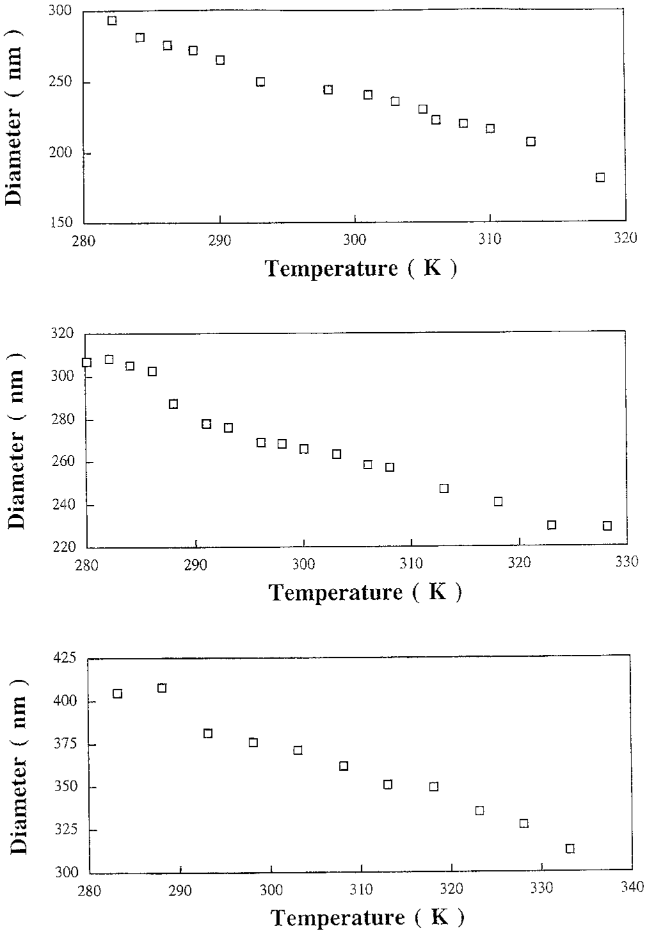
Statistical copolymers of *N*-isopropylacrylamide and acrylamide containing varying amounts of the latter monomer were studied as anchored steric stabilizers. Their

θ-temperatures in pure water in free solution as determined by light scattering are listed in Table 1. The temperature dependence of DLS particle size of electrosterically stabilized latexes coated by the copolymers of differing compositions are presented in Figs. 1 and 2. It is apparent that the three latexes for which data are presented in Fig. 1 all displayed large decreases in the DLS average particle size over relatively small increments in temperature. These copolymers contained from 0.9 down to 0.4 mole fraction of NIPAM. This type of behaviour is symptomatic of the occurrence of coil-to-globule transitions. Reference to the data presented in Table 1 shows that the large contraction in size occurred under better than θ-solvency conditions. This implies that the transitions for these copolymers are driven by *n*-clustering, just as they are for homopolymer PNIPAM [1]. The core sizes of the latex particles are presented in Table 2. Although there was some variation in core diameter, it is stressed that, as discussed below, the observed decreases in measured DLS sizes are solely those of the interfacial chains and are independent of the latex core diameters, which are essentially temperature independent. All that any difference in core size does is to move the graph of the temperature dependence of the DLS size up or down the ordinate axis, without changing its slope.

Table 1 Conventional theta-temperatures of poly(NIPAM-*stat*-AM) copolymers in water

Mole fraction of NIPAM in copolymer	θ/K
1.00	306
0.90	317
0.46	370
≤ 0.45	> 373

Fig. 1 The temperature dependence of the DLS particle size for latexes coated with copolymers of NIPAM and AM. From top to bottom: 0.90; 0.46; 0.41 mole fraction of NIPAM



The DLS size versus temperature of a latex coated by a copolymer containing a mole fraction of AM of 0.75 is shown in Fig. 2, as is that for a latex coated by homopolymer PAM. It is apparent that the absolute values of the slopes of the two lines are similar, although that for the copolymer coated latex appears to be marginally larger than that for PAM coated latex. The decrease in size of the PAM coated latex may be attributed to the decrease in solvency of the water for the PAM on heating.

