

Poly(ethylene Oxide) × Polyacrylamide. Which One is More Efficient to Promote Drag Reduction in Aqueous Solution and Less Degradable?

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ABSTRACT: The hydrodynamic drag reduction (HDR) in aqueous solutions containing very small amounts of poly(ethylene oxide) (PEO) and polyacrylamide (PAM, 0–100 ppm) was studied under turbulent flow. In this condition, the polymers undergo severe mechanical degradation and lose their capacity to promote drag reduction. The interpretations from a molecular point of view of the mechanical degradation of these flexible polymers under turbulent flow are not consensual. To avoid effects of polymer entanglement and to correlate the mechanical degradation with the intrinsic characteristics of the polymer chain, a polymer concentration lower than 2 ppm was used. For this purpose, a highly accurate rheometer con-

taining a double-gap cell was used to determine the mechanical degradation kinetics. The kinetics was measured directly from the loss of the polymer's capability to promote drag reduction. The comparisons of degradation kinetics for PEO and PAM in aqueous solution allow us to conclude that the stabilities of the two polymers are similar. This new interpretation can be useful to understand the relative mechanical stability of flexible polymers under drag reduction conditions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1844–1850, 2008

Key words: kinetics of polymer degradation; drag reduction; poly(ethylene oxide); polyacrylamide

INTRODUCTION

Frictional drag results in dissipation of energy, and for many years scientists and technologists have attempted to devise methods to minimize this effect. B.A. Toms found that a very dilute high-molecular weight polymer solution under turbulent flow required a lower pipe flow pressure gradient than the pure solvent to produce the same flow rate.¹ Hydrodynamic drag reduction (HDR) levels may reach 80% under laboratory conditions.² Consequently, the phenomenon has become of considerable engineering interest, mainly in pumping processes.^{3–7}

Modeling HDR in macromolecular systems is necessarily complex, as both turbulence effects and the extremely dilute nature of the solutions involved need to be taken into account.^{3,8} Although the existence of HDR has been recognized for many years, and the phenomenon is hydrodynamically well char-

acterized, a molecular understanding of the role of added polymer in HDR processes is still rudimentary.⁹ There are many different theories for the HDR phenomenon based on molecular approach considerations. Consensually, the theories assume that the added macromolecules under high shear undergo dynamic chain elongation and absorb the energy of the dissipative eddies formed in the flow.^{10,11} According to Tabor and de Gennes,¹² the polymer affects the evolution of the vortices cascade by storing up in the chain some of the turbulence energy. In this way, the macromolecules prevent both loss of fluid kinetic energy and the formation of eddies which results in HDR.⁴ The chain elongation occurs when the shear rate in a turbulent flow is greater than the reciprocal of the molecular relaxation time.^{10,13}

Experimental studies of this phenomenon are generally performed during pipe flow, where levels of HDR are related to the magnitude of the pressure drop along the tube. Although this kind of experiment provides realistic and quantitative testing of polymer inducing HDR, the experimental systems are usually voluminous, and the measurements are both sample and time consuming. Studies on HDR have been also focused on the visualization of structures produced during drop impact against a

