Hydrophobically end-capped polyethyleneoxide urethanes: 2. Modelling their association in water

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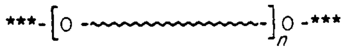
Associative thickeners of the end-capped polyethyleneoxide urethane type are well known to form aggregates in aqueous solutions but there is a lack of studies dealing with the determination of the association mechanisms and with the size and form of these aggregates. We show for a given example that a combination of light scattering and viscosity experiments may produce a rather good description of these phenomena by interpreting them through theories of association and models of branched polymers. It is concluded that the aggregates look like statistically branched polymers, the junction points being formed by the association of approximately four hydrophobic chain ends.

(Keywords: aggregation; association mechanisms; polyethyleneoxide urethanes)

INTRODUCTION

In a previous work[1], we have compared the associative behaviour of three thickeners in aqueous solution. These samples have the following chemical structure



where paraffinic end groups ***, diisocyanate moieties ○, and poly(oxyethylene) blocks (POE), are linked together by urethane bonds.

Careful characterization of the chemical nature of the different parts and of the molecular weight distributions allowed us to draw some general relations between the chemical properties of the product and its aggregation in water. The main conclusion is that the average hydrophobicity of the chains determines the extent of association, and the broader the molecular weight distribution, the higher is the aggregate polydispersity. The aim of the present paper is to discuss a general methodology allowing interpretation of the light scattering and viscosity measurements in order to obtain a description of the aggregate size and form. This methodology is described here in the case of one of the previously studied polymers[1] which gives rise to a relatively low polydispersity of aggregates in water.

REVIEW OF THEORY

When a polymer self-associates in solution, the first problem is to calculate the average association number N and the polydispersity of the aggregates. The second step is the determination of their size and form.

Aggregation number

General expressions. According to Elias[2], one can define two extreme association models called 'closed association' and 'open association'. In the model I 'closed association' or cooperative association, an equilibrium between unassociated molecules or unimers M_I and aggregates M_N of N molecules is considered:

$$N\,\mathrm{M_I} \rightleftharpoons \mathrm{M}_N \qquad (1)$$

N is not concentration dependent.

In the model II 'open association' similar to that used to describe a polycondensation reaction, aggregation is assumed to take place by successive steps according to the equilibria:

$$\begin{aligned} \mathrm{M_I} + \mathrm{M_I} &\rightleftharpoons \mathrm{M_{II}} \\ \mathrm{M_{II}} + \mathrm{M_I} &\rightleftharpoons \mathrm{M_{III}} \\ \mathrm{M_{III}} + \mathrm{M_I} &\rightleftharpoons \mathrm{M_{IV}} \qquad (2) \\ &\vdots \\ \mathrm{M}_{N-1} + \mathrm{M_I} &\rightleftharpoons \mathrm{M}_N \end{aligned}$$

For model I:

$$(K_o)_{I,N} = [\mathrm{M}_N]/[\mathrm{M_I}]^N \quad (\mathrm{l\,mol^{-1}})^{N-1} \qquad (3)$$

For model II:

$$(K_o)_{I,II} = [\mathrm{M_{II}}]/[\mathrm{M_I}]^2 \quad (\mathrm{l\,mol^{-1}}) \qquad (4)$$

$$(K_o)_{II,III} = [\mathrm{M_{II}}]/[\mathrm{M_I}][\mathrm{M_{II}}] \quad (\mathrm{l\,mol^{-1}}) \qquad (5)$$

$$\vdots$$

$$(K_o)_{N-1,N} = [\mathrm{M}_N]/[\mathrm{M}_{N-1}][\mathrm{M_I}] \quad (\mathrm{l\,mol^{-1}}) \qquad (6)$$

and if the different association steps are assumed to be equivalent, the system is defined by one constant:

$$(K_o)_{I,II} = (K)_{II,III} = (K)_{N-1,N} = K_o \qquad (7)$$

The weight fraction of unimers is:

$$W_I = \frac{C_I}{\sum C_N} = \frac{C_I}{C} \qquad (8)$$

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(where C_I and C are the unimer and the total polymer concentrations respectively). W_I can be calculated in both models by the expression:

$$\ln W_I = \int_{C=0}^{C} \left[\frac{M_{IW}}{M_W} - 1\right] \frac{dC}{C} \qquad (9)$$

where M_{IW} and M_W are the weight average molecular weight of the unimer and associated polymer respectively. If the concentration dependence of M_W is known, it may be possible to deduce the most appropriate model, in fact:

if W_1 is small, in the mole concentration range explored, M_w must be independent of C in the case of model I,

if W_1 is close to 1, such a criterion cannot be used, and it is easy to demonstrate that in model I, M_w increases with C according to:

$$M_w = (1 - N)\frac{M_{IW}^2}{1000C}\left(\frac{1000C}{K_o N M_{IW}}\right)^{(1/N)} N M_{IW} \qquad (10)$$

