



*Dedicated to the memory of
Dr. Henry V. Kehiaian (1929–2009)*

CLUSTERING IN POLY(OXYETHYLENE) AQUEOUS SOLUTIONS

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In the present paper, the aqueous solutions of poly(oxyethylene) in different experimental conditions were investigated by viscometry and rheometry. The clusters formation was evidenced for fresh prepared samples which were not stirred or submitted to sonication. The time evolution of the viscoelastic parameters demonstrates that the history of the sample influences the aggregation process. The present results, corroborated with literature data, show that clusters originate from the chain-chain associations due to repulsive hydrophobic interactions between the methylene groups and water molecules as well as to attractive hydrogen bonding between the structural units of the polymer and water molecules.

INTRODUCTION

Poly(oxyethylene) (POE) has attracted considerable interest due to its unique properties: the ability to adsorb at particle interfaces,¹⁻³ the hydrophilicity, biocompatibility and lack of toxicity being used in cosmetics and many industrial and biomedical applications.⁴

POE is a nonionic polymer which has both hydrophobic and hydrophilic segments, having a simple basic forming unit: $[-\text{CH}_2-\text{CH}_2-\text{O}-]_x$. The presence of an oxygen atom changes entirely the nature of the interactions and therefore the thermodynamics of POE macromolecules when dissolved in various solvents (water or several organic solvents). When dissolved in water, POE is characterized by hydrophilic interactions (hydrogen bonding of water molecules to the oxygen atoms on the polymer) and hydrophobic interactions (the $-\text{CH}_2-\text{CH}_2-$ groups repel water), being able to form clusters or aggregates.⁵ The origin of the cluster formation is still debated. Some authors considered that impurities of water are responsive

for the aggregation of POE chains.⁶ In others studies, the aggregation was attributed to crystallization of POE chains,⁷ or phase transition phenomena (aqueous solutions of POE present low critical temperature) which produces a polymer rich phase,⁸ interchains physical cross-links due to the intense hydrogen bonding,⁹ and chain ends effects.¹⁰ Polik and Burchard⁷ investigated aqueous POE solutions in the temperature range from 20°C to 90°C by light scattering and concluded that different structures, *i.e.*, aggregates of high and low density, closed to the thermodynamic equilibrium, are present into solution. The coexistence of high density particles (spherulites) and of low density aggregates (noncrystalline microgel particles) was discussed in terms of hydrophobic interactions between the polymer and solvent.

The ability of POE to form aggregates is influenced by: molecular weight and concentration of polymer,¹¹ history of the sample and the method to prepare the solutions,^{12,13} temperature,^{12,13} and solvent nature.^{11,12} Static and quasi-elastic light scattering experiments have shown that POE

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chains also aggregate in organic solvents such as acetonitrile, dioxane, benzene, carbon tetrachloride,¹⁴ chloroform¹⁵ or methanol.^{10,11,16}

POE can be coupled to hydrophobic molecules to produce nonionic surfactants. The effect of nonionic surfactants on the POE – crosslinked poly (acrylic acid) interpolymer complexes in water was recently investigated by FTIR spectroscopy as well as by surface tension, viscosity and pH measurements.¹⁷ PAA interacts with small molecules of nonionic surfactants above a critical aggregation concentration which is smaller than the critical micelle concentration. The addition of nonionic surfactants changes the hydrophilic-hydrophobic balance, the free surfactant molecules can interact with the free micelles in solution thus the static and dynamic behaviour of such systems becomes very complex. In aqueous formulations, the hydrophobic groups interact to form a transient network giving unique rheological properties to the solutions.¹⁸

The present paper evidences the cluster formation of POE in aqueous solutions in different experimental conditions by following the viscoelastic properties at low shear stress.

RESULTS AND DISCUSSION

Viscometric behaviour

The intrinsic viscosity, $[\eta]$, can be determined by using the classical Huggins equation:

$$\eta_{sp}/c = [\eta]_H + k_H \cdot [\eta]_H^2 \cdot c \quad (1)$$

where η_{sp}/c is the reduced viscosity and k_H , the Huggins constant. These parameters offer information about the dimension and shape of macromolecules in solution, as well as on hydrodynamic interactions between different segments of the same polymer chain.

