HAL
open science

Mechanical Degradation Onset of Polyethylene Oxide Used as a Hydrosoluble Model Polymer for Enhanced Oil Recovery

A. Dupas, Isabelle Hénaut, Jean-François Argillier, Thierry Aubry

To cite this version:

A. Dupas, Isabelle Hénaut, Jean-François Argillier, Thierry Aubry. Mechanical Degradation Onset of Polyethylene Oxide Used as a Hydrosoluble Model Polymer for Enhanced Oil Recovery. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 2012, 67 (6), pp.931-940. 10.2516/ogst/2012028 . hal-00815882

HAL Id: hal-00815882

https://ifp.hal.science/hal-00815882v1

Submitted on 19 Apr 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles
Copyright © 2013, IFP Energies nouvelles
DOI: 10.2516ogst/2012028

Dossier

Challenges and New Approaches in EOR
Défis et nouvelles approches en EOR

Mechanical Degradation Onset of Polyethylene Oxide Used as a Hydrosoluble Model Polymer for Enhanced Oil Recovery

A. Dupas[1], I. Hénaut[1], J.-F. Argillier[1] and T. Aubry[2]

1 IFP Energies nouvelles, 1-4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France
2 LIMATB-Equipe Rhéologie, Université de Bretagne Occidentale, 6 avenue Victor Le Gorgeu, CS 93837, 29238 Brest Cedex 3 - France
e-mail: adeldupas@gmail.com - isabelle.henaut@ifpen.fr - jean-francois.argillier@ifpen.fr - Thierry.Aubry@univ-brest.fr

Résumé — Seuil de dégradation mécanique de solutions de polymères utilisés en récupération assistée des hydrocarbures — Les polymères hydrosolubles comme les polyacrylamides peuvent être utilisés en récupération assistée des hydrocarbures (Enhanced Oil Recovery (EOR)) par injection de polymère. Cette technique vise à augmenter la production de brut en le poussant du réservoir vers un puits producteur à l'aide d'une solution de polymère suffisamment visqueuse. Les polymères utilisés à cet effet ont des masses moléculaires supérieures à 10^6 g/mol, ce qui les rend sensibles à la dégradation. En raison des débits élevés utilisés lors de leur injection, mais aussi en raison des taux d'élongation élevés rencontrés dans le réservoir, les polymères peuvent se rompre et perdre leurs propriétés viscosifiantes. Dans la littérature, il a été clairement montré, pour des solutions diluées en régime laminaire, que la dégradation des macromolécules n'était initiée qu'au-delà d'un taux d'élongation critique noté $\dot{\varepsilon}_c$, et que ce taux d'élongation était une fonction puissance de la masse moléculaire du polymère : $\dot{\varepsilon}_c \approx M_w^{-k}$. La présente étude expérimentale de la dégradation mécanique a été menée sur des solutions d'oxydes de polyéthylène pour comprendre la dégradation mécanique non seulement en écoulement laminaire ou turbulent, mais aussi en régime dilué et semi-dilué, ainsi qu'en bon ou mauvais solvant. Il a été mis en évidence que la dégradation mécanique affecte principalement les longues chaînes, qu'elle est favorisée à concentrations élevées et en mauvais solvant. Les résultats montrent également que la décroissance de la viscosité élongationnelle à faibles taux de déformation, due à la dégradation, est semblable à celle de la viscosité de cisaillement ; elle est en revanche beaucoup plus marquée à forts taux d'élongation.

Abstract — Mechanical Degradation Onset of Polyethylene Oxide Used as a Hydrosoluble Model Polymer for Enhanced Oil Recovery — *Water soluble polymers such as polyacrylamide are used in polymer flooding, which is an advanced technique of Enhanced Oil Recovery (EOR). It aims at improving crude oil displacement in reservoir by pushing it with a viscous injected fluid. Polymer flood is challenged by mechanical degradation of long macromolecules during intense flows. Many studies reported that above a critical extensional rate* $\dot{\varepsilon}_c$*, polymer chains can break and lose their rheological properties. The molecular weight (M) dependence of* $\dot{\varepsilon}_c$ *for dilute solutions in laminar flows was shown to follow a power law:* $\dot{\varepsilon}_c \approx M_w^{-k}$*. An experimental study has been performed to investigate the onset of mechanical degradation in both laminar and turbulent flows and for both dilute and semi dilute polyethylene oxide aqueous solutions. It reveals that the exponent k strongly depends on the concentration and flow regimes and also on solvent quality. Results show that mechanical degradation mainly affects long chains, that it is favoured at high concentrations, under poor solvent conditions. They also evidence that the extensional viscosity at low strain rates decreases to the same extent as shear viscosities due to mechanical degradation. However, the decrease of the extensional viscous properties at high strain rates is much more pronounced.*

INTRODUCTION

The classical oil recovery process (use of initial pressure in the well and water flooding) is used to produce a small fraction of the crude oil initially present in the field (around 30% on average). To improve performance, the oil industry has developed advanced techniques, namely Enhanced Oil Recovery (EOR) techniques. For example, in polymer flooding, macromolecules are used to increase the viscosity of brine significantly and improve the displacement of oil in the reservoir. At present, the main polymer used in EOR application is high molecular weight synthetic hydrolyzed polyacrylamide, HPAM with a molecular weight up to 18×10^6 g/mol. Polymer concentrations used lie between 200 and 2000 ppm [1]; corresponding to either dilute or semi-dilute solutions [2]. The major limitation of this EOR technique is the flow induced mechanical degradation. This phenomenon can occur during the injection at high flow rates and also in the reservoir where elongationnal flows take place. The scission of large molecules in strong turbulent (injection process) or laminar (reservoir) flows can result in significant viscosity loss, which hinders the efficiency of the EOR technique [3].

