

# Influence of Grafted Copolymer Structures (Polyacrylamide-g-polyoxide) on Drag-Reduction

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**ABSTRACT:** This article reports the results of experiments to synthesize a family of copolymers based on polyacrylamide (PAAM), poly(ethylene oxide) (PEO), and poly(propylene oxide) (PPO) to obtain PAAM-g-PEO and PAAM-g-PPO copolymers with varied grafted chain lengths and contents. The influence of the chemical structure, composition, and molecular architecture on the drag-reduction properties was evaluated. The PAAM-g-PEO systems were prepared by solution polymerization using hydrogen peroxide as initiator, whereas the PAAM-g-PPO systems were obtained by micellar polymerization using potassium persulfate as initiator and sodium dodecyl sulfate as surfactant agent. The synthesized polymers were

characterized by carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR) and size-exclusion chromatography. The drag-reduction tests were carried out in a capillary viscosimeter in bench scale, and the performance was expressed in terms of drag-reduction percentage (%DR). The results suggest that, a determined chemical structure for each copolymer family evaluated probably promotes the ideal conformation of the chains under flow, favoring each polymer's drag-reduction action. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2502–2510, 2011

**Key words:** drag-reduction; water-soluble polymers; poly(alkylene oxide); macromonomer; copolymerization

## INTRODUCTION

The rapid growth of energy demand in many applications has increased interest in improving existing energy saving methods and developing new ones. Pumping fluids through pipes requires significant amounts of energy, and savings can be attained by techniques to reduce the fluid's drag inside the pipe.<sup>1</sup> These techniques have wide applications, such as in transport of crude oil in pipelines, especially when the distance is long or the volume is high<sup>2–5</sup>; fire fighting, to increase the water jet radius; management of runoff in storm drain systems<sup>2,3</sup>; district heating and cooling systems (DHC) to replace individual household systems, to reduce maintenance costs and minimize peak electricity demands<sup>6,7</sup>; spraying of pesticides in agricultural activities<sup>8</sup>; biomedicine, to improve blood flow in partially blocked arteries<sup>2,3</sup>; and oil drilling operations. In this last case, the drilling paths are becoming increasingly complex, particularly in deepwater offshore operations, horizontal drilling and drilling in unconsolidated formations, all of which require drilling fluids that, beyond

the normal lubrication functions, have low drag and can support high shear rates and temperatures without causing damage to the formation.<sup>9,10</sup>

In this context, the use of polymer additives to reduce flow resistance to minimize load loss has received considerable attention in recent years. The phenomenon of drag-reduction during transport of fluids is caused by the addition of a small quantity of a polymer with high molar mass to the fluid. This can significantly reduce the pressure loss during flow and the need for energy to maintain this pressure.<sup>6</sup> Some studies have demonstrated that the efficiency of the various polymers used is related to their flexible linear structures with high molar mass, enabling them to conform and align in the flow direction, thus reducing the drag.<sup>3,6,11</sup>

Many studies have been conducted to shed light on how polymer additives reduce drag. Among the factors studied are how the chemical structure, molar mass, and hydrodynamic volume of the polymer, interactions with solvents, thermodynamic conditions of the system, and level of turbulence influence the flow characteristics.<sup>3,12–15</sup> Various theories have been proposed to describe the drag-reduction mechanism, such as those that relate this phenomenon with the polymer's radius of gyration or salvation capacity.<sup>4,5</sup>

Studies to investigate drag-reduction have often focused on molecules of poly(ethylene oxide) (PEO), polyacrylamide (PAAM), and their derivatives. In

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recent years, interest has been growing particularly in PAAM derivatives, and significant scientific and commercial advances have been made, especially in applications involving properties of water-soluble associations, such as colloidal stability, emulsification, flocculation, formulation of paints, manufacture of paper and cosmetics, production of hydrocarbons, and formulation of drilling fluids.<sup>16,17</sup> In this area, research into the synthesis and characterization of polymers, such as PAAM-base copolymers, has been conducted to elucidate the way they reduce drag and thus to contribute to the development of new technologies to improve operational efficiency and reduce costs of oil exploration and production.<sup>18-20</sup>