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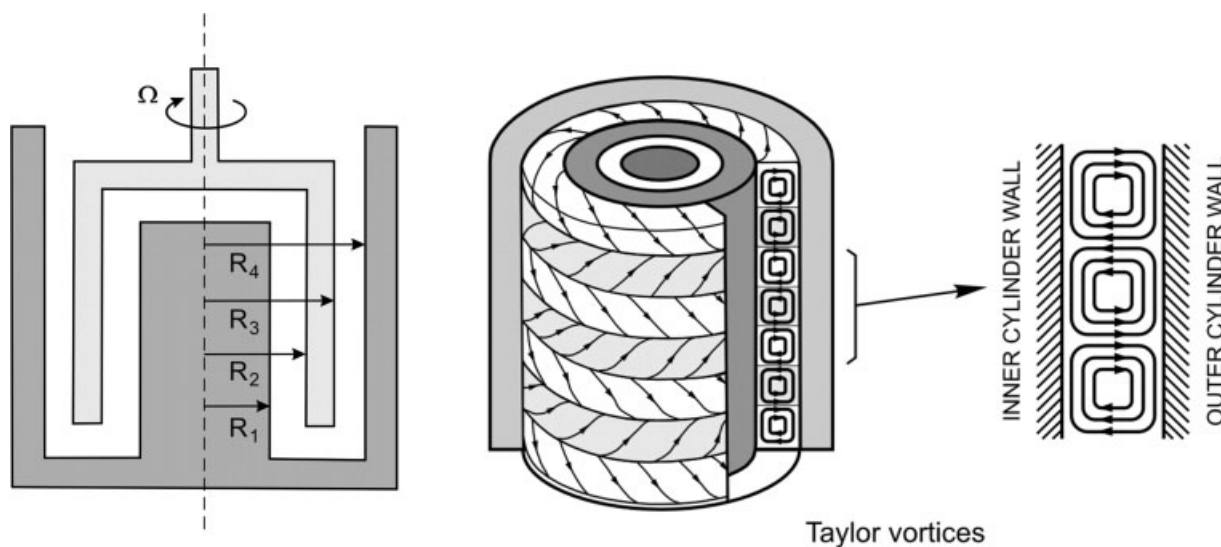


Figure 1 Schematic representations of the double-gap cell, and the Taylor vortices formed in the outer compartment (adapted from Nijman, J. Taylor flow in concentric cylinder system, Technical note of Thermo Fisher Scientific).

shallow polymer solution.^{14,15} Recently, Nakken et al.¹⁶ reported excellent HDR results using a rheometer containing a double-gap cell. The sample fills the two gaps formed between the inner and outer cylindrical surfaces of the rotor and the stationary cup. The centrifugal forces in the two compartments are different and at low angular velocities, Couette and Searle flows are experienced by the fluid at the inner and outer side of the rotor, respectively. On increasing the angular velocity, the first instability (named as Taylor flow) is encountered in the liquid in the outer compartment (Fig. 1), which consists of two counter-rotating pairs of vortices overlapped with the Couette flow.^{17,18}

According to Taylor,¹⁹ the instability of the flow when the inner cylinder is rotating and the outer is fixed (corresponding to the situation of the flow at the outer gap in a double-gap cell) is reached when,

$$P = 0.0571 \left(1 - 0.652 \frac{t}{R_4} \right) + 0.00056 \left(1 - 0.652 \frac{t}{R_4} \right)^{-1} \quad (1)$$

where

$$P = \frac{\pi^4 v^2 (R_3 + R_4)}{2 \Omega^2 t^3 R_4^2}, \quad (2)$$

t is the thickness of the annulus, v is the kinematic viscosity, Ω is the angular velocity and R_3 and R_4 are indicated in Figure 1. Therefore the onset of the

instability is determined when the angular velocity is

$$\Omega = \left(\frac{\pi^4 v^2 (R_3 + R_4)}{2 t^3 R_4^2 P} \right)^{\frac{1}{2}} \quad (3)$$

On increasing the angular velocity, beyond the onset point, the Taylor vortices become wavy and smaller secondary vortices appear (named as Gortler vortices). The onset point for the Taylor vortices is clearly observed by sudden increase in the applied shear stress. The flow field becomes eventually chaotic if the velocity is increased further.¹⁶ Under such hydrodynamic conditions, the drag reduction effect caused by macromolecules in solution can be directly determined from the difference between the applied shear stress for the solution and for the pure solvent.

Several articles involving drag reduction by polymers^{16–18,20,21} and macromolecules formed by self-assembly of surfactants (worm-like micelles)²² in Taylor flows have been published. The most attractive aspect of this technique is the high reproducibility and accuracy that is better than $\pm 2.5\%$.¹⁶ Moreover, the technique is suitable to investigate effects of mechanical polymer degradation under HDR conditions.

Although there are numerous investigations on mechanical degradation of polymers solutions in turbulent flow, the results are conflicting.²³ In aqueous solution, poly(ethylene oxide) (PEO) and polyacrylamide (PAM) are the most efficient drag reducers.