When submitted to shear, macromolecules do not stretch significantly, whereas, when submitted to extension, they can elongate drastically and break. This is the reason why mechanical degradation of polymer solutions was mainly studied in extensional flows. Two kinds of extensional devices are reported in the literature:

- devices with a stagnation point such as cross slots, four roll mills or opposed jets. In the vicinity of the stagnation point, the residence time is very high and macromolecules can extend completely at strain rates much larger than the relaxation rate and then break. Extensional flows of this type are called Quasi-Steady State Flow (QSSF) [4];
- devices with an abrupt contraction (or divergence) in which the sudden acceleration of a polymer solution across an orifice generates a Fast Transient Flow (FTF). In this type of flow, the residence time is often smaller than the polymer relaxation time and mechanical degradation may occur even though macromolecules are only partially extended [5].

The mechanical degradation onset takes place when a critical scission strain rate $\dot{\varepsilon}_c$, is reached. The subscript c stands for "critical", since a critical velocity is needed for chain scission to occur. For dilute solutions, a so-called scaling law between $\dot{\varepsilon}_c$ and the molecular weight M has been evidenced:

$$\dot{\varepsilon}_c \approx M^{-k} \tag{1}$$

In Quasi-Steady State Flows, Odell and Keller [4] found experimentally that $k = 2$, in agreement with theory. Indeed, if macromolecules are considered as a series of N monomers connected by bonds of length b and if they are assumed to adopt a totally stretched conformation, then the tension is maximum in the middle of the chain [6]. When the tension T_c exceeds the intensity of a covalent bond, the chain breaks at the middle and the critical tension T_c in a solvent of viscosity η is:

$$T_c \propto \eta b N^2 \dot{\varepsilon}_c \tag{2}$$

As the number of monomers is proportional to the molecular weight, the extensional strain rate at the mechanical degradation onset is expressed as follows:

$$\dot{\varepsilon}_c \propto \frac{T_c}{\eta M^2} \tag{3}$$

In transient flows, where partially stretched macromolecules can break, the exponent k was found to be equal to 1 [5, 7].

Besides, several studies based on Brownian dynamics simulations have shown that hydrodynamic interactions could influence mechanical degradation in FTF flows, but not in QSSF ones [8-10].

All the above-cited references concerned dilute polymer solutions under laminar conditions. As for turbulent flows, to our knowledge, only Vanapalli *et al.* [11] established a relationship between a critical scission strain rate $\dot{\varepsilon}_c$ and molecular weight M, for polyethylene oxide dilute solutions:

$$\dot{\varepsilon}_c \approx \frac{U_c}{D} \approx M^{-1.23 \pm 0.12} \tag{4}$$

with U_c: critical mean velocity in the pipe of diameter D.

Scission scenarios have also been studied by Gel Permeation Chromatography (GPC) and optical methods (birefringence and dynamic light scattering) [7, 9, 12-14]. Using such techniques, the scission of isolated macromolecules in QSSF and FTF laminar flows has been confirmed to occur at the chain midpoint. Merill and Horn [15] also observed a mid-scission of polymer chains in dilute solutions under turbulent conditions.

Even though semi-dilute polymer solutions are very often encountered in industrial applications, *e.g.* in oil recovery applications their mechanical degradation has been much less investigated. Keller *et al.* [16] have studied the degradation of semi-dilute polymer solutions in Quasi-Steady State Flows. Birefringence measurements showed that the flow was unstable, particularly close to the stagnation point. Besides, under such conditions, Gel Permeation Chromatography (GPC) highlighted a random scission phenomenon [17]. For a fast transient laminar flow of semi-dilute polymer solutions, a relationship between a critical scission strain rate $\dot{\varepsilon}_c$ and molecular weight M was established by Nghe *et al.* [18] using a microfluidic device:

$$\dot{\varepsilon}_c \approx M_w^{-k} \tag{5}$$

with k equal to 1.7 ± 0.3. This result suggests a stronger dependence of critical elongation rate with chain length for semi-dilute solutions than for dilute polymer solutions.

In the present paper, the mechanical degradation onset of polyethylene oxide solutions has been investigated experimentally, focussing on the influence of physico-chemical parameters (concentration regime, molecular weight, solvent quality) in laminar and inertial flow regimes. The main originality of the work presented in the manuscript is that mechanical degradation has been investigated for a given polymer in both dilute and semi-dilute regimes, in poor and good solvents and under laminar but also turbulent conditions, which is rarely explored in the literature. Moreover the effect of mechanical degradation on both shear and extensional properties has been investigated in this study.

1 EXPERIMENTAL SECTION

1.1 Chemicals

Polyethylene Oxide (PEO) samples with a molecular weight ranging from 1×10^6 and 8×10^6 g/mol were supplied by *Sigma Aldrich* and used as such. SEC/MALLS analysis confirms a polydispersity index about 1.8. The solutions were prepared using the following procedure: under high magnetic stirring, PEO powder was dissolved in distilled water during a few minutes; the solution was then homogenized under gentle stirring at constant velocity, during 1 day or 1 week, depending on the solution concentration. Stirring was moderate in order to minimize degradation during the preparation step.

For each molecular weight, the overlap concentration c^*, which defines the crossover between dilute and semi-dilute regimes, was determined using rheological measurements carried out with a Low Shear viscometer at 20°C. Actually, c^* was defined experimentally as the maximum concentration for which the Huggins equation is valid:

$$\frac{\eta_r - 1}{C} = [\eta] + k'[\eta]^2 C \tag{6}$$

with:

- η_r is the relative viscosity (ratio solution viscosity/solvent viscosity);
- $[\eta]$ is the intrinsic viscosity of the polymer;
- C is the polymer concentration;
- k' is the Huggins coefficient characterizing the ability of polymer chains to aggregate in a solvent (pair interactions).

