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# Insight into Clustering in Poly(ethylene oxide) Solutions

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ABSTRACT: The clustering phenomenon has been observed in many macromolecular systems. Poly(ethylene oxide) solutions are characterized by a clustering effect that has been extensively discussed in the literature. Its origin has remained elusive. Using small-angle neutron scattering from PEO solutions in various deuterated solvents, the possible causes of clustering that have been given in the literature are analyzed here. These include impurities in water, possible PEO crystallization, a subtle phase transition whereby a concentrated phase coexists with free polymer coils, hydrogen-bond physical cross-linking, and finally chain ends effect. We have shown that under the experimental conditions considered here (4% PEO weight fraction) the mostly forgotten chain ends effect is at the origin of clustering in poly(ethylene oxide) solutions.

## Introduction

Poly(ethylene oxide) is one of the most researched water-soluble synthetic polymers. This attention stems from the simplicity of the PEO macromolecule's basic forming unit, the monomer $-(CH_2CH_2O)-$. The presence of an oxygen atom changes entirely the nature of the interactions and therefore the thermodynamics of PEO when dissolved in various solvents. This synthetic polymer is often mentioned as a good and simple enough (and therefore tractable) model for biopolymers. When dissolved in water, PEO is characterized by hydrophilic interactions (hydrogen bonding of water molecules to the oxygen atoms on the polymer) and hydrophobic interactions (the $CH_2CH_2$ groups repel water). PEO can dissolve in water only because water molecules form a sheath around the PEO macromolecule. This is reminiscent of the hydration layer around proteins. Disturbance of this water layer results in the onset of phase separation (seen as a clouding up of the sample) in PEO/water solutions and is the cause of the denaturation of proteins. Dissolution of the hydration layer exposes the hydrophobic groups forcing a phase transition in both cases. PEO/water solutions are known to phase separate at high temperatures.

The hydration layers around the PEO chains have been investigated.[1−3] Models presented consist of cagelike structures whereby the hydrophobic $CH_2CH_2$ groups are shielded from contacting water molecules similarly to hydrate structures. Two to three water molecules per monomer form the first layer.[2] The oxygen−oxygen interdistance on the PEO chain matches the oxygen−oxygen interdistance in the structure of pure water. This is the principal reason why PEO dissolves in water for a wide range of temperatures and concentrations. Its homologues, PMO ($-CH_2O-$) and PPO ($-CH(CH_3)CH_2O-$), are not soluble in water because of the poor match in oxygen−oxygen interdistances. The possibility that PEO forms helical structures in water has also been mentioned in the literature.[2]

When dissolved in water (as well as other solvents), PEO forms characteristic clusters (also referred to as aggregates) that have been the subject of intense investigations.[4−12] This clustering phenomenon has been observed in many other systems such as polyelectrolyte solutions, clay dispersions, living polymerization, polypeptide chains in proteins, etc. The subject of the clusters' origin has been elusive and remains an open question.

Most studies have observed clusters in PEO solutions and presented possible reasons as to their origin and behavior. Some of these reasons include impurities in water,[8] crystallization of the PEO groups,[6] a low-temperature phase transition producing a polymer-rich phase,[5] interchain physical cross-links due to intense hydrogen bonding, chain ends effect, etc. The chain ends effect has been considered once[10] but dismissed right away on the basis of a doubtful argument. These various possibilities have been carefully investigated and are discussed here along with new convincing evidence. Available clues are analyzed and conclusions are presented for our experimental conditions.

Many published investigations[13−17] have focused on the thermodynamics of the phase separation of PEO/water solutions and presented models to predict phase diagrams. PEO/water solutions are characterized by a closed loop immiscibility island above 100 °C. These models have not considered clustering at all. The only model that has attempted to explain clustering[5] (the de Gennes model) used a thermodynamic argument.

## The Approach Used Here

The main investigative tool used in our approach is small-angle neutron scattering (SANS). SANS is a useful probe covering a large size range between a few nanometers and a fraction of a micrometer. This scale covers the sizes of polymer chain thermodynamics (tens of nanometers) and clusters (micrometer). SANS measurements are made in inverse (Fourier) space which is characterized by the scattering "wavevector" $Q = (4\pi/\lambda)\sin(\theta/2)$, where $\lambda$ is the neutron wavelength and $\theta$ is the scattering angle. All of our measurements were made at the National Institute of Standards and Technology Center for Neutron Research (NCNR). The usefulness of the SANS technique stems from the partial deuteration method in which deuterated solvents are used in order to enhance the contrast of PEO.