Therefore, the mechanical degradation of these polymers has been studied and compared, to find correlations between the polymer structure and the energy of the flow.^{24–26} Although some of these articles concluded that PAM is more stable than PEO, there are several aspects that are still unclear.

The rheometer with double-gap geometry was used to investigate PEO and PAM kinetics of degradation in very diluted aqueous solutions. In such condition, the decrease in the polymer molecular weight can be measured directly from the loss in its capability to produce HDR.

EXPERIMENTAL METHODS

Experimental apparatus

Rheological measurements were performed with a Haake Instruments RheoStress 1 rheometer. Measurements were made using a double-gap geometry (Taylor-Couette cell) (Fig. 1) with the active rotor height, $H = 55.0$ mm and with radii $R_1 = 17.75$ mm, $R_2 = 18.35$ mm, $R_3 = 20.99$ mm, and $R_4 = 21.7$ mm. The double-gap cylindrical cell placed in the liquid rotate about the axis of the cylinder, while the sample holder is stationary. The volume of liquid sample (11.5 mL) was kept fixed in all the experiments, and the temperature of the system was maintained at $25.00 \pm 0.01^\circ\text{C}$ by a constant temperature circulating apparatus. The angular velocity was changed from 0 to 1200 rpm. During the experiments of induced mechanical degradation, the angular velocity was maintained constant at 1200 rpm, and the shear stress of the solution was simultaneously measured. The shear viscosity of the solutions was measured using an Ostwald viscometer-50, and the density of the solutions was measured using a density meter (Anton Paar, DMA 58).

Polymer solutions

The aqueous polymer solutions were prepared by an adaptation of the procedure suggested by Little and Wiegand.²⁷ Samples of PEO with nominal molecular weights of 5×10^6 g mol⁻¹ (Aldrich) and PAM 5×10^6 g mol⁻¹ (BDH) were weighed and then sprinkled over a large area of water to avoid clumping of the particles. At 3 h intervals, the solutions were gently stirred using a glass rod to avoid polymer degradation. This procedure was also repeated during the following day. Stock solutions were initially prepared and then diluted to the required polymer concentration. All of the experiments were carried out using analytical grade water from a Millipore Milli-Q Gradient filtration system. Because of the high accuracy required, the diluted solutions were prepared by weighing within ± 1 mg.

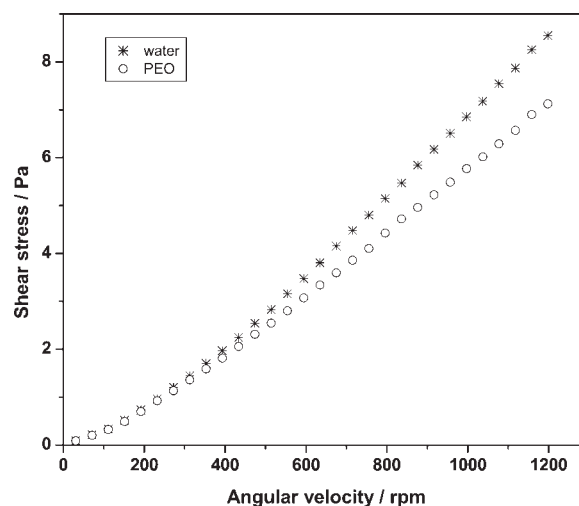


Figure 2 Flow curves (shear stress \times angular velocity) for pure water and for a solution containing 20 ppm of PEO (5×10^6 g mol⁻¹). The onset of the Taylor vortices is observed at $\Omega = 200$ rpm.