Figs. 1 and 2 present the plots of the reduced viscosity as a function of concentration at 30°C for two samples of POE having different number average molecular weights (M_n) (Table 1).

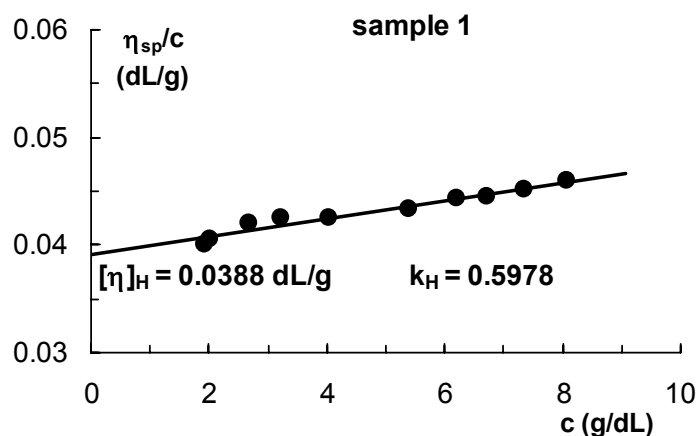


Fig. 1 – The reduced viscosity (η_{sp}/c) as a function of POE concentration for sample 1 (Table 1) in water.

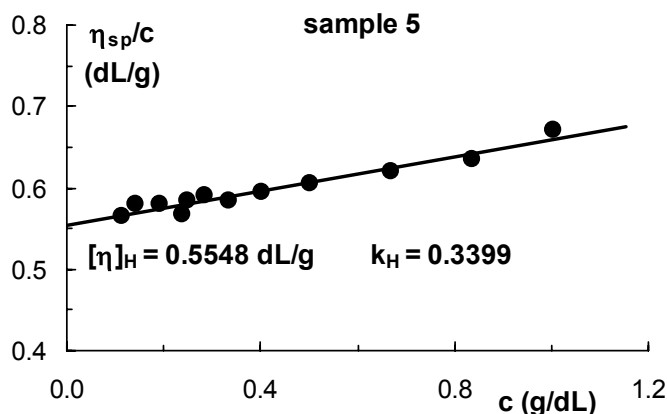


Fig. 2 – The reduced viscosity (η_{sp}/c) as a function of POE concentration for sample 5 (Table 1) in water.

Table 1 gives the intrinsic viscosity and the Huggins constants for all samples having different molecular weights. For low molecular weight samples ($M_n \leq 10^4$ g/mol), it can be observed that the Huggins constant is higher than 0.5, indicating the formation of associated structures.

Rheological behaviour

The aggregation process can be monitored by rheometry using oscillatory deformation tests, when the measured complex shear modulus (G^*) can be followed through its real and imaginary components, *i.e.*:

$$G^*(t) = G'(t) + iG''(t) \quad (2)$$

where the elastic (or storage) modulus G' is a measure of the reversibly stored deformation energy and the viscous (or loss) modulus G'' represents a measure of the irreversibly dissipated energy during one cycle.

The loss factor, $\tan \delta$:

$$\tan \delta = \frac{G''}{G'} \quad (3)$$

is a dimensionless parameter associated with the degree of viscoelasticity of the sample, being a measure of the ratio between the lost energy to the stored energy in a cyclic deformation.

Prior to rheological measurements of POE solutions, suitable shear amplitude was determined by measuring the shear stress dependence of moduli to ensure the linearity of dynamic viscoelasticity. Fig. 3 shows that the linear viscoelastic region is reached for shear stresses between 0.04 Pa and 98 Pa. The large range for the linear viscoelastic regime is characteristic to structured polymer samples.