TABLE 1

Overlap concentration and intrinsic viscosity of PEO solutions investigated

Polymer	c^* (ppm)	$[\eta]$ ($cm^3.g^{-1}$)
PEO 2×10^6 $g.mol^{-1}$	1 800	1 100
PEO 4×10^6 $g.mol^{-1}$	1 000	1 900
PEO 7×10^6 $g.mol^{-1}$	800	2 300
PEO 8×10^6 $g.mol^{-1}$	480	3 500

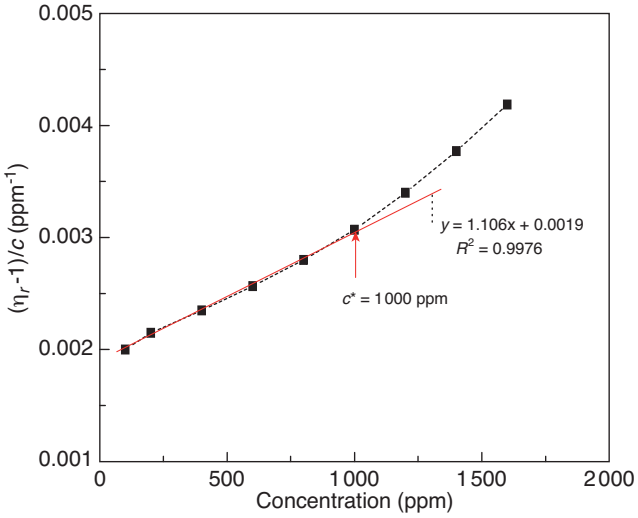

Figure 1

Reduced specific viscosity as a function of polymer concentration: determination of the overlap concentration c^* and intrinsic viscosity of 4 MDa PEO.

An example of c^* determination is given in Figure 1 and c^* values for all PEO chains studied in this work are gathered in Table 1.

1.2 Device Used to Induce Degradation

The American Petroleum Institute has developed a capillary device in order to study mechanical degradation of polymer solutions used in oil recovery. Such a device has been built by IFP Energies nouvelles according to the RP63 convention.

Samples are poured in a cylindrical tank and then flow through a contraction followed by a capillary geometry. Flow is governed by a controlled pressure ranging between 0.5 and 20 bar *(Fig. 2)*. For each pressure, the volumetric flow rate Q is determined by the measurement of the collected volume as a function of time.

In laminar flow, Poiseuille's law enables to determine the apparent shear rate at the wall:

$$\dot{\gamma}_w \approx \frac{4Q}{\pi R^3} \tag{7}$$

with R: capillary internal radius.

Using Cogswell approach [19], a characteristic average extensional rate $\dot{\varepsilon}$ at the entrance of the capillary can be determined:

$$\dot{\varepsilon} = \frac{\dot{\gamma}_w \tan\theta}{2} \tag{8}$$

with θ: half angle of converging die.

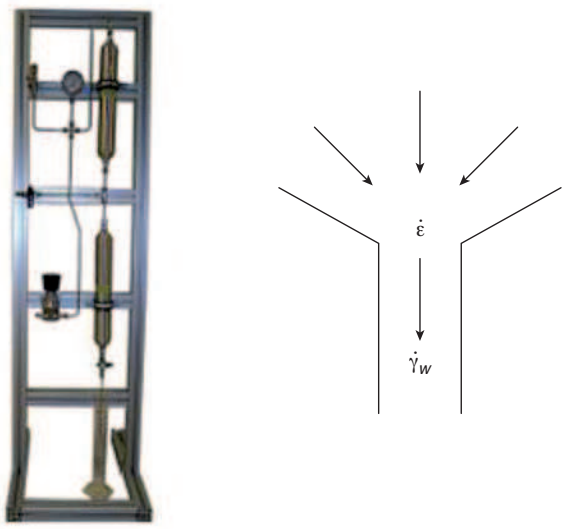

Figure 2

Picture and schematic representation of the API device used to induce mechanical degradation.

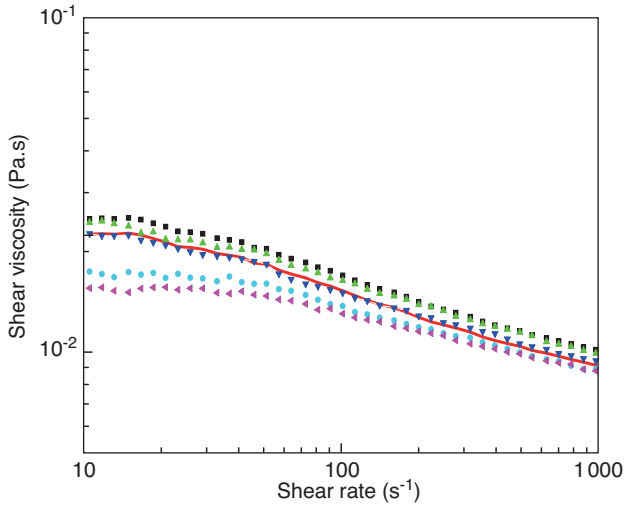

Figure 3

4 MDa-PEO semi-dilute solution at c = 3 000 ppm: shear viscosity as a function of shear rate: ■ native solution, (solid red line) calculated flow curve corresponding to a viscosity loss of 90% relative to viscosity of the native sample, and solutions degraded at different velocities: ▲ 2.7 m.s^{-1}, ▼ 7 m.s^{-1}, ● 12.2 m.s^{-1}, ◀ 17 m.s^{-1}.

Actually, this extensional rate is proportional to the mean velocity U, which can therefore be used to characterize the imposed laminar flow:

$$U = \frac{Q}{\pi R^2} \tag{9}$$

In turbulent regime, Poiseuille's law is no longer valid and no macroscopic shear rate can be determined. Instead, the friction velocity U^* is commonly used to characterize the turbulence strength. It is related to the mean velocity U:

$$U^* = U \times \sqrt{\frac{f}{2}} \tag{10}$$

with f: Fanning friction factor. This dimensionless factor characterizes the head loss due to friction (viscous component) in turbulent flow.

In the range of turbulent Reynolds numbers used, f was found to be constant. The mean velocity can therefore be chosen to characterize the intensity of the turbulent flow.

Therefore, in this study, the mean velocity U was chosen to characterize both laminar and turbulent flows.