Elias and Bareiss[2,3] have calculated $M_w = f(C)$ in model II:

$$M_W^2 = M_{IW}^2 + 4000(K_o)[M_{IW}^2/M_{In}]C \qquad (11)$$

where M_{In} is the number average molecular weight of the unimer.

Light scattering. For such systems, light scattering is probably the best method to determine the concentration dependence of M_w. At a given concentration and at zero angle, light scattering obeys the well known expression

$$\frac{K^*C}{\Delta I} = \frac{1}{M_w} + 2A_2C + 3A_3C^2 + \cdots \qquad (12)$$

where K^* is the product of different optical constants and $\Delta I = I - I_0$, I and I_0 being the scattered intensities by the solution and the solvent respectively. A_2, A_3 are the different virial coefficients. In the concentration range where aggregation occurs, it is generally impossible to neglect these virial terms and if A_2 and A_3 are unknown, $M_w = f(C)$ cannot be directly calculated from equation (12).

One may either hypothesize using the virial coefficient values or try by successive approximations to determine A_2 and A_3 values which permit the variations of M_w to be compatible with an association model and with equations (11) and (12).

Nevertheless, such an analysis may be dangerous without crosschecking the results. A first crosscheck may be based on the value of W_I. If the $M_w = f(C)$ variation has been obtained by adjusting the A_2 values, a W_I value may be calculated by integration of equation (9). From equations (3) and (4)–(7), the weight fraction of each species of aggregation number N is given by:

$$W_N = \left(\frac{CW_I 1000}{(M_I)_w} K_0\right)^{N-1} N W_I \qquad (13)$$

The first value of W_I introduced in equation (13) must lead to $\sum W_N = 1$. If this is verified, the model can be considered to be valid. For model II, one can deduce the different average molecular weights according to

$$M_n = 1 \Big/ \sum_N \frac{W_N}{N W_{IW}} \qquad (14)$$

$$M_W = \sum_N W_N N M_{IW} \qquad (15)$$

$$M_Z = \frac{\sum_N W_N N^2 M_{IW}^2}{\sum_N W_N N M_{IW}} \qquad (16)$$

Such a distribution is characteristic of the step association and leads to a polydispersity index $M_w/M_n = 2$, which is well known in a polycondensation process. The closed association model corresponds to two distributions centred around M_I and NM_I.

Size and form of the aggregates

In *Figure 1*, we have schematized different possible structures of aggregates. The most compact aggregates (model **a**) are those obtained by association of N polymer molecules all of whose chain ends are gathered in a central hydrophobic microdomain. Model **b** corresponds to stars where only one end moiety by chain is bound in the hydrophobic core. In model **c**, we assume that aggregates have a comb-like structure. Model **d** corresponds to statistically branched polymers. In the less compact model **e** the molecules are associated by two extremities and form a large linear macromolecule.

One must point out that in all these models the association is assumed to be due only to the hydrophobic extremities and the possible effects of poly(oxyethylene) main chains[4] and urethane moieties are neglected.

If the molecular weight of the aggregates is well known at each concentration, we can attempt to determine the best scheme from the measurement of their dimensions (radius of gyration, intrinsic viscosity) and by using the branched polymer theories.

Zimm and Stockmayer[5] have defined a structure parameter g:

$$g = \frac{R_{gb0}^2}{R_{gL0}^2} \qquad (17)$$

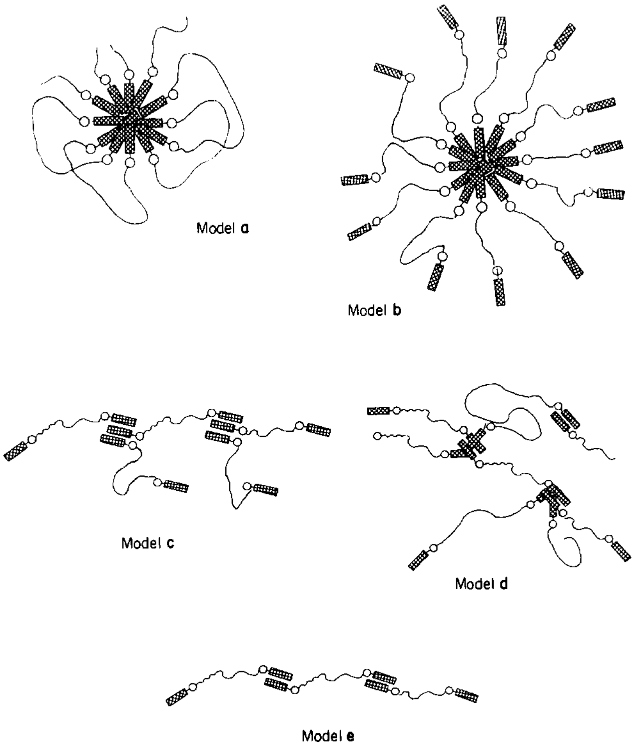


Figure 1 Different possible schemes of aggregation

where R^2_{gb0} and R^2_{gL0} are the squares of the radii of gyration. Indices b and L refer to branched and linear macromolecules of the same molecular weight respectively. The index 0 means that such a relation works in the θ conditions.

In good solvents, expression (17) becomes

$$g = \frac{R^2_{\mathrm{gb0}}\alpha^2_{\mathrm{L}}}{R^2_{\mathrm{gL0}}\alpha^2_{\mathrm{b}}} \tag{18}$$

where α_{b} and α_{L} are the expansion coefficients and R^2_{gb} and R^2_{gL} the square radii of gyration in the given solvent. If α_{b} is assumed to be very close to α_{L}, the expression becomes:

$$g = \frac{R^2_{\mathrm{gb}}}{R^2_{\mathrm{gL}}} \tag{19}$$

By analogy a viscosimetric structure parameter g' can be defined from the intrinsic viscosities.

$$g' = \frac{[\eta]_{\mathrm{b}}}{[\eta]_{\mathrm{L}}} = \frac{[\eta]_{\mathrm{b}}}{KM^a_{\mathrm{L}}} \tag{20}$$

$[\eta]_{\mathrm{l}} = KM^a_{\mathrm{L}}$ is the Mark–Houwink law of the linear polymer. By applying the classical Fox–Flory[6] law:

$$[\eta] \propto \frac{R^3_{\mathrm{gL}}}{M} \tag{21}$$

$$g' = g^{3/2} \tag{22}$$

There is much theoretical work on the calculation of g for different schemes of branched polymers.

(1) For star polymers (schemes a and b), Stockmayer and Fixmann[7] have proposed

$$g = \frac{3p-2}{p^2} \tag{23}$$

where p is the number of branches. In model **b**, $p = N$ and M_{L} of the linear homologous polymer is

$$M_{\mathrm{L}} = NM_{\mathrm{l}} \tag{24}$$

In model **a**, one may assume that a loop of molecular weight M_{l} is equivalent to two branches of molecular weight $M_{\mathrm{l}}/2$. Then $p = 2N$.

(2) For comb-like polymers with trifunctional junction points (model **c**) g calculated by Orofino[8] is:

$$g = \frac{3}{p}\left[\frac{r}{r+1}\right]^2 + \frac{1}{r+1} \tag{26}$$

where p is the total number of grafts and r is the ratio of the graft length to the mean space between two junction points.

By applying Orofino's model to the aggregates of associative polymers and assuming that there is only one unimer between two trifunctional junctions, we have $r = 1$ and $p = (N-1)/2$.

(3) If one assumes that associative aggregates are equivalent to statistically branched polymers, Zimm and Stockmayer's expression for tetrafunctional branching may be used:

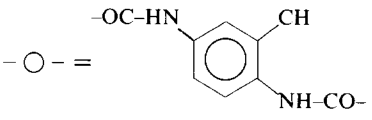
$$g = \left[1 + \frac{m}{6}\right]^{0.5} + \frac{4m}{3\pi} \tag{27}$$

In the case where each hydrophobic chain end is involved in a junction (model **d**): the average branching per chain m is given by $m = (N-1)/3$.

APPLICATION TO THE CASE OF AN ASSOCIATIVE POLYMER

Review of experimental results

We will apply the above theories to the case of polymer B studied in our previous work[1]. Its chemical composition is



$\star\star\star\ = \mathrm{CH_3(CH_2)_{11}}$

and ∿∿∿ = POE

Its weight average molecular weight is $M_{\mathrm{w}} = 13\,500$ and the polydispersity index is 1.8.