RESULTS AND DISCUSSION

For the flow curves, reproducibility better than $\pm 2\%$ (for six measurements) was obtained using the double-gap cell filled with pure water, in the range of angular velocity between 0 and 1200 rpm. Figure 2 shows comparative results of the shear stress (τ) variation as a function of the angular velocity (Ω) for pure water and for 20 ppm of aqueous PEO solution ($M_w = 5 \times 10^6$ g mol⁻¹). In the laminar region ($\Omega < 150$ rpm), practically no difference is observed in the flow curve for both liquids. The polymeric solution is so diluted that it behaves as a Newtonian fluid. The onset of the Taylor instability is almost the same for both liquids ($\Omega \cong 200$ rpm), which means that the polymer chains have no influence on the counter rotating pairs of vortices. Even beyond this point, no difference can be detected up to $\Omega = 400$ rpm. Beyond this point, the applied shear stress is always lower for PEO solution in comparison with pure water, and this is due to the HDR promoted by the PEO molecules. The percentage of HDR can be readily determined using eq. (4):

$$\% \text{HDR} = \left(\frac{\tau_s - \tau_p}{\tau_s} \right)_{\Omega} \times 100 \quad (4)$$

where τ_s and τ_p , are the shear stress for the solvent and for the polymer solution, respectively.

In the case shown in Figure 2, the percentage of HDR increases as Ω is increased and a maximum value ($\cong 16\%$) is reached at $\Omega = 1200$ rpm.

PEO and PAM have very flexible chains and therefore they also have a high capability to stretch under high shear. For a comparative HDR study, the

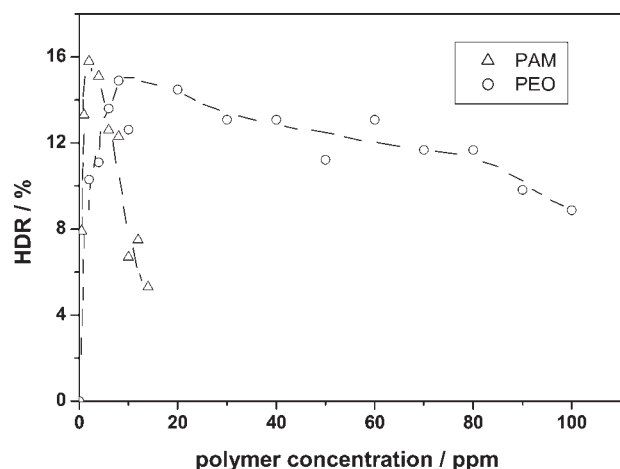


Figure 3 Percentage of HDR as a function of the polymer concentration for aqueous solution containing PEO and PAM. Both polymers have the same molecular weight ($5 \times 10^6 \text{ g mol}^{-1}$). The dashed lines are used as a guideline for the eyes, and the standard deviation is $\cong \pm 0.4\%$.

same polymer molecular weight was used ($5 \times 10^6 \text{ g mol}^{-1}$), and their concentrations were changed in the range in which HDR is effective. Figure 3 shows the efficiency, in terms of %HDR, for both polymers as a function of their concentration, at $\Omega = 1200 \text{ rpm}$. The maximum percentage of HDR (%HDR_M) for both polymers is almost the same $\cong 16\%$. However, the concentration of PAM ($c_{\text{MPAM}} = 2 \text{ ppm}$) necessary to obtain %HDR_M is much lower than that required by PEO (c_{MPEO} is in the range between 10 and 20 ppm). Beyond c_{MPAM} , the percentage of HDR decreases sharply, due to the large increase of the shear viscosity of the PAM solutions. In the case of PEO solutions, the dependence of the shear viscosity on the concentration is much lower than that for

PAM solutions (see the inset in Fig. 6). The higher viscosity of PAM is associated with the more expanded chain in aqueous solution in comparison with the PEO ones.

The polymer overlap concentration, c^* , can be determined from the relation: $c^*[\eta] = 1$. The values for the intrinsic viscosity measured for PEO and PAM are 3 and 116 dL g^{-1} , and the values for c^* are $\sim 86 \text{ ppm}$ and 3330 ppm, respectively. Therefore, $c_M \ll c^*$, indicates that the HDR effect is associated with the elongation of isolated chains. Under high shear, polymeric chains can undergo intense mechanical degradation. As demonstrated by de Gennes,²⁸ the critical polymer concentration in which the polymer acts as a drag reducing agent is highly dependent on the polymerization degree. Therefore, under such conditions, the HDR effect can disappear in very short time due to the rapid decrease in the polymer molecular weight. This is one of the engineering problems in pumping fluids in closed circuits, which use polymers as HDR agents.²⁹