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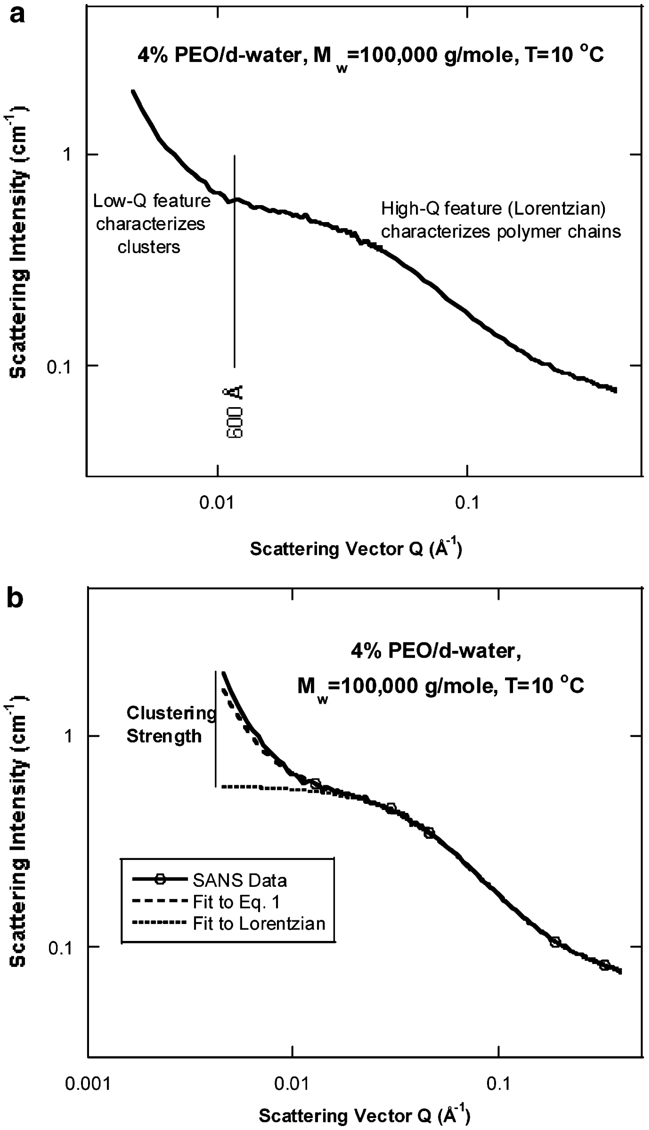

**Figure 1.** (a) Small-angle neutron scattering from a 4% (weight fraction) poly(ethylene oxide) polymer ($M_w = 100\ 000$ g/mol) in deuterated water and at a temperature $T = 10$ °C. The 4% weight fraction corresponds to the semidilute regime where polymer chains overlap. (b) SANS data and results of fits to eq 1 are shown. Fits to a Lorentzian form (last two terms only in eq 1) are also included. The clustering strength is defined as the first term in eq 1 for $Q = 0.004$ Å.

PEO samples were purchased from Polymer Source and dissolved in deuterated solvents (the PEO macromolecules contained no deuteration). The PEO supplier performed gel permeation chromatography (GPC) to characterize the molecular weights. The molecular weights used in our experiments are described in the following sections. The various deuterated solvents (d-water, d-benzene, d-methanol) were purchased from Sigma-Aldrich. Deuterium atoms replace hydrogen atoms in the deuterated solvents.

## A Typical Example

Figure 1a illustrates a typical SANS spectrum from a 4 wt % PEO/d-water (weight-average and number-average molecular weights of $M_w = 100\ 000$ and $M_n = 96\ 000$ g/mol, respectively) for a temperature $T = 10$ °C. The low-*Q* feature characterizes the large size clusters, and the high-*Q* feature characterizes the polymer chains. One notes that only the tail of the low-*Q* feature is seen in our spectrum. For this reason, precise cluster sizes cannot be obtained from our data; only lower bounds can be estimated. Dynamic light scattering (DLS) is suitable for estimating cluster sizes.