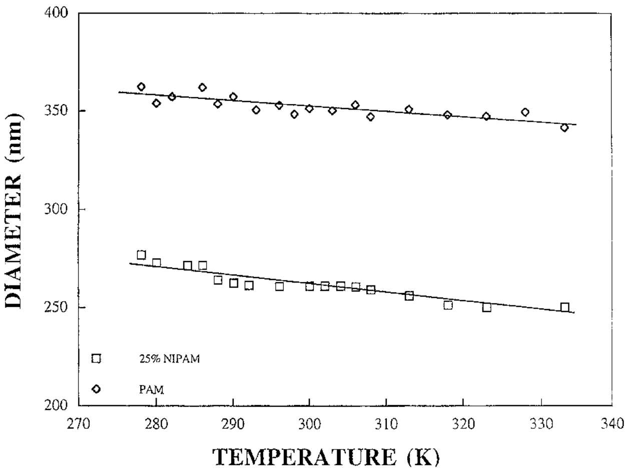


Fig. 2 The temperature dependence of the DLS particle size for latexes coated with i) □ copolymer containing 0.25 mole fraction of NIPAM and ii) ◇ with homopolymer PAM

Table 2 Electron microscopic values of the core latex particle sizes

Mole fraction of NIPAM in copolymer	core diameter/nm
0.90	165
0.46	170
0.41	290
0.25	150
0.00	250

No coil-to-globule transition would be expected to be observed in this case under better than θ-solvency conditions and this expectation is confirmed by the relatively small decrease in DLS size observed for this sample. This result for homopolymer PAM implies that the latex coated by the copolymer containing a mole fraction of 0.75 AM also exhibited little, if any, *n*-clustering.

Figure 3 summarizes the absolute values of the slopes of the linear regions of the temperature dependence of the DLS particle size for the latexes presented in Figs. 1 and 2 as a function of the mole fraction of NIPAM in the copolymer stabilizers. This comparison of the slopes is only meaningful because of the similar molecular weights of the ensheathing polymers. It should be noted that these anchored interfacial chains, as was shown previously [1], do not adopt a brush-like (i.e., extended) conformation. Rather, their interfacial conformation is more coil-like.

The DLS size that is measured is the sum of the core latex particle diameter plus two layers of interfacial chains, one on either side of the particle. The temperature dependence of the size of the core latex particle is negligible over the range studied and so the changes observed on heating are those of the interfacial chains, irrespective of the core latex particle diameter. It is independent of the number of copolymer chains attached to the latex particle. Note that only those sections of the plots at temperatures greater than 16 °C were used in determining the slopes. The linear least squares plot drawn in Fig. 3 for the PNIPAM/AM copolymers is somewhat arbitrary since a more complex shape might well be followed. Whatever shaped curve is appropriate, however, the following conclusion remains unaltered: *n*-clustering is seemingly not detectable experimentally once the mole fraction of NIPAM in the copolymer is reduced to or falls below *ca.* 0.25. Stated another way, the observation that *n*-clustering is detectable up to such a high mole fraction of the diluent monomer as 0.75 contains the qualitative implication that the value of '*n*' in the *n*-clusters of PNIPAM must be quite small, certainly less than 10; were that not so, *n*-clustering would disappear at much lower levels of AM in the copolymer than were in fact observed.

Theoretical sequence distribution in poly(NIPAM-*stat*-AM)

To narrow down the likely value of '*n*' in the *n*-clusters of PNIPAM, it is necessary to resort to the calculated sequence distribution of monomers in the copolymers. If the monomers AM and PNIPAM are denoted respectively by 0 and 1, then what are required are the relative populations of the diad (0110), triad (01110) tetrad (011110) and pentad (0111110) sequences of NIPAM at the overall mole fraction of NIPAM where *n*-clustering just ceases to be observable. Such results are shown in Fig. 4. The values

Fig. 3 Effect of copolymer composition on the moduli of the slopes of the plots of latex particles size versus temperature for i) □ AM as the diluting monomer and ii) * NEAM as the diluting monomer