Several authors have compared the relative mechanical stability of PEO and PAM in aqueous solution under HDR conditions.^{24–26} A key point for comparison is the choice of the experimental parameters associated with both polymers. In this study, the same molecular weight of PEO and PAM was used ($5 \times 10^6 \text{ g mol}^{-1}$), and to assure that the degradation of the polymer results in immediate loss of HDR capability, the initial concentrations of PEO and PAM were studied in the range of maximum HDR (close to c_{MPEO} and c_{MPAM}). In such low concentration, the rheometer containing the double-gap cell is quite suitable to investigate the kinetics of polymer degradation.

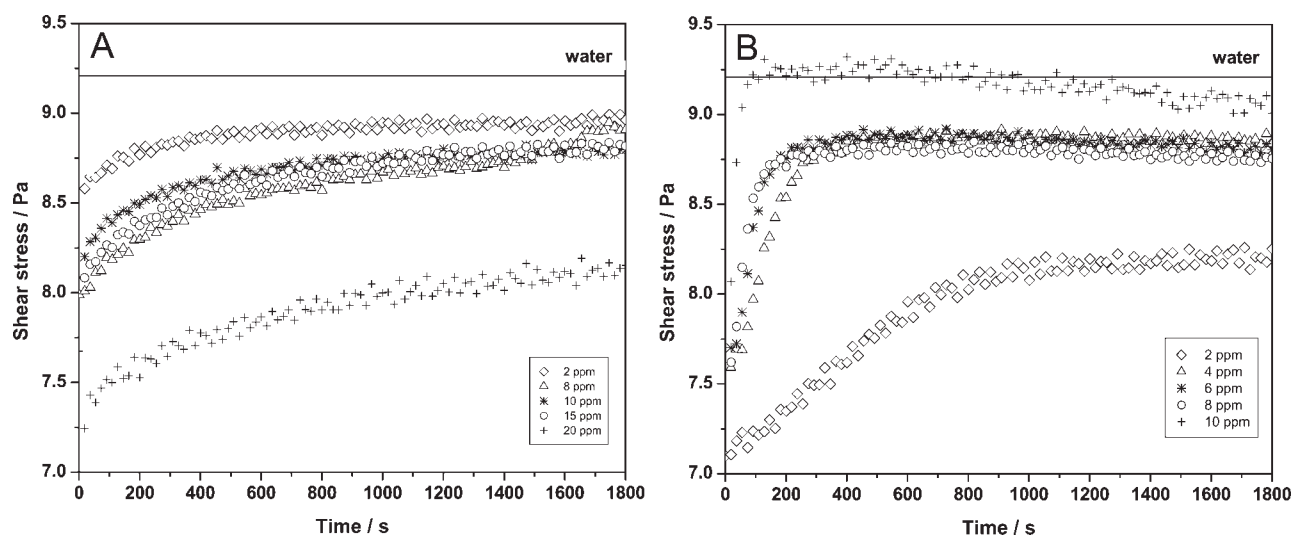


Figure 4 Dependence of the applied shear stress at $\Omega = 1200 \text{ rpm}$ as a function of time for different concentrations of (A) PEO and (B) PAM ($5 \times 10^6 \text{ g mol}^{-1}$). The shear stress for pure water is also indicated in the figures. The standard deviation for the shear stress is $\cong \pm 0.3 \text{ Pa}$.

Figure 4 shows the variations of the shear stress, necessary to keep $\Omega = 1200$ rpm, as a function of the time. The study was performed in duplicate and good reproducibility was observed. The solutions of both polymers showed intense degradation up to 800 s, because the applied shear stress increases as the scissions of polymer chains result in loss of the HDR capability. After a long period, it is expected that the applied shear stress (at $\Omega = 1200$ rpm) for the solutions reach that for pure water, $\tau = (9.2 \pm 0.5)$ Pa (indicated in both graphics in Fig. 4). For PEO [Fig. 4(A)], not only the HDR efficiency increases as the concentration is increased (up to 20 ppm) but also the time necessary for complete loss of HDR. This behavior is in agreement with that obtained by McCormick and coworkers.²⁴ However, an opposite trend is observed in the case of PAM solution [Fig. 4(B)], in which an apparently shorter time is required for complete loss of HDR as PAM concentration is increased. The different behavior is explained in terms of the dependence of HDR as a function of the polymer concentration (Fig. 3). In the case of PAM, the maximum HDR efficiency is observed in a narrow range of PAM concentrations. Therefore, as the mechanical degradation is measured directly from the capability of the polymer to reduce the hydrodynamic drag, an apparent faster loss of HDR for PAM is observed.