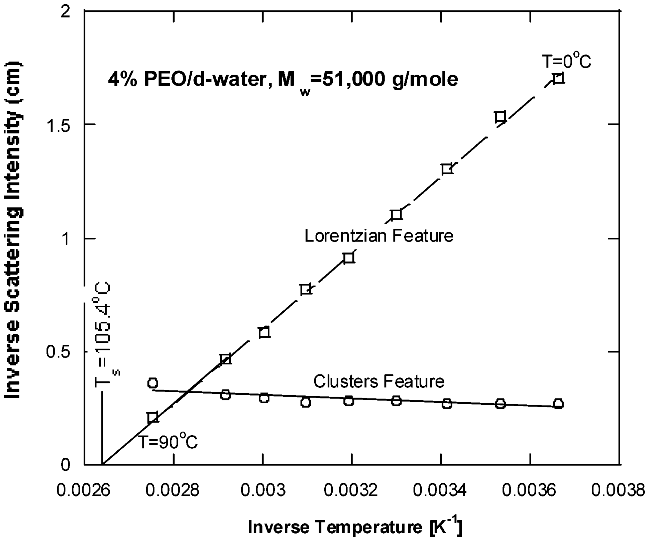

**Figure 2.** Variation of the inverse intensity $C^{-1}$ vs inverse temperature $T^{-1}$ (in K) shown in the top curve gives an estimate of the spinodal phase separation temperature $T_s$. The bottom curve shows the variation of $A^{-1}$ vs inverse temperature $T^{-1}$. Error bars are of the same size as the symbols.

To characterize our results, the following functional form is fitted to the data:[12]

$$I(Q) = A/Q^n + C/\{1 + (QL)^m\} + B \qquad (1)$$

The first term describes Porod scattering from clusters, and the second term is a Lorentzian function describing scattering from polymer chains. This second term characterizes the polymer/solvent interactions and therefore the thermodynamics. The two multiplicative factors *A* and *C*, the incoherent background *B*, and the two exponents *n* and *m* are used as fitting parameters. The final parameter *L* is a correlation length for the polymer chains. SANS data as well as fits are shown in Figure 1b. It is found that $L = 19.88 \pm 0.14$ Å, $n = 2.98 \pm 0.04$, and $m = 1.91 \pm 0.01$. DLS gave a cluster size of $1.36 \pm 0.20$ $\mu$m at ambient temperature for the 4% PEO/d-water sample.

The clustering strength is defined as $A/Q^n$, where *A* and *n* are fitting parameters and $Q = 0.004$ Å$^{-1}$ (a low-enough *Q* value). It is shown in Figure 1b. The correlation length *L* as well as the coefficient *C* in eq 1 increase with increasing temperature *T* due to increased composition fluctuations when approaching phase separation. The PEO/d-water system is characterized by a lower critical solution temperature (LCST); i.e., it phase separates upon heating. The spinodal (phase separation) temperature $T_s$ can be accurately estimated from the intercept of a $C^{-1}$ vs $T^{-1}$ plot of data taken at various temperatures as shown in Figure 2. In the case shown, corresponding to 4% PEO/d-water ($M_w = 51\ 700$, $M_n = 48\ 500$ g/mol), one finds $T_s = 105.4 \pm 0.5$ °C.

The clusters scattering feature (represented by the scale factor *A* in eq 1) is seen to decrease with increasing temperature. However, clusters persist even at high temperatures. Measurements made in a high-pressure cell show that clusters are still present even at $T = 150$ °C, i.e., way above the LCST for the polymer solution.

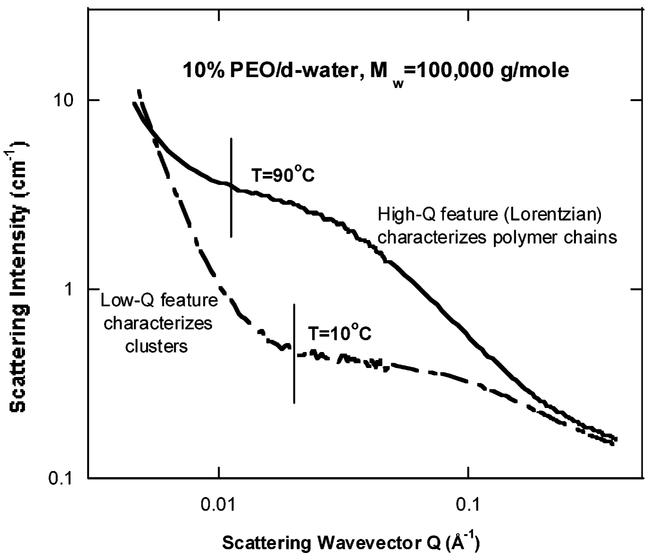

**Figure 3.** SANS data from a 10% PEO/d-water solution. The top curve shows clearly that clusters persist even above the crystallization temperature of PEO (66 °C).