Also, the loss tangent is nearly constant, *i.e.*, $\tan \delta \cong 3$, which means an important degree of elasticity due to some structures formed in POE solutions.

Fig. 4 shows the evolution of viscoelastic moduli as a function of time for a fresh prepared aqueous solution of 2 g/dL POE (sample 3) submitted to a very small stress (0.04 Pa). After thousand seconds, G' and G'' start to increase and after additionally thousand seconds they reach values which are higher with 3 orders of magnitude than the initial ones. This behaviour can be attributed to the aggregation process which occurs in POE solutions.

Table 1

The characteristics of the studied POE samples at 30°C

Sample	$M_n \times 10^{-4}$ (g/mol)	$[\eta]_H$ (dL/g)	k_H
1	0.04	0.0388	0.5978
2	0.4	0.1230	0.5423
3	1	0.2250	0.5141
4	2	0.4093	0.3875
5	3.5	0.5548	0.3399
6	8	1.1866	0.3489

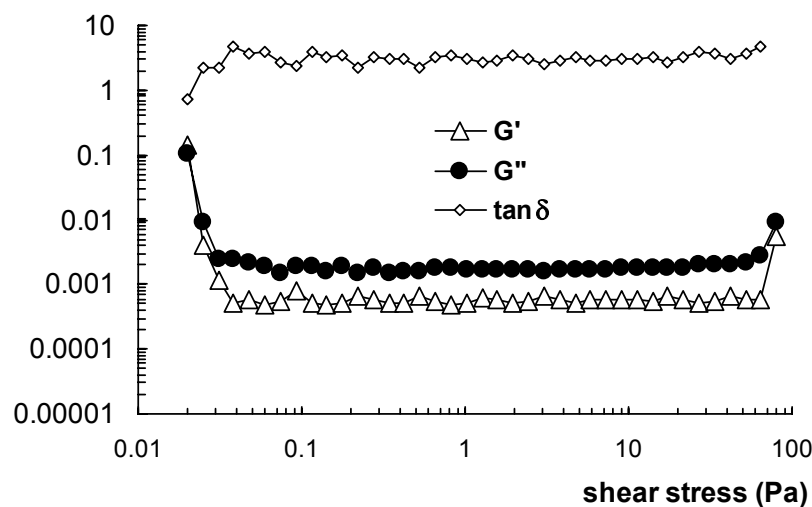


Fig. 3 – Amplitude sweep test (at constant oscillation frequency of 1 rad/s) for a solution of 2 g/dL POE (sample 3, Table 1) at 25°C.

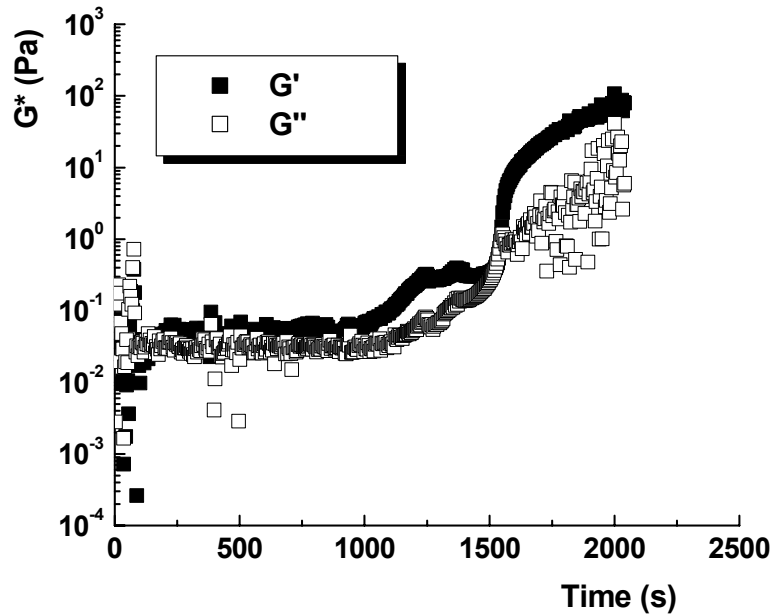


Fig. 4 –The evolution of the viscoelastic moduli as a function of time for 2 g/dL POE (sample 3) in water at a shear stress of 0.04 Pa.