1.3 Rheological Characterization

Shear rheological measurements were performed using the AR2000 rheometer (*TA Instruments*). Temperature was maintained at 20°C. A logarithmic shear rate sweep was applied to the samples from 1 to 100 s^{-1} in 3 minutes. For semi-dilute solutions, the cone and plate geometry (4 cm plate diameter, 1°59 cone angle) was chosen. For dilute solutions, a larger cone and plate geometry (6 cm plate diameter, 1°59 cone angle) was used. Non-degraded as well as degraded samples were tested; a sample was considered as degraded as soon as its Newtonian viscosity was decreased by 10%, as illustrated in Figure 3, for a 4 MDa PEO solution, for which the viscosity loss of 10% is reached at the critical velocity U_c = 7 m.s^{-1}.

Extensional properties of all samples were determined using the microfluidic device EVROC® (Extensional Viscometer and Rheometer On-a-Chip) from *RheoSense*. It is composed of a channel presenting a planar and hyperbolic contraction *(Fig. 4)* equipped with miniaturized pressure transducers. Several studies have underlined the advantages of such microfluidic devices [20-24]. In EVROC system, an extensional rate $\dot{\varepsilon}$ is imposed through a controlled flow rate Q, the resulting extensional pressure drop ΔP_{ext} is measured and the extensional viscosity η_{ext} can be inferred:

$$\Delta P_{ext} = \frac{\upsilon}{Q} \eta_{ext} \dot{\varepsilon}^2 \tag{11}$$

where υ is a characteristic volume [25, 26]. Data for extensional and shear viscosities are often compared using the Trouton number Tr:

$$Tr = \frac{\textit{extensional viscosity}}{\textit{shear viscosity}} \tag{12}$$

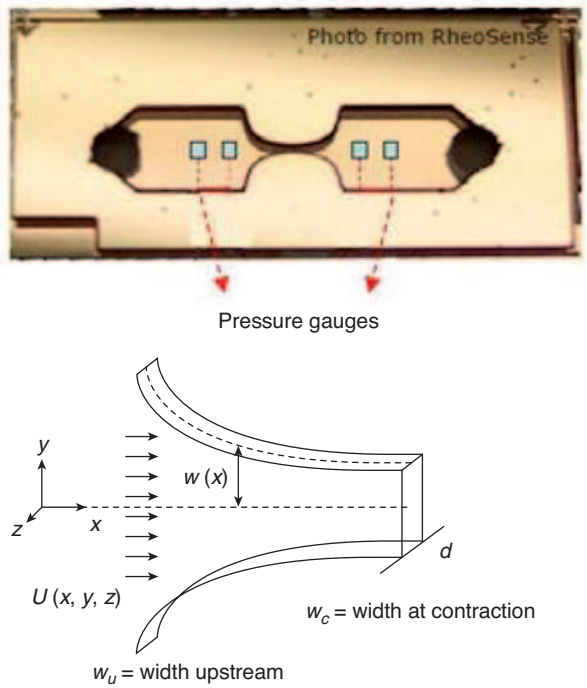

Figure 4

Schematic representation of planar hyperbolic contraction of the microfluidic EVROC RheoSense device [33].

For a Newtonian fluid under planar extension, Trouton number is equal to 4.

2 RESULTS AND DISCUSSION

2.1 Mechanical Degradation of Dilute Solutions

2.1.1 Molecular Weight Dependence

The first experiments were made on dilute PEO solutions prepared at a weight concentration of 500, 600 and 750 ppm. For each sample, the critical mean velocity U_c has been plotted as a function of the weight-averaged molecular weight M *(Fig. 5, Tab. 2)*, the following power law dependence was obtained:

$$U_c \approx M_w^{-1} \tag{13}$$

These results are in accordance with the scaling law suggested in the literature for dilute solutions in Fast Transient Flows.

Reynolds numbers at the entrance of the capillary geometry have been estimated for all tested conditions. Their values are given in Table 3. The data indicate that flows applied to low molecular weight solutions were turbulent whereas flows applied to high molecular weight ones were laminar. The results plotted in Figure 5 show that the exponent k remains constant despite the difference in flow regime, which suggests that the mechanism of degradation of partially extended macromolecules in FTF is the same under laminar or turbulent conditions.

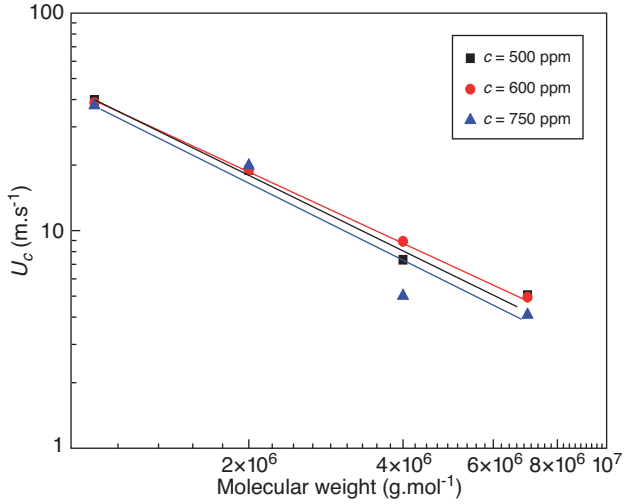

Figure 5

Mean critical velocity U_c as a function of molecular weight in inertial flow (API device), for dilute aqueous PEO solutions.

TABLE 2

k exponent and correlation coefficient for dilute PEO aqueous solutions degraded with API system

Concentration (ppm)	k exponent
500	$k = 1.10$, $R^2 = 0.989$
600	$k = 1.06$, $R^2 = 0.999$
750	$k = 1.22$, $R^2 = 0.957$

TABLE 3

Critical velocity and Reynolds number at the onset of degradation for dilute PEO aqueous solutions

	c = 500 ppm		c = 600 ppm		c = 750 ppm	
	U_c (m.s^{-1})	Re	U_c (m.s^{-1})	Re	U_c (m.s^{-1})	Re
POE 1 × 10^6 g.mol^{-1}	40	32 300	38.7	30 700	37.6	26 000
POE 2 × 10^6 g.mol^{-1}	19	9 300	18.9	9 000	19.9	7 300
POE 4 × 10^6 g.mol^{-1}	7.3	3 200	8.9	3 400	5.0	1 700
POE 7 × 10^6 g.mol^{-1}	5.1	1 500	4.9	1 530	4.1	1 090