## Impurities in Water

It has been suggested that PEO clusters are due to impurities in water.[8] This claim has been addressed before and settled.[11,18] To remove impurities, the PEO/water solution (not just water) was filtered in some published experiments.[8−10] This filtering process affected (i.e., broke down) the clusters. Clusters, however, were seen to re-form[11,18] after hours to days. Careful dynamic light scattering (DLS) experiments have clearly shown a clusters diffusion (slow) mode and an individual chains diffusion (fast) mode.[11,18]

## PEO Crystallization

PEO crystallizes in water only at temperatures below 66 °C and concentrations above 50%.[13] Our low concentration (semidilute) regime should not show crystallization. However, because crystallization would appear as a low-$Q$ feature (just like clusters), we investigate this issue here. A plot of the SANS data (Figure 3) at a temperature (90 °C) well above the crystallization temperature shows that clusters persist at high temperatures. They persist even at 150 °C (with measurements made in a high-pressure cell). This simple observation proves that the formation of clusters is not due to PEO crystallization. Claims that clusters may be due to crystallization at low temperatures (below 66 °C) and to other aggregation processes at high temperatures[6] are also not founded. This conclusion is based on the smooth variation of the clusters feature (in the SANS data) across the 66 °C temperature. In fact, the signature of crystallization is completely different from that due to clusters. Crystallization is characterized by a steep $A/Q^4$ variation over orders of magnitude in $Q$, whereas our data show a weaker $A/Q^n$ variation with $n = 3.2$ and a plateau region at intermediate $Q$ as shown in Figure 3.

## Concentrated Phase of a Phase-Separated System

Phase separation in polymer solutions occurs either upon heating (LCST behavior) or upon cooling (upper critical solution temperature or UCST). It is well-known that the PEO/d-water system is characterized by an LCST (above 100 °C). Actually, the high-temperature portion of the phase diagram is a closed loop immiscibility island (phase separation then remixing upon heating above 100 °C). However, the high-temperature portion of the phase diagram is of no interest here.

The de Gennes model[5] hypothesizes that PEO could also phase separate at temperatures below 70 °C and that this (lower portion) UCST is characterized by a high-concentration phase and a dilute-concentration phase coexisting in equilibrium (along a tie line). Standard UCST behavior involves phase separation into a high-concentration phase and a dilute phase of *collapsed* coils. The idea put forward[5] is that of a UCST phase separation into a high-concentration phase and a dilute concentration of *swollen* coils. This theoretical idea is based on the possibility of attractive interactions inside a large group of monomers (i.e., clusters would contribute a negative energy in the free energy expansion), but there is no apparent physical reason for this effect.

One obvious argument against this model[5] is the fact that if PEO/water solutions were characterized by a miscibility gap between a UCST (around 70 °C) and an LCST (around 100 °C), the high-$Q$ SANS intensity (fitting parameter $C$ in eq 1) would increase and then decrease between these two temperatures. Figure 2 shows a monotonic variation throughout the entire temperature range. Another (even stronger) argument against the hypothesis that clusters may be the concentrated phase of a phase-separated system is presented in the chain ends effect section.

## Hydrophobic Interactions

Hydrogen bonding could form physical “cross-linking” of the oxygen sites across neighboring PEO chains (mediated through water molecules). If this happened in our case, one would obtain a short characteristic distance between cross-links (say, of the order of 100 Å or less). There is no evidence for that effect in our case (4% PEO weight fraction). Figure 1a shows that the crossover from the low-$Q$ feature to the high-$Q$ feature occurs around 600 Å ($\sim 2\pi/0.01$). This is of the order of the total chain size and therefore much larger than typical cross-link interdistances. This observation suggests that interchain cross-linking is not at the origin of the clustering observed in our experimental conditions. As described in the next section, the chain ends effect is the major cause of clustering in our case. In other experimental conditions, other effects (such as hydrogen bonding) may contribute and/or cause clustering.