In *Figure 2*, we have reproduced the Zimm–Plot obtained for a concentration range between 10^{-4} and $10^{-2}\,\mathrm{g\,cm^{-3}}$ and in *Figure 3*, the concentration dependence of the reduced viscosity η_{red} of polymer B is compared with that obtained for a POE sample of the same molecular weight.

Aggregation number

One obtains from the ratio (K^*C/I) at zero angle, apparent values of M_{w}, M_{wapp} (see expression (12)):

$$\frac{1}{M_{\mathrm{wapp}}} = \frac{1}{M_{\mathrm{w}}} + 2A_2C + \cdots \tag{28}$$

(see *Figure 4*).

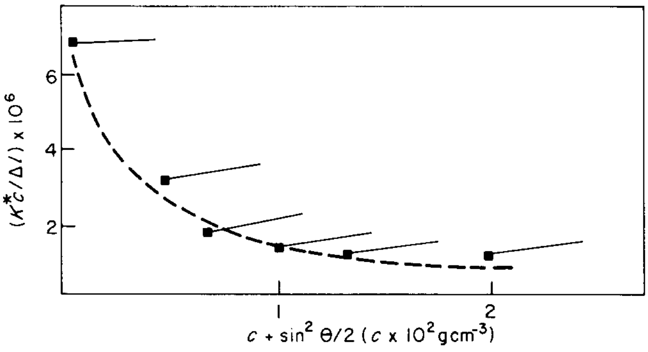


Figure 2 Zimm plot of polymer B in water

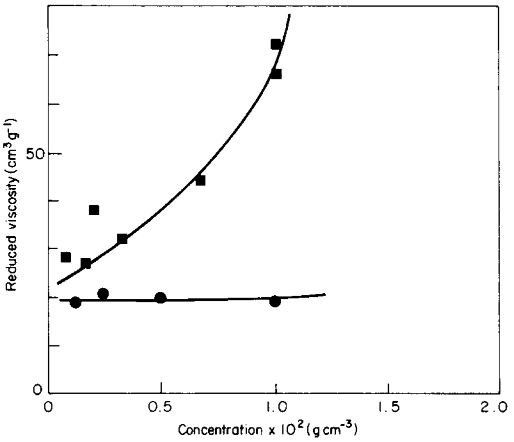


Figure 3 Concentration dependences in water of the reduced viscosity of polymer B (■) and polyethyleneoxide of the same molecular weight (●)

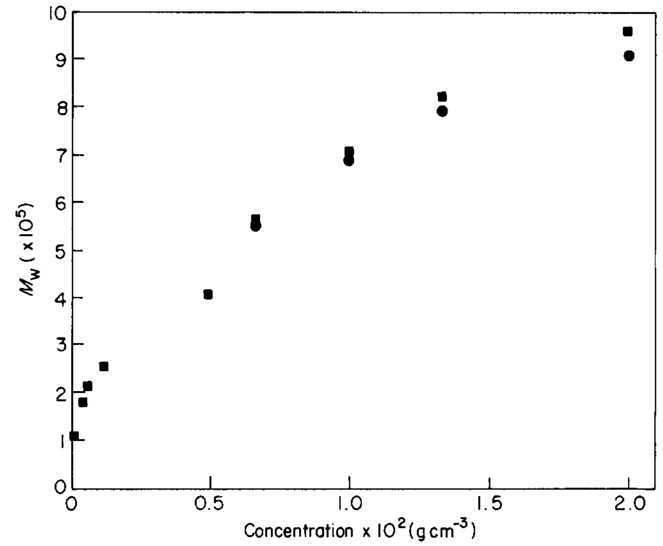


Figure 4 Concentration dependences of M_{wapp} (●) and M_w (■) calculated for polymer B in water (see text)