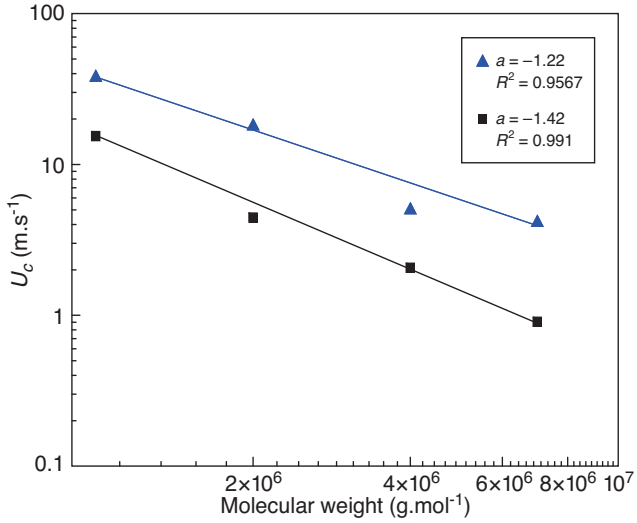

Figure 6

Critical velocity U_c as a function of molecular weight in laminar flow for 750 ppm PEO solutions in water (▲) and in 60/40 glycerine/water (■).

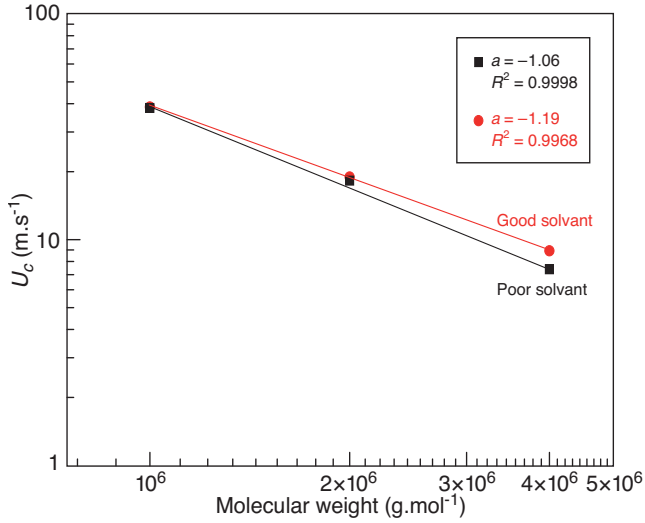

Figure 7

Mean critical velocity U_c as a function of molecular weight in inertial flow (API device), for dilute PEO solutions at c = 600 ppm prepared with water (●) and 20/80 glycerine/water (■).

2.1.2 Influence of Solvent Quality

Some published works have suggested that the mechanical degradation of polymers in poor solvents was easier than in good solvents [27-30]. In order to study the effect of solvent quality, experiments have been performed with the API device using 40/60 and 80/20 w/w water/glycerine solvent mixtures, glycerine being added to make the solvent poorer.

PEO solutions have been prepared in a 40/60 water/glycerine mixture at a concentration of 750 ppm in weight. The mean critical velocity U_c has been plotted as a function of M in Figure 6. A power law dependence has been obtained:

$$U_c \approx M_w^{-k} \tag{14}$$

with k = 1.4. Thus, the presence of glycerine has increased k, confirming that poor solvents facilitate mechanical degradation. These experiments were carried out under laminar conditions for all molecular weights tested, because of the rather high viscosity of a 40/60 water/glycerine solvent. Complementary tests were done with solvents containing less glycerine, therefore of lower viscosity, in order to investigate the influence of solvent quality on mechanical degradation taking place in turbulent regime. PEO dilute solutions have been prepared in 80/20 water/glycerine at a concentration of 600 ppm in weight. The critical mean velocity U_c as a function of M was shown to follow a power law:

$$U_c \approx M_w^{-k} \tag{15}$$

with k = 1.2 *(Fig. 7)*. Those results suggest that poor solvents facilitate mechanical degradation not only under laminar but also under turbulent conditions. Moreover, it seems that the mechanisms responsible for mechanical degradation in dilute polymer solutions are similar in laminar and turbulent flows (same k exponent). At last, it can also be noticed that the decrease in critical velocity due to the addition of glycerine is more pronounced for the highest molecular weight polymers.

2.2 Mechanical Degradation of Semi-Dilute Solutions

As already mentioned in introduction, polymers used as thickening agents in EOR applications may be added at relatively high concentrations in water, forming semi-dilute or concentrated solutions in which macromolecules are entangled. The study of mechanical degradation of PEO

TABLE 4

Critical velocity characterizing the onset of mechanical degradation for semi-dilute PEO aqueous solutions

	U_c (m.s^{-1})		
M_w (g.mol^{-1})	c = 2 000 ppm	c = 3 000 ppm	c = 4 000 ppm
1 × 10^6	36	29.5	17
2 × 10^6	17	16	6.35*
4 × 10^6	13*	7*	0.53*
7 × 10^6	3*	1.6*	
8 × 10^6	1.3*	0.7*	

* Degradation under laminar conditions.

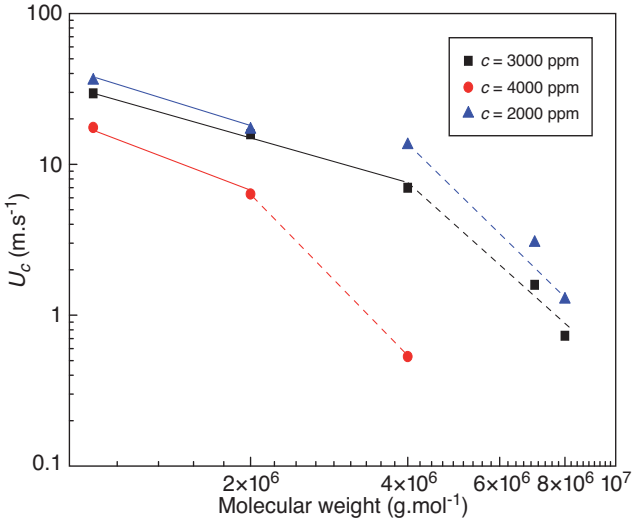

Figure 8

Critical velocity U_c as a function of molecular weight for semi-dilute aqueous PEO solution: straight line for turbulent flow and dotted line for laminar flow.