## Chain Ends Effect on Cluster Formation

Most PEO polymers are end-capped with an $-OH$ group at one end and an $-OCH_3$ group at the other end. This relates to the common synthesis scheme used to polymerize ethylene oxide. To test the chain ends effect on clustering, a set of three PEO samples were purchased (also from Polymer Source) in which the end groups were either $-OCH_3$ on both ends, $-OH$ on both ends, or an $-OH$ on one end and an $-OCH_3$ on the other end. All three samples were of comparable molecular weights ($M_w$ around 51 000 g/mol and narrow molecular weight distributions), and the same polymer weight fraction of 4% was used for PEO/d-benzene, PEO/d-water, and PEO/d-methanol solutions. The same experimental conditions were used for all three samples.

Figure 4a shows the SANS data in the case of 4% PEO/d-benzene at 50 °C. Clustering (the low-*Q* feature) is clearly affected by changing the polymer chain end groups. It even disappears completely in the case of $-OCH_3$ on both ends. The effect is large. Figure 4a also shows that changing end groups does not affect the high-*Q* feature which characterizes chain thermodynamics. Parts b and c of Figure 4 present the 4% PEO/d-water and 4% PEO/d-methanol cases at 50 °C. The 50 °C temperature was chosen in order to avoid sample crystallization in the PEO/d-methanol case observed at lower temperatures. Changing chain ends in the PEO/d-water case (Figure 4b) reduces but does not eliminate clustering completely. This is related to the solvation sheath around PEO chains. This sheath may be either distorted close to chain ends or even "broken" (incomplete solvation) at spots.

Figure 5 summarizes the clustering strength (i.e., the low-*Q* feature) for the 50 °C temperature data for the various solvents and the various polymer chain end groups. The clustering strength is defined as $A/Q^n$, where $A$ and $n$ are fitting parameters and $Q = 0.004$ Å$^{-1}$ (a low-enough $Q$ value). This figure summarizes the most salient results presented in this paper.

The notation (for example HO−PEO−OH) used in Figure 5 is not rigorously correct because one of the oxygen atoms (at one or the other HO− end) belongs to the PEO and should not be double counted. The simple case of ethylene glycol $HO-CH_2CH_2O-H$ (or antifreeze) shows that the oxygen atom belongs to the monomer and not to the end group. Our notation has been chosen for convenience.

This end group series of experiments contains the other argument mentioned above that goes against the notion that clusters are the concentrated phase of a phase-separated system. If clusters were to form because of a thermodynamic driving force, they would depend only on temperature and concentration and not on the chain ends effect. Moreover, Figure 4a−c shows that the clusters feature (low *Q*) changes drastically whereas the polymer chains feature (high *Q*) does not change at all. These two features cannot correspond to two thermodynamic phases in equilibrium.

## Interpretation of the Results

In the PEO/d-water case, when varying chain ends, one sees that strongest clusters are obtained when both chain ends are $-OCH_3$ and weakest ones are obtained when both chain ends are −OH. This can be understood on the basis of the hydrophobic nature of the $-OCH_3$ group. The (hydrophilic) −OH groups are perfectly happy staying dissolved in water, whereas the (hydrophobic) $-OCH_3$ groups cannot stay dissolved. They have to seek and "stick" to a $-CH_2CH_2-$ group on a polymer chain and "hide" in the "cage" structure that water forms around these groups (see Figure 6). Water forms a hydration sheath structure wherein the hydrophobic $-CH_2CH_2-$ groups are shielded.[2] When both chain ends are −OH groups, one obtains mostly dissolved polymer chains. When both chain ends are $-OCH_3$, one obtains a network whereby chain ends are (randomly) sticking (tethered) to other chains. Finally, with different chain ends, one obtains a branched structure whereby one chain end is sticking to another polymer and the other end is left free to dangle. This branched structure extends to the size of the clusters (fraction of a micrometer to a few micrometers depending on concentration