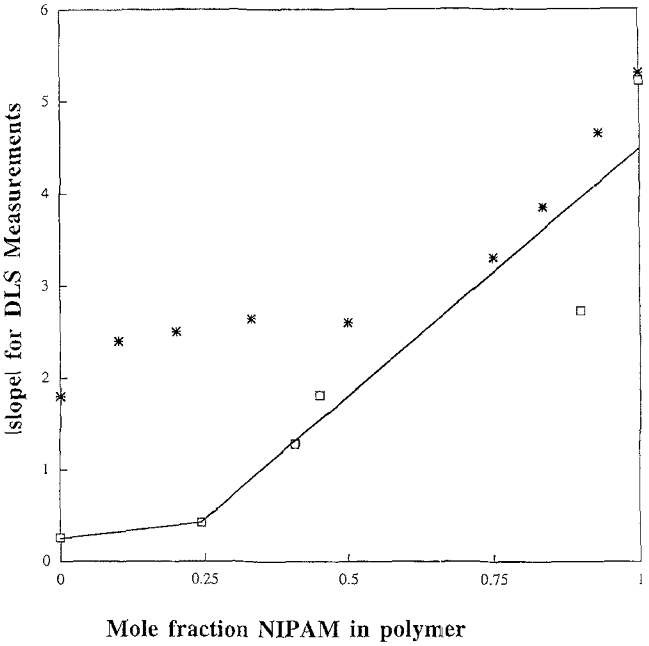
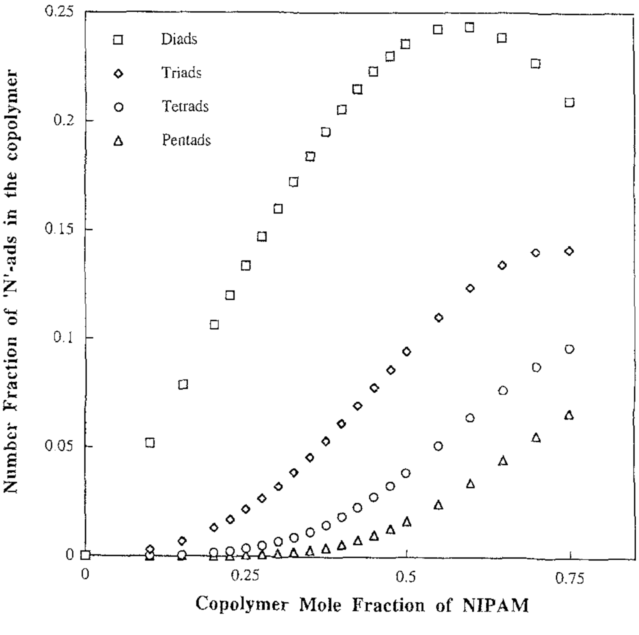


Fig. 4 Calculated relative populations of the distribution of sequences (*n*-ads) for copolymers of AM and NIPAM at various copolymer compositions: □ diads; ◇ triads; ○ tetrads; △ pentads



were calculated using the formulae given by Bovey [12]. It is apparent that at a mole fraction of NIPAM of 0.25, the incidence of pentads of NIPAM is relatively small. This means that too few pentads are present in the copolymer chains to induce the n-clustering phenomena. For this reason pentads (i.e., $n = 5$) can reasonably be eliminated as the lower bound required for n-clustering. In contrast, diads of NIPAM show a relatively high incidence at this mole fraction and there seems to be nothing at the mole fraction of NIPAM of 0.25 to connect the diad concentration to the loss of n-clustering phenomena. This result agrees with the discussion and experimental evidence presented previously [1] that affirm that binary segmental interactions are repulsive in better than θ-solvents and so cannot be responsible for n-clustering and the observed coil-to-globule transitions. The data presented here suggests that triads or tetrads ($n = 3$ or 4) of NIPAM are necessary for the occurrence of n-clustering. These sequence calculations, however, are unable to discriminate unequivocally between the two possible values of 'n'. Nonetheless, the value of $n = 3$ is preferred as the more likely lower bound for two reasons: First, model building with space filling models suggests that the close packing of the isopropyl moieties into protomicelles can be accomplished without undue steric strain for $n = 3$ whereas such packing seems far more difficult for $n = 4$; Secondly, the incidence of tetrads of NIPAM is quite small in an absolute sense at a mole fraction of NIPAM of 0.25 and so their concentration is probably insufficient to drive a coil-to-globule transition in better than θ-solvents.