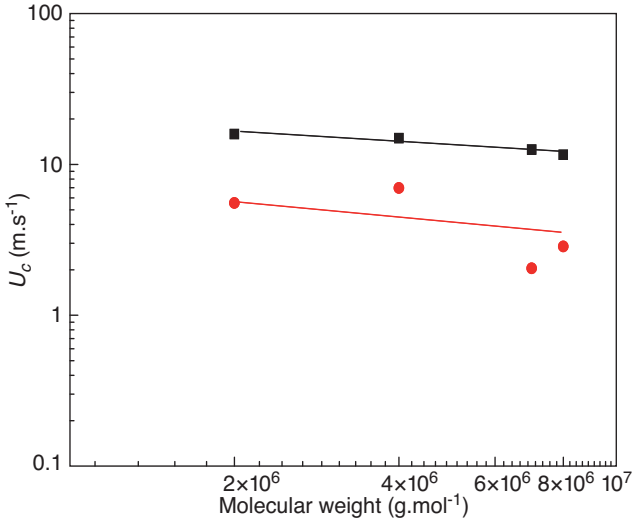

Figure 9

Critical velocity U_c as a function of molecular weight for semi-dilute PEO aqueous solutions in laminar flow at $c/c^* = 2$ (■) and $c/c^* = 3$ (●).

semi-dilute solutions was performed in this work. Three series of PEO solutions with molecular weight ranging from 10^6 to 8×10^6 g/mol were prepared in distilled water at concentrations of 2 000, 3 000 and 4 000 ppm. They have been degraded using the API device. The critical mean velocities have been gathered in Table 4.

The critical mean velocities have been plotted as a function of molecular weight in Figure 8. A power law dependence,

$$U_c \approx M_w^{-k},$$

has been obtained but with an exponent k different from that obtained for dilute solutions, in qualitative agreement with previous works on mechanical degradation of polyacrylamide in porous media [31]. For semi-dilute solutions the k exponent depends on the flow regime: $k = 1$ for turbulent regime and $k = 3$ for laminar flow *(cf. Tab. 5)*. Besides, it should be noticed that U_c values are lower for semi-dilute solutions than for dilute solutions, meaning that entangled polymer chains are particularly affected by mechanical degradation. The greater efficiency of mechanical degradation in semi-dilute solutions could be due to microscopic mechanisms (influence played by entanglement points) or to the macroscopic effect of viscosity. To discriminate these two potential effects, we plotted ηU_c as a function of M_w. In laminar regime, taking into account viscosity, k decreases from 3 to 2 but is still higher than 1, suggesting that the entanglement network certainly contributes to facilitate the mechanical degradation of polymer chains. Indeed, the presence of numerous network junctions increases the number of constraints exerted on a chain and also the number of potential scission points. This explanation is in accordance with the random scission scenario validated by GPC analysis for degraded semi-dilute polymer solutions [17].

However, the results of these experiments have been analyzed at constant concentration, hence corresponding to different entanglement densities for the different molecular weights investigated. Therefore, in order to get a more physically relevant analysis, results have been plotted at constant c/c^*, that is at fixed entanglement density. The critical velocities then appear to be the same for all molecular weights *(Fig. 9)*. This result shows that, for a given entanglement density, the mechanical degradation of polymer chains is not influenced by the molecular weight of the overall polymer but rather by the molecular weight between entanglements, which is in accordance with De Gennes's theory [32].

TABLE 5

k exponent and correlation coefficient for semi-dilute PEO aqueous solutions degraded with API system

	k exponent	
Concentration (ppm)	Turbulent flow	Laminar flow
2 000	$k = 1.08$ $R^2 = 1$	$k = 3.18$ $R^2 = 0.9646$
3 000	$k = 1.04$ $R^2 = 0.9942$	$k = 3.08$ $R^2 = 0.9738$
4 000	$k = 1.5$ $R^2 = 1$	$k = 3.6$ $R^2 = 1$

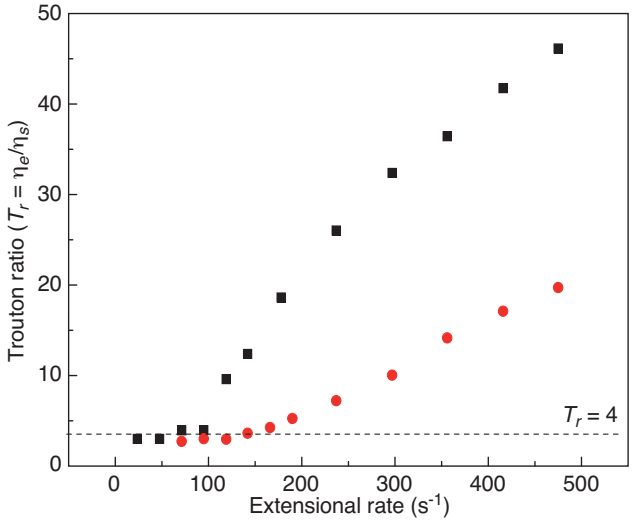

Figure 10

EVROC data for 2 000 ppm, 4 MDa-PEO aqueous solutions dissolved in Canadou (50:50): (■) native solution (●) solution degraded in laminar flow (API system).