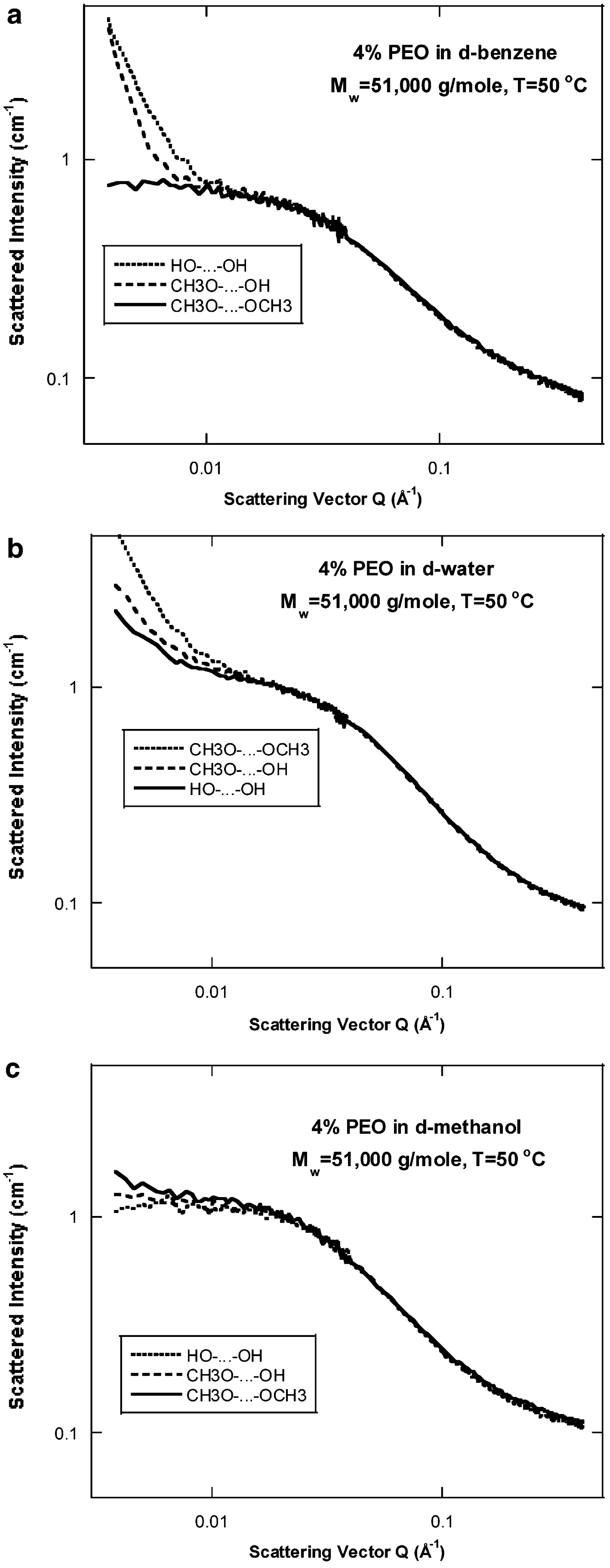

**Figure 4.** (a) SANS intensity for the 4% PEO/d-benzene case at 50 °C and for the three different chain end groups. Note that clusters disappear completely in the $CH_3O-PEO-OCH_3$ case. (b) SANS intensity for the 4% PEO/d-water case at 50 °C and for the three different chain end groups. Note that clusters become smaller for the HO−PEO−OH case. (c) SANS intensity for the 4% PEO/d-methanol case at 50 °C and for the three different chain end groups. Note that there is no cluster formation in this case.

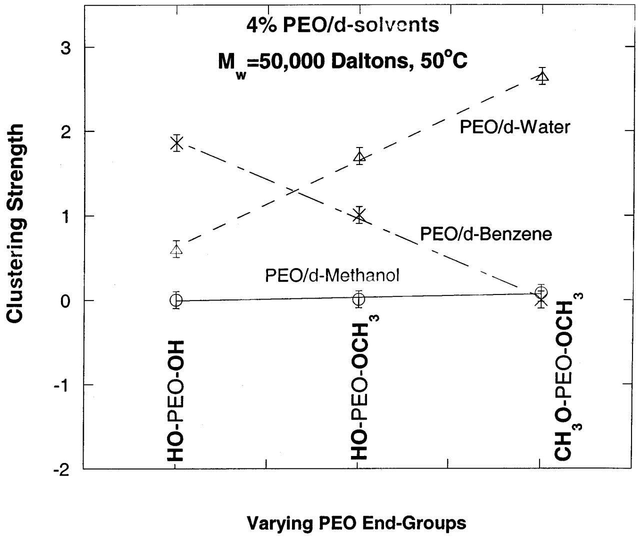

**Figure 5.** Variation of the clustering strength (obtained for the low-$Q$ feature in the scattering) with PEO varying end groups at 50 °C. The clustering strength is defined as the first term in eq 1 with $Q = 0.004$ Å. Error bars are small.