Note that the foregoing discussion is strictly limited to the determination of the lower bound for 'n'. This follows because it is not yet known whether n-clusters involve just localised triads (or tetrads) of NIPAM segments acting alone or whether these triads interact with other NIPAM segments located at some distance along the backbone of the chain but placed contiguous to the triads by chain coiling. If the latter occurs, the triads could interact with monads or diads of NIPAM monomers, which are present at relatively high absolute concentrations, or, even possibly the less frequent triads. Other interactions would seem to be too rare statistically to be important. This line of reasoning would suggest that an upper bound for 'n' in n-clustering is likely to be $n = 6$, always remembering that if this coiling mechanism is operative, values of 'n' equal to 4 or 5 are far more likely statistically.

de Gennes and coworkers [2, 3] anticipated that the value of 'n' was likely to be relatively small (i.e., $n \leq 10$) for protomicelles compared with the aggregation numbers of conventional micelles, where typically values of order say 50–100 are found. There are likely to be at least two reasons for this difference. First, the size of the hydrophobic moieties (e.g., isopropyl groups) is small compared with the size of the usual surfactant hydrophobes (e.g., dodecyl); it is known that a reduction in the tail size to say, octyl reduces the micellar aggregation number from say, 50–100 for dodecyl to around 10 [13]. This reduction is presumably associated with the reduction in space filling capacity of the tails within the micellar cores. Second, the constraints resulting from the connectivity of the backbone atoms to which the hydrophobic moieties are attached function effectively as a high interfacial tension, restraining the growth of the protomicelles.

Coil-to-globule transitions of copolymers of N-isopropylacrylamide and N-ethylacrylamide

Statistical copolymers of NIPAM with NEAM were prepared after it was found that interfacial homopolymer PNEAM chains gave n-clustering in better than θ-solvents that led to coil-to-globule transitions. Thus PNEAM becomes only the second interfacial homopolymer reported to-date to exhibit the phenomenon of n-clustering in water. The θ-temperature of homopolymer PNEAM in water was measured as 73 °C. The data for the absolute values of the slopes of the average DLS particle size as a function of the mole fraction of NIPAM in the copolymer are shown in Fig. 3, along with those for the AM copolymers discussed previously. It is interesting to note that at low mole fractions of both AM and NEAM, the effects of the presence of the two diluting monomers on the n-clustering of PNIPAM were relatively similar. At most, AM as a diluting monomer was only marginally more effective than NEAM. This similarity in observed behaviour suggests that mixed protomicelles composed of ethyl and isopropyl groups are not readily formed in copolymers of NIPAM and NEAM. It is apparent that if the measured absolute value of the slope can be correlated directly with the strength of n-clustering, then the decrease in the magnitude of the slope for the NEAM copolymers is greater than would be expected purely on the basis of the relative mole fraction of the diluent monomer. Put another way, the experimental slopes for the diluting NEAM monomer exhibited significant positive deviations from "ideal" mole fraction behaviour. Here "ideal" behaviour is defined as a direct proportionality between the measured absolute value of the slope and the mole fraction of NIPAM in the copolymer over the entire mole fraction range for which n-clustering is observed. "Positive" deviations are defined here as providing a greater reduction in slope for a given mole fraction of PNIPAM than an ideal system. Such positive deviations suggest that n-clustering is an autocatalytic phenomenon: the formation of some n-clusters promotes the formation of even more clusters. This might be interpreted as favouring the model of n-cluster formations that involves the coiling of the chain back in upon itself but this interpretation is far from conclusive.

Conclusions

Studies of interfacial coil-to-globule transitions occurring in better than θ-solvents for the statistical copolymers of NIPAM with AM have shown that the transition occurs down to copolymers containing as little as 0.25 mole fraction of NIPAM but is lost at lower NIPAM mole fractions. Sequence calculations suggest that the lower bound for the value of 'n' in the n-clusters of interfacial PNIPAM is $n = 3$ (or perhaps 4). This implies a likely upper bound if chain coiling is involved of $n = 5$ or 6. Interfacial PNEAM chains were found to exhibit n-clustering phenomena; this is only the second interfacial polymer to be shown to display this effect. Statistical copolymers of NIPAM and NEAM exhibited n-clustering over the entire compositional range.

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