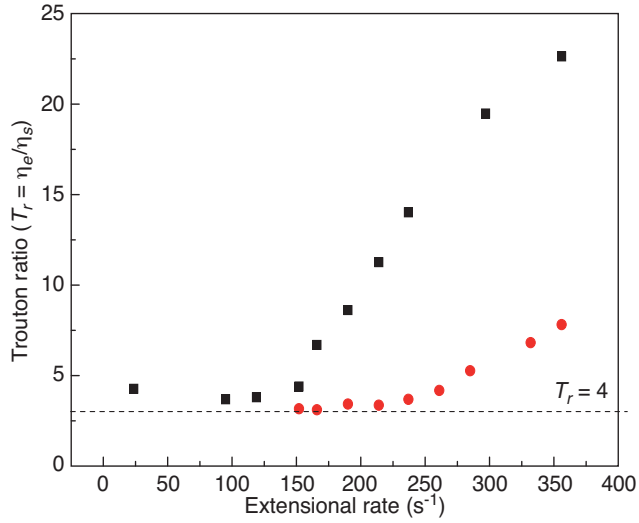

Figure 11

EVROC data for 600 ppm, 4 MDa-PEO aqueous solutions dissolved in Canadou (50:50): (■) native solution (●) solution degraded in turbulent flow (API system).

2.3 Effects of Mechanical Degradation on Rheological Properties

In order to study how mechanical degradation affects extensional properties, two representative degraded solutions (at the degradation onset corresponding to 10% Newtonian shear viscosity loss) were characterized with the EVROC® microfluidic device: a 600 ppm, 4×10^6 g/mol PEO dilute solution degraded in turbulent flow ($k = 1$) and a 2 000 ppm, 4×10^6 g/mol PEO semi-dilute solution degraded in laminar flow ($k = 3$). The extensional response of each degraded sample was compared to that of the non-degraded solution (*Fig. 10, 11*). To gain accuracy, a viscosifying agent (sugar syrup, at sample/sugar syrup weight ratio 50/50) was added to all samples after degradation and before testing with EVROC®. Shear and extensional viscosities have been measured; the data are presented in Table 6. Results show that Trouton number is in accordance with the theoretical value of 4 for a planar extension. The extensional viscosity of degraded samples is 10% lower than that of the non-degraded solution, which shows that extensional viscosities are affected by mechanical degradation to the same extent as shear viscosities.

TABLE 6

Comparison between shear and extensional viscosity of degraded and non-degraded PEO aqueous solutions at 23°C

Solutions	Degradation conditions	Shear viscosity (mPa.s)	Extensional viscosity (mPa.s)	Trouton ratio
PEO 4 MDa c = 600 ppm in water/sugar syrup = 50/50	Non degraded	7.2	27.6	4.06
	Degraded in inertial flow (API system)	6.1	24.2	3.96
PEO 4 MDa c = 2 000 ppm in water/sugar syrup = 50/50	Non degraded	13.2	52.5	3.97
	Degraded in laminar flow (API system)	11.5	42.0	3.70

At higher extensional rates, macromolecules or network get stretched and become more resistant to flow; pressure drops then strongly increase, as shown in Figures 10 and 11. Moreover, the results show that degraded samples lead to much smaller pressure drops than non-degraded ones. This significant effect of mechanical degradation might greatly impact the pushing efficiency in reservoir and would deserve further investigation.

CONCLUSION

The experimental study confirms that above a critical extensional rate $\dot{\varepsilon}_c$, polymer chains can break. The critical extensional rate $\dot{\varepsilon}_c$, characterizing the mechanical degradation onset, was shown to be a power-law function of the weight average molecular weight M_w:

$$\dot{\varepsilon}_c \approx M_w^{-k} \tag{16}$$

This scaling law, which is well established for dilute solutions in laminar flows, was shown to be also valid under turbulent conditions. For an abrupt contraction flow, for which chains are partially extended when they break, the exponent k was found to be equal to 1 both under laminar and turbulent conditions. Moreover, in such Fast Transient Flows, macromolecules have been shown to be affected by solvent quality: k was evidenced to be higher under poor solvent conditions. Besides, the mechanical degradation of longer chains was shown to be more affected by solvent quality.

Experiments were also performed on semi-dilute solutions, for which macromolecules are entangled in a network. In this case, k has been shown to depend on the flow regime: $k = 3$ in laminar flows and $k = 1$ in turbulent ones.

The results suggest that the mechanisms of mechanical degradation are not the same in dilute and semi-dilute regimes. Mechanical degradation is most likely enhanced in semi-dilute solutions, because of numerous mechanical constraints exerted on chains at entanglement points. As far as extensional properties of polymer solutions are concerned, they have been shown to strongly weaken after degradation, both for dilute and semi-dilute solutions.

Finally, the results of this work show that mechanical degradation may have a detrimental effect on polymer solutions. It particularly affects the longer chains in semi-dilute solutions, which are encountered in EOR applications. In order to validate chain scission scenarii, molecular weight distribution measurements are needed and will be carried out in a near future.

REFERENCES

1 Thomas S. (2008) Enhanced Oil Recovery - An Overview, *Oil Gas Sci. Technol.* **63**, 1, 9-19.

2 Fujita H. (1990) *Polymer Solutions*, Elsevier, Amsterdam.

3 Sorbie K.S. (1991) *Polymer-Improved Oil Recovery*, Blackie & Son, Glasgow.

4 Odell J.A., Keller A. (1986) Flow-Induced Chain Fracture of Isolated Linear Macromolecules in Solution, *J. Polym. Sci. B Polym. Phys.* **24**, 1889-1916.

5 Nguyen T.Q., Kausch H.H. (1988) Chain Scission in Transient Extensional Flow Kinetics and Molecular-Weight Dependence, *J. Non-Newton. Fluid Mech.* **30**, 2-3, 125-140.

6 Nghe P. (2009) Ecoulements de Fluides Complexes en Géométrie Microfluidiques, *Thèse*, Université Pierre et Marie Curie.

7 Nguyen T.Q., Kausch H.H. (1992) Chain Extension and Degradation in Convergent Flow, *Polymer* **33**, 12, 2611-2621.

8 Knudsen K.D., Cifre J.G.H., De LaTorre J.G. (1996) Conformation and Fracture of Polystyrene Chains in Extensional Flow Studied by Numerical Simulation, *Macromolecules* **29**, 10, 3603-3610.