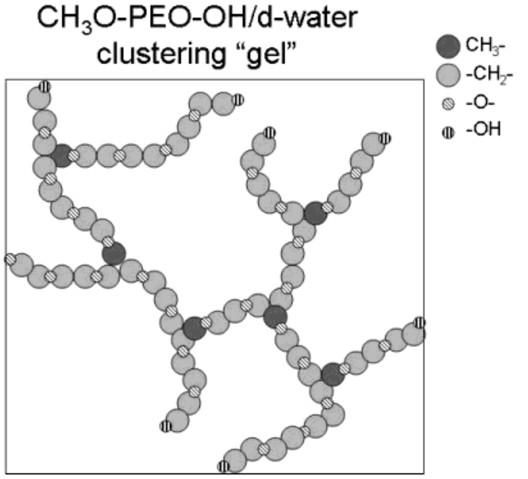

**Figure 6.** Schematic rendering (not to scale and not realistic) of the PEO/d-water clusters in the case with different chain ends ($-OCH_3$ and $-OH$). The $-OH$ end groups stay dissolved in water, whereas the $-OCH_3$ end groups are expelled from water regions and end up sticking to other hydrophobic ($CH_2CH_2$) groups on the PEO chain. PEO chains are tethered at one end.

and temperature). This picture becomes even clearer when we consider the case of PEO/d-benzene.

In the PEO/d-benzene case, the trend observed for PEO/d-water when varying chain ends is reversed (see Figure 5). Strongest clusters are obtained when both chain ends are $-OH$, and weakest clusters are obtained when both chain ends are $-OCH_3$. This can be understood on the basis of the benzophobic (disliking benzene) nature of the $-OH$ group and the benzophilic (liking benzene) nature of the $-OCH_3$ group. More generic terms that apply to all solvents (not just benzene) could be lyophobic and lyophilic. When both ends are $-OCH_3$, polymer chains are happy staying dissolved in benzene. With $-OH$ groups at both chain ends, this group cannot stay dissolved and seeks an oxygen atom on the polymer chain and sticks to it. One obtains again a network formed of polymer chains where both ($-OH$) ends are stuck (tethered) to random spots on other chains. The intermediate case of different ends again corresponds to a branched structure whereby chains are tethered through one of their ends only to other chains; the second end remains free to dangle. What is interesting is that, in analogy to the hydration sheath in the case of PEO/d-water, there must be a benzenation sheath in the case of PEO/d-benzene in which a benzene structure must form around the $-CH_2CH_2-$ polymer groups to bridge and isolate the (benzophobic) oxygen atoms on the PEO chains. There is a direct analogy between the PEO/d-water and the PEO/d-benzene systems; both are LCST systems and move closer to phase separation as temperature is increased. This is observed as an increase in the high-$Q$ intensity feature (scale factor $C$ in eq 1) as temperature is increased.

In the PEO/d-methanol case where both the $-OH$ and the $-OCH_3$ groups like the solvent, clustering is nonexistent (see Figure 5). Whatever the ends are on the PEO chain, the polymer stays dissolved because methanol contains both a hydrophilic end group ($-OH$) and a hydrophobic one ($-CH_3$).

The picture that comes out of these investigations is clear but not perfect. For instance, in the PEO/water case with $-OH$ end groups where chains are supposed to dissolve happily, some clustering remains (the clustering strength is not zero) as seen in Figure 4b. In this case, the hydration structure must get terribly distorted close to the chain ends as well as elsewhere along the chain, and perfect dissolution cannot occur. One must remember that PEO "barely" dissolves in water and that its neighboring homologues PMO and PPO do not dissolve at all in water. Moreover, the chain ends effect seems to be effective for our experimental conditions (4% PEO weight fraction), but the major cause of clustering may change for other conditions. For example, we know that for weight fractions above 50% PEO crystallization will not be negligible. Also, for the PEO/d$-$water case (especially for nondilute concentrations), the hydration tube around the PEO chains may become less effective in which case the interchain hydrogen-bonding effect may become dominant.