Studies reveal that the relationship between the structure of a PAAM and its copolymers affects its drag-reducing properties. The side chain of polymers influences the friction reduction behavior, as has been verified by the favoritism of the presence of the linear pendant and long groups, causing the molecules to be more flexible. However, more voluminous side chains do not present very significant results.<sup>6</sup>

These last observations prompted this study, which evaluates the influence of different structures of graft copolymers of PAAM and PEO (hydrophilic character) or poly(propylene oxide) (PPO) (hydrophobic character), as pendant chains, on the drag-reducing properties of their aqueous solutions when submitted to flow in a capillary tube system. Due to the dissimilar characteristics of the pendant chains chosen, it is desired to observe if there is some influence of the conformation of the pendant chain on the drag-reduction qualities. Laboratory-synthesized samples of PAAM grafted with polyoxides were used, with varying chain lengths and incorporation contents in the main chain. Then the drag-reduction percentages were correlated with the structure, architecture, and composition of the molecules.

## EXPERIMENTAL

### Synthesis

A family of PAAM copolymers grafted with poly(alkylene oxide) by varying both the molar mass of the copolymer and the type, content, and molar mass of the grafted chain were obtained. The PEO used were three commercial brands: Ultrapeg 300 and Ultrapeg 600, with molar mass of  $\sim 300$ – $600$  g/mol, respectively, and Atepeg 1000, with molar mass of  $\sim 1000$  g/mol, supplied by Oxiteno (São Paulo, SP, Brasil). Two commercial brands of PPO were also used: Dowfroth 250 and Polyglycol Fluent-Mat 612, with respective molar mass of  $\sim 300$  g/mol and  $1000$  g/mol, supplied by Dow (São Paulo, SP, Brasil). Finally, the 97% acrylamide, stabilized with cupric ions, was supplied by Sigma Aldrich (São Paulo, SP).

Before synthesizing the copolymers, it was necessary to carry out a series of preliminary steps to obtain the poly(alkylene oxide) macromonomers, namely PEO methacrylate and PPO methacrylate. The step to obtain the macromonomers was carried out in two substeps: (1) synthesis of methacryloyl chloride, and (2) synthesis of poly(alkylene oxide) methacrylate.

### Synthesis of methacryloyl chloride

This consisted of reacting benzoyl chloride and methacrylic acid in a molar proportion of 1.4 : 1 along with 10% (p/v) of hydroquinone. The final product was distilled from the system at a temperature range of 80 to 110°C. The methacryloyl chloride was then redistilled at 98°C.

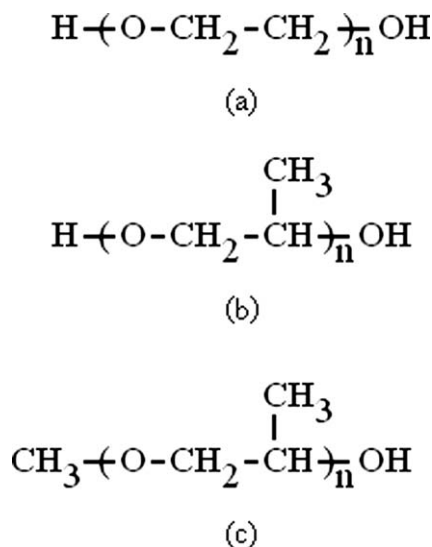
### Synthesis of poly(alkylene oxide) methacrylate

The functionalization of the poly(alkylene oxide) for formation of the poly(alkylene oxide) methacrylate consisted of reacting methacryloyl chloride and polyoxide, previously dried in toluene, in the presence of pyridine (sequestration agent of chloridric acid). Figure 1 shows the chemical structure of the poly(alkylene oxides) used in this work, which have mono and difunctional structures.