The final modulus, G_{max}^* , when the aggregation process reaches an equilibrium (the viscoelastic moduli show plateau values) that can be determined by fitting the experimental data with a Boltzmann sigmoid equation (Microcal Origin version 6.0):

$$G^*(t) = G_{max}^* + \frac{G_{min}^* - G_{max}^*}{1 + \exp((t - t_0)/dt)} \quad (4)$$

where t_0 is the time at which

$G^*(t) = \frac{G_{max}^* - G_{min}^*}{2}$ and G_{min}^* represents initial modulus.

The obtained Boltzmann sigmoid curves offer a better image of the variation of the viscoelastic moduli and the corresponding loss tangent in time (Figs. 5 and 6).

Interesting features can be seen from Figs. 4-6. At the beginning of the experiment, the sample keeps its characteristics and the rheological parameters remain constant. After 1000 s, the clustering process starts and evolves rapidly during the next thousand seconds.

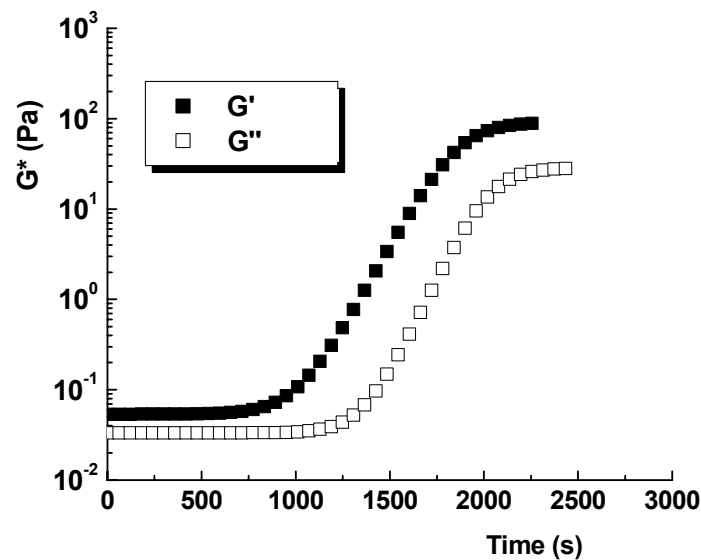


Fig. 5 –The parameters from Fig. 4 fitted with a Boltzmann sigmoid equation.

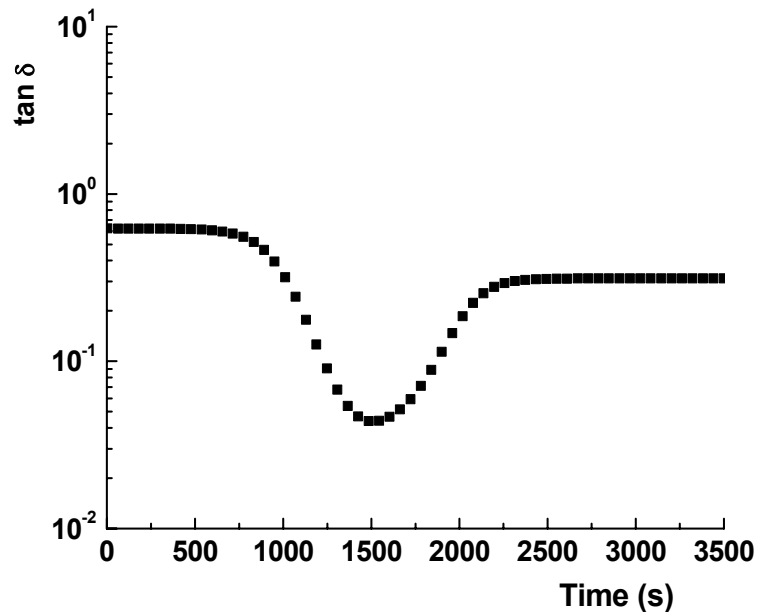


Fig. 6 – The time dependence of the loss tangent for 2 g/dL POE (sample 3) in water at constant shear stress (0.04 Pa).