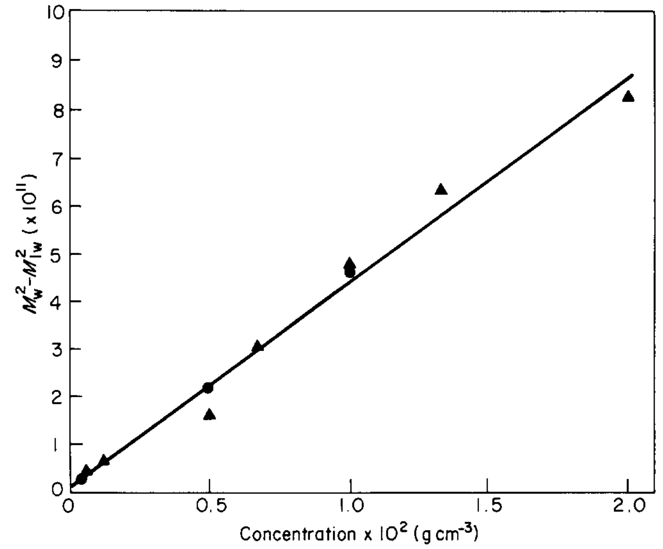


Figure 5 Variation of $(M_w)^2 - (M_l)_w^2$ as a function of concentration C, calculated by adjusting A_2 (●) or by complete integration of equation (16) (▲)

By using M_{wapp} in the place of M_w in expression (9), we obtain very low values of W_l, and, since M_W is not independent of C (as discussed above), this means that model II is the most appropriate. If so, $(M_w^2 - M_l^2)$ must be a linear function of concentration (expression (11)). One must find by successive approximations a value of the second virial coefficient which allows calculation, from M_{wapp}, values of M_w leading to such behaviour. *Figure 5* shows that this can be obtained by taking $A_2 = 1.4 \times 10^{-6}$ in equation (28). The value of the equilibrium constant $K_0 = 4.3 \times 10^5\ \mathrm{l\,mol^{-1}}$ is then deduced from the slope of this straight line. With this value, one can calculate W_n, the weight fraction of species of aggregation number N as a function of W_l, by equation (14) and by adjusting N_l at each concentration to obtain $\sum W_N = 1$. The term $[M_w^2 - M_l^2]$ can then be determined from these W_N values by using relation (15) and the values obtained in this way (see *Figure 5*) are in very good agreement with the previous ones. This means that the W_l values derived from relation (9) are close to those adjusted to obtain $\sum W_N = 1$. Then the self-consistency of the interpretation is well demonstrated and we can conclude that polymer B self-associates in water according to a model of open association. The low value of second virial coefficient $A_2 = 1.4 \times 10^{-6}$ seems to be rather reasonable since the lower critical solution temperature (*LCST*) of the aqueous solution of this polymer is +313 K. At the room temperature at which experiments were carried out, the reduced temperature

$$T_{\mathrm{red}} = (T - LCST/LCST)$$

is low.

Moreover the linear angular dependences of $(K^*C/\Delta I)_C$ at each concentration indicate that the polydispersity index of aggregates is approximately 2, in agreement with predictions (15)–(17) for model II.

Size and form of aggregates

We will assume that R_{gL} and $[\eta]_{\mathrm{L}}$ scale with M for linear unassociated polymer B as for POE in water[9,10]:

$$R_{\mathrm{gL}} = 0.26M^{0.55} \qquad (29)$$

$$[\eta]_{\mathrm{L}} = 0.054M^{0.66} \qquad (30)$$

Such laws have been obtained for samples of very low polydispersity. It is well known that the radius of gyration deduced from light scattering corresponds to the Z average molecular weight while intrinsic viscosity corresponds to the viscosimetric average, M_v:

$$M_v = [\sum_N W_N N (M_l)^a]^{1/2a} \qquad (31)$$

Then R_{gL} and $[\eta]_{\mathrm{L}}$ are calculated from the M_Z and M_v values of the aggregates at each concentration, respectively.

On the other hand, one has to compare the intrinsic viscosities while the experiments give at each concentration the reduced viscosity. Since the aggregation number is concentration dependent, one must determine approximate values of $[\eta]$ by assuming a constant value for the Huggins constant. Experimental points in *Figure 7* are calculated with $K = 0.4$ but a value $K = 0.6$ leads to slightly lower intrinsic viscosities.

In *Table 1*, we compare the values of structure parameter g obtained either from R_g or from $[\eta]$ values. Both methods lead to results in rather good agreement and g is found to be an increasing function of the concentration.