The macromonomer synthesis method varied slightly in function of the functionality of the poly(alkylene oxide). To modify the difunctional polyoxides (PEO 600, PEO 1000, and PPO 1000), it was used molar proportions of 0.54 : 1 and 0.5 : 1 of pyridine and methacryloyl chloride, respectively, for PEO and PPO, whereas to modify the monofunctional polyoxide (PPO 300), molar proportions of 1.04 : 1 and 1 : 1 of pyridine and methacryloyl chloride were used, respectively, for PEO and PPO. The reactions were carried out in dry toluene, under stirring in an ice bath until the formation of precipitated pyridine chloride. The pyridine hydrochloride was separated from the polyoxide macromonomer solution by filtration. The toluene present in the solution was removed by rotating evaporation at a temperature of  $65 \pm 5^\circ\text{C}$ .<sup>21,22</sup>

### Synthesis of the copolymers

The acrylamide and poly(alkylene oxide) copolymers were obtained by free radical polymerization in aqueous solution, with initiation by thermal dissociation. The reactions were carried out at 65°C, in distilled and deionized water deaerated for 15 min in an ultrasound bath under a nitrogen atmosphere. The systems composed of acrylamide and PEO (PAAM-g-PEO) were obtained by polymerization in solution, using 3% acrylamide and hydrogen



**Figure 1** Chemical structure of (a) difunctional PEO, (b) difunctional PPO, and (c) monofunctional PPO.

peroxide as the initiator in mass proportions from 0.3 to 1.5% in relation to the acrylamide. The systems composed of acrylamide and PPO (PAAM-g-PPO) were obtained by micellar polymerization, using acrylamide and potassium persulfate as the initiator, in the same concentrations mentioned, and sodium dodecyl sulfate (SDS) as surfactant agent, in a concentration of 3%.

The polyoxide feed content was varied up to 40% by mass in relation to the total monomer concentrations. In the case of copolymerization with the difunctional polyoxide macromonomers, double the amount of polyoxide was added in relation to the theoretical quantity calculated to obtain the copolymer in the desired mass proportion. As this was copolymerization with a monofunctional polyoxide macromonomer, the quantity of macromonomer utilized was equal to the theoretical quantity calculated to obtain the copolymer in the desired mass proportion. The copolymers were purified by successive dissolutions in distilled and deionized water and precipitations in methanol.

### Characterization

#### Size-exclusion chromatography (SEC)

The commercial polyoxides and synthesized polymers were characterized regarding average molar mass by SEC, using a Waters model 600 C chromatograph with four Polysep-GFC-P columns in series, covering a broad molar mass range. A quantity of 50  $\mu\text{L}$  was injected of each polymer solution at 0.5% (p/v) in the mobile phase, which consisted of a saline solution of 0.1M sodium nitrate ( $\text{NaNO}_3$ ) and 0.02% (p/v) sodium azide ( $\text{NaN}_3$ ), utilized as a fungicide agent. The samples injected were filtered in a

Durapore (Millipore) hydrophilic membrane with 0.45- $\mu\text{m}$  mesh. The working flow was 0.6 mL/min at an oven temperature and refraction index detector temperature of 40°C. Six PAAM standard samples, supplied by American Standard, were used for calibration. The number average molar mass ( $\langle M_n \rangle$ ) and weight average molar mass ( $\langle M_w \rangle$ ), in g/mol, were: (1) 4,250,000 and 9,000,000; (2) 465,300 and 1,140,000; (3) 141,000 and 367,000; (4) 44,400 and 71,000; (5) 13,700 and 21,900; (6) 7,600 and 11,530, respectively.

### Carbon 13 nuclear magnetic resonance (13 C-NMR)

The synthesized copolymers were characterized regarding composition by carbon 13 nuclear magnetic resonance (13 C-NMR), at a frequency of 75 MHz, using a Varian Mercury Vx 300 device. The analysis was performed with the polymer solutions at a concentration of  $\sim 50$  g/L in distilled and deionized water/deuterated water. The standard solvent TSP was used as calibration reference.

### Drag-reduction performance

#### Load loss test

The load loss test was performed in a capillary viscosimeter and consisted of forcing the polymer solution through a tube under pressure, according to the method described in a previous work.<sup>23</sup>

The concentrations evaluated were 0.05, 0.10, and 0.15 g/L. The test was conducted in an ample flow speed range, which was achieved by varying the input pressure from 5 to 50 psi with intervals of 2.5 psi, and from 50 to 65 psi with intervals of 5 psi. Therefore, the behavior of the polymer solution regarding load loss per capillary length was determined in an ample Reynolds number range.

The measurements were taken in duplicate for each solution. The distilled and deionized water was analyzed before the measurements of each solution to verify the cleanliness of the tube so that the results could be used to calculate the relative drag-reduction percentage.