After 2000 s, the viscoelastic moduli and the loss tangent present a plateau value, when the clustering reaches an equilibrium state.

Fig. 7 gives the viscosity-time dependence for 2 g/dL POE solution (sample 3) which was not stirred and not submitted to sonication as compared with the same sample which was sonicated for 5 minutes before the rheological test. By sonication, the clusters which are formed in

POE solution are destroyed and the viscosity is ten times smaller at the beginning of the test as compared with the same sample which was not submitted to sonication.

The sample which was not stirred and not submitted to sonication starts to aggregate after 1000 s and the final viscosity reaches a plateau which is with 3 orders of magnitude higher than the initial value.

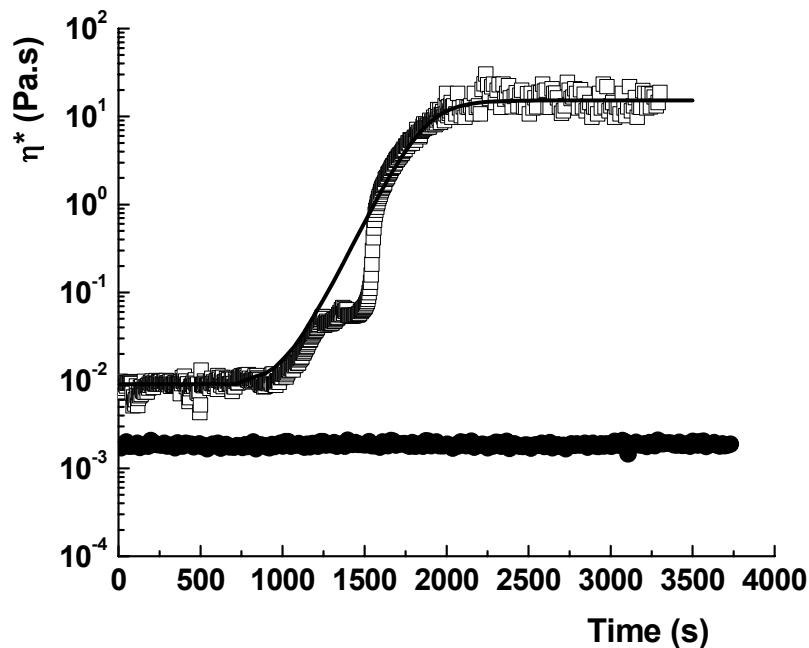


Fig. 7 – Viscosity as a function of time for 2 g/dL POE solution (sample 3) which was not stirred and not submitted to sonication (open symbol) as compared with the same sample which was sonicated for 5 min before the experiment (full symbol). The solid curve was calculated using the Boltzmann equation (eq. 4).

Literature presents sometimes contradictory data concerning the aggregation of POE in solution and this can be due to the sample history. Kinugasa *et al.*¹⁰ did not observe clustering in centrifuged and filtered POE solutions, whereas Zhou and Brown¹⁶ evidenced clusters formation by measuring the fresh prepared solutions without any other experimental procedures. It was also

confirmed that filtration of solution before the experimental tests removes the clusters and aggregates and these structures reappear in time.¹⁹

The viscometric and rheological data indicate the occurrence of an aggregation process in POE solutions which can be discussed as summarized in Fig. 8.