9 Sim H.G., Khomami B., Sureshkumar R. (2007) Flow-induced Chain Scission in Dilute Polymer Solutions: Algorithm Development and Results for Scission Dynamics in Elongational Flow, *J. Rheol.* **51**, 6, 1223-1251.

10 Hsieh C.C., Park S.J., Larson R.G. (2005) Brownian Dynamics Modeling of Flow-induced Birefringence and Chain Scission in Dilute Polymer Solutions in a Planar Cross-slot Flow, *Macromolecules* **38**, 4, 1456-1468.

11 Vanapalli S.A., Islam M.T., Solomon M.J. (2005) Scission-induced Bounds on Maximum Polymer Drag Reduction in Turbulent Flow, *Phys. Fluids* **17**, 095108.

12 Nguyen T.Q., Kausch H.H. (1986) Degradation of a Polymer-Solution in Transient Elongational Flow - Effect of Temperature, *Colloid Polym. Sci.* **264**, 9, 764-772.

13 Odell J.A., Muller A.J., Narh K.A., Keller A. (1990) Degradation of Polymer-Solutions in Extensional Flows, *Macromolecules* **23**, 12, 3092-3103.

14 Odell J.A., Keller A., Muller A.J. (1992) Thermomechanical Degradation of Macromolecules, *Colloid Polym. Sci.* **270**, 4, 307-324.

15 Horn A.J., Merill E.W. (1984) Midpoint Scission of Macromolecules in Dilute Solution in Turbulent Flow, *Nature* **312**, 140-141.

16 Keller A., Muller A.J., Odell J.A. (1987) Entanglements in Semi-dilute Solutions as Revealed by Elongational Flow Studies, *Prog. Colloid Polym. Sci.* **75**, 179-200.

17 Muller A.J., Odell J.A., Carrington S. (1992) Degradation of Semidilute Polymer-Solutions in Elongational Flows, *Polymer* **33**, 12, 2598-2604.

18 Nghe P., Tabeling P., Ajdari A. (2010) Flow-induced Polymer Degradation Probed by a High throughput Microfluidic Set-up, *J. Non-Newton. Fluid Mech.* **165**, 7-8, 313-322.

19 Cogswell F.N. (1972) Converging Flow of Polymer Melts in Extrusion Dies, *Polym. Eng. Sci.* **12**, 1, 64-73.

20 Li Z., Yuan X.F., Haward S.J., Odell J.A., Yeates S. (2011) Non-linear dynamics of semi-dilute polydisperse polymer solutions in microfluidics: effects of flow geometry, *Rheol. Acta* **50**, 3, 277-290.

21 Rodd L.E., Scott T.P., Boger D.V., Cooper-White J.J., McKinley G.H. (2005) The Inertio-elastic Planar Entry Flow of Low-viscosity Elastic Fluids in Micro-fabricated Geometries, *J. Non-Newton. Fluid Mech.* **129**, 1-22.

22 Rodd L.E., Lee D., Ahn K.H., Cooper-White J.J. (2010) The Importance of Downstream Events in Microfluidic Viscoelastic Entry Flows: Consequences of Increasing the Constriction Length, *J. Non-Newton. Fluid Mech.* **165**, 1189-1203.

23 Rodd L.E., Cooper-White J.J., Boger D.V., McKinley G.H. (2007) Role of the Elasticity Number in the Entry Flow of Dilute Polymer Solutions in Micro-fabricated Contraction Geometries, *J. Non-Newton. Fluid Mech.* **143**, 2-3, 170-191.

24 Wang J., James D.F. (2011) Lubricated Extensional Flow of Viscoelastic Fluids in a Convergent Microchannel, *J. Rheol.* **55**, 5, 1103-1126.

25 Binding D.M. (1988) An Approximate Analysis for Contraction and Converging Flows, *J. Non-Newton. Fluid Mech.* **27**, 2, 173-189.

26 Pipe C.J., McKinley G.H. (2009) Microfluidic rheometry, *Mech. Res. Commun.* **36**, 1, 110-120.

27 Harrington R.E., Zimm B.E. (1965) Degradation of Polymers by Controlled Hydrodynamic Shear, *J. Phys. Chem.* **69**, 1, 161-175.

28 Johnson W.R., Price C.C. (1960) Shear Degrdation of Vinyl Polymers in Dilute Solution by High-speed Stirring, *J. Polym. Sci.* **45**, 145, 217-225.

29 Minoura Y., Kasuya T, Kawamura S. (1967) Degradation of Poly(ethylene oxide) by High-speed Stirring, *J. Polym. Sci. A-2 Polym. Phys.* **5**, 1, 125-142.

30 Rodriguez F., Winding C.C. (1959) Mechanical Degradation of Polyisobutylene Solutions, *Ind. Eng. Chem.* **51**, 10, 1281-1284.

31 Noik C., Delaplace P., Muller G. (1995) Physico-Chemical Characterics of Polyacrylamide Solutions after Mechanical Degradation through a Porous Medium, *SPE International Symposium on Oilfield Chemistry*, San Antonio, Texas, 14-17 Feb., *SPE Paper* 28954, pp. 93-100.

32 De Gennes P.-G. (1979) *Scaling Concepts in Polymer Physics*, Cornell University Press, New York.

33 Pipe C.J., Kim N.J., McKinley G. (2007) Microfluidic Rheometry on Chip, *4th Annual European Rheology Conference (AERC 2007),* Napoli, Italy, 12-14 April.

Final manuscript received in April 2012
Published online in January 2013

Copyright © 2013 IFP Energies nouvelles

Permission to make digital or hard copies of part or all of this work for personal or classroom use is granted without fee provided that copies are not made or distributed for profit or commercial advantage and that copies bear this notice and the full citation on the first page. Copyrights for components of this work owned by others than IFP Energies nouvelles must be honored. Abstracting with credit is permitted. To copy otherwise, to republish, to post on servers, or to redistribute to lists, requires prior specific permission and/or a fee: Request permission from Information Mission, IFP Energies nouvelles, fax. +33 1 47 52 70 96, or revueogst@ifpen.fr.