Hanratty and coworkers³⁰ proposed that the loss of HDR during the mixing of PAM solutions with water can be associated with the disruption of polymeric clusters. To avoid such possible aggregation effect, as mentioned earlier, the polymeric solutions were used with concentrations lower than c^* . Some authors who studied the relative mechanical stability of PEO and PAM under turbulent flow, concluded that PAM is more stable than PEO.^{25,26} Explanations based on microscopic properties are common. Vana-palli et al.²⁵ attributed the higher stability of PAM to the higher estimated values of the bond strength in comparison with PEO. Scissions of not only C—C bonds are involved in degradation of both polymers but also C—O bonds are involved in the case of PEO. However, the average bond enthalpy for C—C (348 kJ mol^{-1}) is lower than for C—O (360 kJ mol^{-1}),³¹ and therefore, this explanation is not plausible. In terms of the entire polymer molecules, some arguments based on the molecular gyration radius are often used as well. Kim et al.²³ and Zakin et al.³² reported that the degradation is higher in a poor polymer solvent than in a good one. Brostow et al.³³ stressed similar interpretation, but they also pointed out that intuitively it is expected that more expanded chains (in a good solvent) should be more vulnerable to suffer scissions, in comparison with more compacted chain (poor solvent). This interpretation was stressed by Nakano and Minoura.^{34,35}

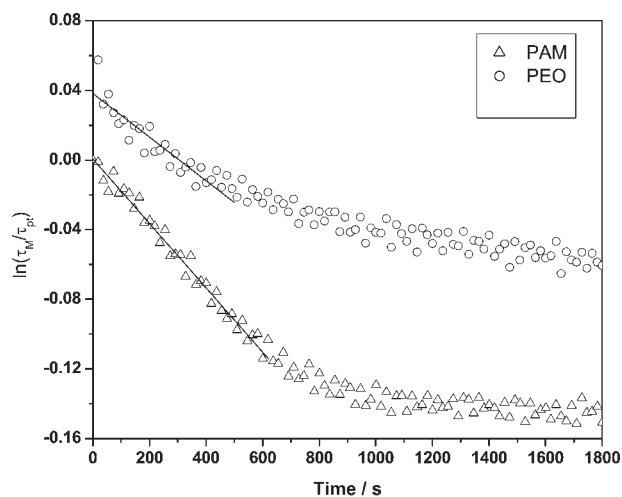


Figure 5 Dependence of $\ln(\tau_M/\tau_{p,t})$ as a function of the time for aqueous solution of PEO and PAM ($5 \times 10^6 \text{ g mol}^{-1}$). The initial concentrations of PEO and PAM are 2 and 8 ppm, respectively. The mechanical degradation was studied at $\Omega = 1200$ rpm.

To obtain a quantitative comparison for PEO and PAM degradation, a kinetic model was applied to describe the mechanical degradation kinetic of polymer based on HDR effect. At a specific Ω , the following considerations were assumed:

1. The chains undergo scissions at the middle.³⁶
2. The concentrations of the two fragments formed during the degradation do not contribute to HDR anymore.
3. The rate of polymer degradation is only dependent on the intact polymer concentration in a specific time ($c_{p,t}$) and a first order kinetics is obeyed:

$$\frac{dc_{p,t}}{dt} = -k_p c_{p,t} \quad (5)$$

or in the integrated form

$$\ln\left(\frac{c_{p,t}}{c_M}\right) = -k_p t \quad (6)$$

where k_p is the polymer degradation rate constant and at $t = 0$, the polymer concentration is c_M .