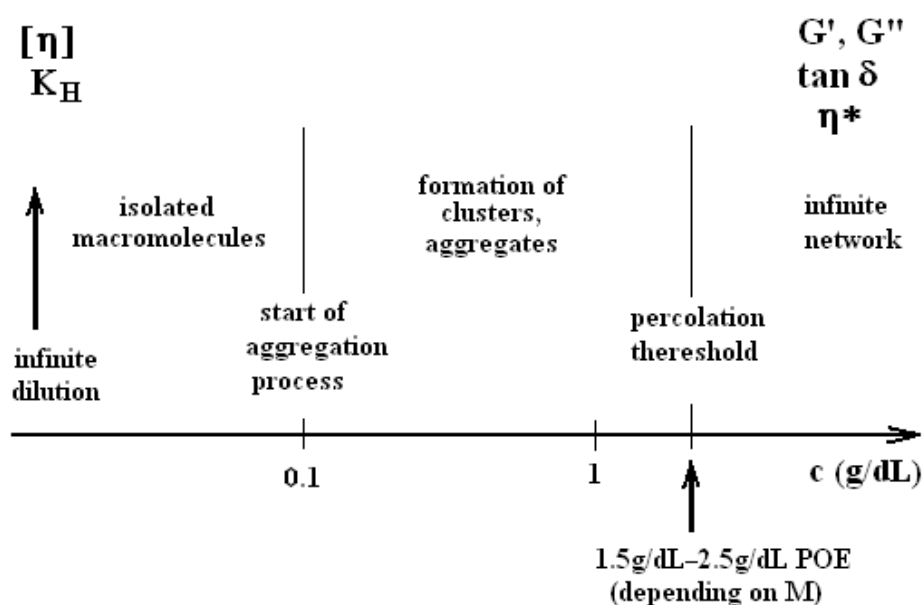


Fig. 8 – Schematic representation of clustering process in POE solutions.

At very low concentrations ($c < 0.1$ g/dL), most of the macromolecular coils are isolated, some of them can be closed to loops, or present in small aggregates (less than 2 % chains). The aggregation process starts for concentrations above 0.1 g/dL, when the formation of clusters or aggregates can occur. The sharp rise of the dynamic moduli (Fig. 5) or of the viscosity (Fig. 7) indicated a percolation threshold when an infinite network of interconnected nodes appears. In addition, for low molecular weight samples, the $-OH$ end groups contribute also to the clustering process by H-bonding between different short chains. The dimensions and the concentration of POE aggregates in aqueous solutions depend on the history of the sample and the aggregation process evolves in time as it is shown in Figs. 4-7. This aspect was evidenced previously by static and quasi-elastic light scattering.¹²

By taking into account the present data and the studies reported in the literature, two type of interactions can be responsive for clusters formation: the repulsive hydrophobic interaction between the $-CH_2$ groups and water molecules, and respectively

the attractive hydrogen bonding between the POE structural units and water molecules.

EXPERIMENTAL PART

Six samples of poly(oxyethylene) with molecular weights in the range 4×10^2 g/mol and 8×10^4 g/mol were purchased from Aldrich (see Table 1). The producer does not mention the polydispersity of POE samples. POE solutions were prepared in filtered deionized water at room temperature, without any stirring, in order to prevent polymer aggregation or degradation.

Viscometric studies were carried out in water at $30^\circ C$ by using an Ubbelohde suspended viscometer. The flow time for the solvent was 156.74 s and the flow volume of the viscometer was greater than 5 mL, making drainage errors unimportant. Flow times were obtained with an accuracy of ± 0.02 %.

The rheological measurements were performed at $25^\circ C$ by using a CVO Rheometer with parallel plate geometry (60 mm diameter and 500 μm gap) and thermal control by Peltier effect.

CONCLUSIONS

Different experiments carried out with aqueous solutions of poly(oxyethylene) have evidenced the formation of supramolecular structures: clusters or aggregates originating from the chain-chain associations.

In dilute solution, the determination of Huggins constant from the slope of the reduced viscosity as a function of polymer concentration, gives information about the aggregation of POE in water.

For a fresh prepared solution of 2 g/dL POE in water, an aggregation can be evidenced by dynamic oscillatory measurements. The viscoelastic parameters (G' , G'' , $\tan \delta$, η^*) change in time due to the clustering process and show a plateau value after a period of time, when an equilibrium state is reached. The aggregates are destroyed by sonication.

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