### Determination of the rheological parameters of the polymer solutions

Aliquots of the polymer solutions (prepared for the drag-reduction test) were set aside before being passed through the capillary viscosimeter, and their rheological behavior was classified by the shape of the curve obtained in the continuous shear tests. The rheological measurements were made in a Haake RheoStress 600 rheometer with a double-gap concentric cylinder system (model DG 41 Ti) (inner cylinder: internal diameter = 35.5 mm and external

diameter = 36.0 mm; outer cylinder: internal diameter = 42.8 mm and external diameter = 43.4 mm; inner cylinder height = 55.0 mm; gap = 5.10 mm; sample volume = 6.3 cm<sup>3</sup>).

In this system, the recipient containing the sample remains still while the cylindrical sensor, immersed in the system, is rotated. The experiments were carried out at 25.0 ± 0.1°C controlled with a thermostatic bath (Haake C25P) coupled to the rheometer.

The samples were analyzed in a shear rate interval of 1000 to 5000 s<sup>-1</sup>, in both directions, and the apparent dynamic viscosity values [Pa.s] and shear rates [s<sup>-1</sup>] were calculated and recorded using the RheoWin program. This enabled plotting the flow rheogram for a defined shear rate interval ( $\dot{\gamma}$ ), which permitted inferring the fluid's behavior and thus defining the mathematical regression that should be applied.

In this work, the regression of the apparent dynamic viscosity ( $\eta$ ) versus shear rate ( $\dot{\gamma}$ ) curves was done through the Ostwald de Waale or power law models. The rheological parameters K [Pa.s<sup>n</sup>], called the consistency index, which indicates the fluid's degree of resistance under flow, and n [adimensional], called the flow index, which physically indicates the separation of the fluid from the Newtonian model, were calculated according to eq. (1), utilizing the RheoWin Data software.

$$\eta = K \times \dot{\gamma}^{n-1} \quad (1)$$

### Determination of the drag-reduction percentage (%DR)

The mathematical treatment of the data obtained by the load loss test and the rheological parameters, until obtaining the load loss curve per the capillary length (DP/L) in function of the Reynolds number, followed the procedure described by Figueiredo, 2006.<sup>23</sup> The performance of the synthesized copolymers as drag-reducing additives was evaluated in terms of drag-reduction percentage, according to eq. (2).

$$\%DR = \frac{\left(\frac{DP}{L}\right)_{\text{water}} - \left(\frac{DP}{L}\right)_{\text{polymerdispersion}}}{\left(\frac{DP}{L}\right)_{\text{water}}} \times 100 \quad (2)$$

where  $\left(\frac{DP}{L}\right)_{\text{water}}$  = pressure loss per capillary length in function of the Reynolds number, for water flow in the capillary viscosimeter;  $\left(\frac{DP}{L}\right)_{\text{polymerdispersion}}$  = pressure loss per capillary length for flow of the polymer dispersion in the capillary viscosimeter.

## RESULTS AND DISCUSSION

### Characterization of the composition of the copolymers

The polyoxides used in this work were first characterized to confirm their molar masses by <sup>1</sup>H-NMR, following the calculation method described in a previous work.<sup>21</sup> Based on the number of repeated units in each sample, molar masses of 580, 1080, 320, and 1060 were determined, respectively, for PEO600, PEO1000, PPO300, and PPO1000, confirming the nominal molar mass values.

The composition of each copolymer was calculated as described previously.<sup>22</sup> Table I presents the mass composition values of the comonomers at the feed (theoretical) and the values calculated for the copolymers in terms of mass composition. Copolymers were obtained with compositions varying in the range of ~ 1–30 wt % of graft chain.

In general the poly(alkylene oxide) content in the copolymer was less than that in the feed, which suggests that an excess quantity of polyoxide must have been fed into the system in relation to the desired composition for the copolymer.

### Characterization of the molar mass of the copolymers

Table II presents the results of the characterization of the average numerical molar mass ( $\langle M_n \rangle$ ) obtained by SEC. The polydispersion values are in the range of 2–5, which are characteristic of the polymerization process employed.