Because of the HDR effect, the concentration of intact polymers is inversely proportional to the applied shear stress ($c_{p,t} \sim 1/\tau_{p,t}$), so that (eq. 6) may be written as

$$\ln\left(\frac{\tau_M}{\tau_{p,t}}\right) = -k_p t \quad (7)$$

where τ_M and $\tau_{p,t}$ are the applied shear stress on the polymer solution at $t = 0$ and at t , respectively.

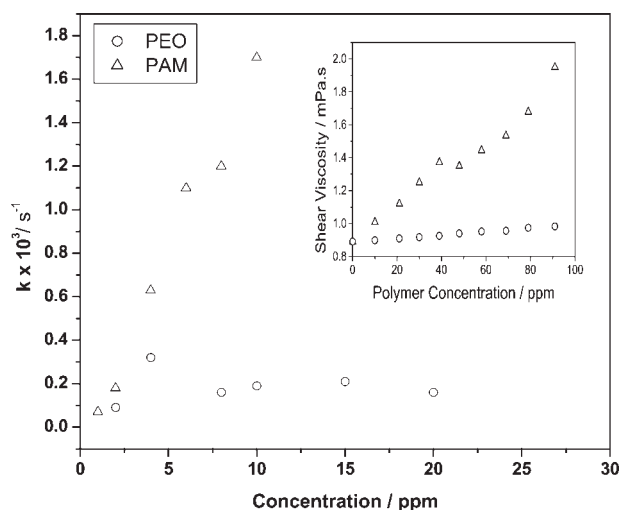


Figure 6 Dependence of polymer degradation rate constant (k_p) for PEO and for PAM as a function of the polymer concentration. Inset: dependence of the shear viscosity of PEO and PAM solutions as a function of polymer concentration.

Figure 5 shows the plot of $\ln(\tau_M/\tau_{p,t})$ as a function of t , for c_{MPEO} and c_{MPAM} (at 20 and 2 ppm, respectively, for PEO and PAM), at $\Omega = 1200$ rpm, in which a linear correlation is observed for the first 800 s. The values for polymer degradation rate constant for PEO and for PAM were $k_{\text{PEO}} = (9 \pm 1) \times 10^{-5} \text{ s}^{-1}$ and $k_{\text{PAM}} = (2 \pm 1) \times 10^{-4} \text{ s}^{-1}$, respectively. Although, the model assumes that k is not dependent on the polymer concentration, a graph of k_p as a function of PEO and PAM concentration can reveal deviations. The graph is shown in Figure 6 and as expected, the deviation is higher in the case of PAM, which has higher shear viscosity than the PEO solutions (inset in Fig. 6). To separate the information about the intrinsic mechanical stability of macromolecule from the effects associated with its concentration, the estimation of the polymer degradation rate constant ($k_{p,0}$) at $c_p \rightarrow 0$ can be determined by extrapolation. The result is interesting as the values for $k_{p,0}$ for both polymers converges to ca. $8 \times 10^{-5} \text{ s}^{-1}$. Apparently, the mechanical degradation in such turbulent conditions is not specific for both flexible polymers. This means that under high shear, the polymer chain is highly elongated and independent of the polymer gyration radius, and therefore, they become equally vulnerable to scission. Measurements of the polymer molecular weight and polydispersity index of the sheared samples using size exclusion chromatography (SEC) can confirm the conclusions stressed here. However, the results obtained until now are still inconclusive due to the very low polymer concentrations used in this work.

CONCLUSIONS

The high sensitivity of the rheometer with the double-gap cell allowed the investigation of the polymer induced drag reduction effects. The method showed to be very suitable for this proposal, as the data obtained were reproducible to better than 2%. The method was also used to compare the kinetics of mechanical degradation of PAM and PEO in aqueous solutions in highly very diluted solutions. The data for mechanical degradation, obtained directly from the loss in the capability of the polymer to produce drag reduction, were adjusted by using a first-order process. The results indicate that the polymer degradation rate constant in infinite dilution is similar for both polymers. Therefore, under turbulent flow, if the chains of PEO and PAM are fully stretched, they are equally vulnerable to undergo scissions.

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