In *Figures 6* and *7* we compare the experimental variations of radius of gyration and intrinsic viscosity as a function of concentration with those calculated with different aggregation models and by using expressions (23)–(27). No model is able to fit the experimental results. The behaviour seems to be rather close to that of a statistically grafted polymer with tetrafunctional

Table 1 Comparison between values of g from DDL (g^*) and viscosimetry (g^{**})

C (g cm^{-3})	0.0005	0.005	0.010	0.013	0.020
R_{gb} (Å)		185	310	350	380
g^*		0.19	0.30	0.36	0.31
$[\eta]$ (cm^3 g^{-1})	27	35	54	–	160
g^{**}	0.25	0.24	0.33		0.47

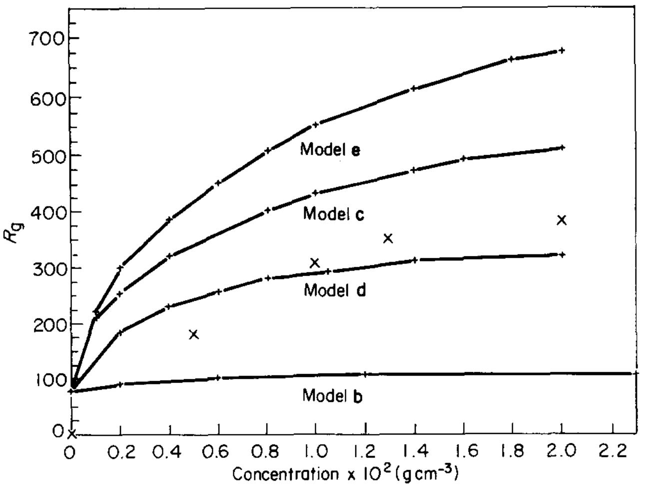


Figure 6 Comparison between experimental variations of $R_g = f(C)$ (×) with the variations calculated for different aggregation models (+)

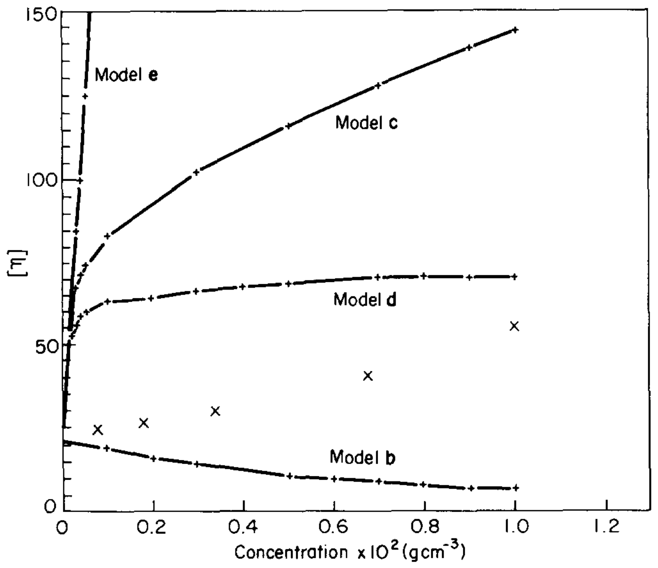


Figure 7 Comparison between experimental variations of $[\eta] = f(C)$ (×) with the variations calculated for different aggregation models (+)

junctions in the case of the radius of gyration but the viscosity seems to indicate a behaviour intermediate between this model and the model **b** of star-like aggregates. This means that the number of chain ends involved in the hydrophobic microdomain is at least equal to 4 but lower than the total aggregation number $N = M_W/M_1$, over the whole range of concentration investigated. Such a result seems to be confirmed by preliminary measurements of fluorescence decay[11] of pyrene, which provides an order of magnitude of the aggregation number inside the hydrophobic core. This number was found to be around 12, which is much lower than the global aggregation number measured by light scattering (80) at the same concentration (2%).

We must point out that we have introduced in our analysis only one equilibrium constant. In fact the polymer under study has a double distribution (80% and 20% w/w of condensation degrees 1 and 2 respectively) and several types of association are involved in the general aggregation process. It will be more interesting to study well defined and monodisperse samples, whose synthesis and characterization are in progress in our laboratory.

CONCLUSION

From an example of an associative polymer we show that it is possible to interpret light scattering and viscosity measurements and obtain an approximate description of the aggregation in water. The case studied is relatively simple and satisfactory results can be obtained from two variable parameters: the second virial coefficient A_2 and an association equilibrium constant K_0. When the polymer is itself a multimodal distribution, the association is difficult to reduce to a unique type of equilibrium and more elaborate fitting methods are necessary.

Such an approach uses the complementarity of both methods, light scattering and viscosity, while the previous attempts to describe association phenomena of these polymers were only based upon viscosity measurements, which seem to be difficult to interpret without knowledge of the molecular weight dependence of the aggregates[12].

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