## Concentration Effects

Concentration effects on chain thermodynamics (the high-$Q$ feature) or on clustering (the low-$Q$ feature) have been discussed before in the literature.[4,11,12] Clusters get stronger with increasing PEO concentration in water. In these published results, "typical" PEO-containing $CH_3O-PEO-OH$ chain ends were used. It should be noted that systematic studies of the concentration effect on clustering of PEO with other chain ends have not been performed. Our investigations (reported here) considered the 4% PEO weight fraction only.

## The Excluded Volume Parameter

The Flory mean-field theory of polymer mixing[19] considers chain statistics as a random walk process along chain segments. The radius of gyration of the polymer chain is given in terms of the number of chain segments $N$ as $R_g \sim N^{\nu}$, where $\nu$ is the excluded volume parameter. Self-avoiding walk corresponds to swollen chains with $\nu = {}^3/_5$, pure random walk corresponds to chains in theta conditions (where solvent$-$solvent, monomer$-$monomer, and solvent$-$monomer interactions are equivalent) with $\nu = {}^1/_2$, and self-attracting walk corresponds to collapsed chains with $\nu = {}^1/_3$. In our scattering case the $m$ and $n$ exponents of $Q$ (see eq 1) are related inversely to the excluded volume parameters ($n = 1/\nu$, $m = 1/\mu$).

Our fitting results for the 4% PEO/d-water solution show from the high-$Q$ exponent $m$ that chains are mostly swollen at low temperatures (excluded volume parameter around $\mu = 0.59$) and change to theta conditions at high temperatures (excluded volume parameter around $\mu = 0.5$) as the spinodal temperature is approached. The same fitting results show that the low-$Q$ exponent $n$ corresponds to a self-attracting walk (excluded volume parameter $\nu$ between 0.42 and 0.33). This is due to the stickiness of the chain ends which produces the clusters. When two monomers belong to the same chain, they appear to follow a self-avoiding walk at low temperature (good solvent behavior) or an unbiased random walk at high temperature ($\Theta$ solvent behavior). When two monomers belong to two different chains (but inside the same cluster), they appear to follow a self-attracting random walk. This is yet another confirmation of the presence of attractive forces (stickiness of the chain ends) inside clusters.

## Conclusions

The clustering effect is pervasive and shows up in many dissolved systems. It is often ignored or overlooked because its basic origin is not understood. Our efforts reported here show that clustering in PEO solutions at 4% weight fraction is due to the chain ends effect. Chain ends are only a small fraction of the polymer architecture (1 in 1000 monomers in our case), but they are the dominant factor driving cluster formation because of hydrophobic forces on chain ends. When chain ends are not happy staying dissolved, they tend to stick to more favorable groups on another polymer chain. (Polymer chains bury their ends where these would be in a happier state.) This creates network structures where both ends are tethered or branched structures where only one end is tethered.

Most of the conclusions on clustering reached here are based on observations of the low-$Q$ SANS feature. The high-$Q$ feature characteristic of chain thermodynamics has been discussed extensively in the literature.[13−17] Now it is apparent that this high-$Q$ feature is due to dangling chains (anchored by their ends) or could be due to free chains in solution (observed at low concentrations at least[11]). Both yield the same scattering signature by SANS and by DLS. GPC and sample centrifugation can, however, differentiate between dangling chains and free chains because they can separate the dense phase from the dilute phase. It is not clear, however, whether this processing (GPC or centrifugation) is breaking down clusters to free up the observed single chains.

It is apparent that the PEO clusters (low-$Q$ SANS feature) are controlled by the chain ends effect (hydrophobic interactions on the chain ends) while polymer chain thermodynamics (high-$Q$ feature) are controlled by hydrogen-bonding interactions. This applies to the experimental conditions presented here (4% PEO weight fraction). The situation may change for other experimental conditions (higher concentrations, for example).

Another observation is that clusters manifest themselves as density fluctuations while chain thermodynamics are driven by concentration fluctuations. For example, a sample with deuterated PEO in d-water would be characterized by a low-$Q$ feature (clusters), but the high-$Q$ feature would vanish to a flat line because the neutron contrast would be zero.

The just-right balance of hydration and hydrophobic forces that makes PEO soluble in water (and other organic solvents) for a wide range of temperatures and concentrations is also at work in many other complex fluid systems. It remains to be seen whether the chain ends effect described here applies elsewhere.

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