The number average molar mass values obtained ranged from 30 × 10<sup>3</sup> to 200 × 10<sup>3</sup> g/mol, respectively, and for an initiator concentration range of ~ 1.5–0.3%. A significant change in the average molar mass values was only obtained when the initiator was nearly tripled. In other words, a small reduction of the initiator concentration, such as from 0.5 to 0.3% or from 1.5 to 1.3%, was not enough to considerably increase the average molar mass of the molecules. Therefore, to obtain greater average molar mass values than those achieved in this study, some modifications in the polymerization process would be necessary, such as changing the initiation system. In particular, polymerizations by redox initiation with cerium ions are indicated to obtain PAAM with higher molar mass.<sup>24</sup>

A comparison of the results obtained for two syntheses (#7 and #8), carried out under the same conditions and that produced PAAM-g-PEO 1000 copolymers shows that the average molar mass values obtained were very different ( $\langle M_n \rangle = 39,000$  and 113,000), suggesting that the control of the structure obtained depend on better control of the synthesis process. As the main goal of this work was to obtain families of copolymers with varied compositions and molar masses, to correlate the influence of these

**TABLE I**  
**Mass Composition of the Monomers at the Feed and of the**  
**Respective Copolymers Obtained**

Polymer (%) <sup>a</sup>	Pendant chain (g/mol)	Composition at the feed (wt %) AAM : PO <sup>b</sup>	Composition of the copolymer (wt %) PAAM : PO <sup>b</sup>
PAAM-g-PEO (1.5%)	1,000	70 : 30	87 : 13
		90 : 10	96 : 4
PAAM-g-PEO (1.3%)	600	90 : 10	90 : 10
PAAM-g-PEO (0.5%) (1)		95 : 5	95 : 5
PAAM-g-PEO (0.5%) (2)		95 : 5	95 : 5
PAAM-g-PEO (0.5%) (3)		90 : 10	89 : 11
PAAM-g-PEO (0.5%) (4)		90 : 10	96 : 4
PAAM-g-PEO (0.5%) (5)		90 : 10	95 : 5
PAAM-g-PEO (0.5%)		70 : 30	62 : 38
PAAM-g-PEO (0.3%)		80 : 20	88 : 12
PAAM-g-PEO (1.3%)		80 : 20	84 : 16
		90 : 10	95 : 5
PAAM-g-PEO (0.3%)	1,000	95 : 5	>1% PO
PAAM-g-PPO (0.3%)		60 : 40	75 : 25
		70 : 30	84 : 16
		80 : 20	83 : 18
		90 : 10	89 : 11
		95 : 5	96 : 4
		95 : 5	95 : 5
PAAM-g-PPO (0.4%)		60 : 40	72 : 28
		70 : 30	76 : 24
		90 : 10	92 : 8
PAAM-g-PPO (0.3%)	300	60 : 40	74 : 26
		80 : 20	86 : 14
		90 : 10	89 : 11
		80 : 20	84 : 16
		70 : 30	78 : 22

<sup>a</sup> Initiator composition in wt % in relation to the acrylamide.

<sup>b</sup> AAM = acrylamide, PAAM = polyacrylamide, PO = poly(alkylene oxide).

variables with their performance as drag-reducers in aqueous solutions, it was not place emphasis on controlling the reaction. The objective in terms of synthesis was achieved, since it was obtained with varied molar masses containing varied graft chain contents with different chemical structures (hydrophilic or hydrophobic) and sizes. As the results obtained by SEC depend not only on the length of the molecule but also on the conformation, the real molar mass of the copolymers should be higher than the so obtained value, because the calibration was made with PAAM that is a linear molecule. However, in general, it is possible to compare the results obtained by SEC if the tendency of molecules expansion is the same. In this work, it is not possible to make a straight comparison between PAAM-g-PEO and PAAM-g-PPO molar masses, because of their differences concerned to the interaction with the solvent: PAAM-g-PEO copolymers present higher interaction with water than PAAM-g-PPO ones.

### Performance in reducing drag

As discussed previously,<sup>23</sup> the results for drag-reduction obtained in our system do not reproduce

the values obtained in large scale loop, using about 200 L of polymer solution. However, it has been useful for testing different polymers that were synthesized in bench scale. The results obtained in our system are far below those normally reported in the literature<sup>25,26</sup> (~ 80% for PHPA).

Figure 2 shows the DP/L versus Re curves for the copolymer solution PAAM-g-PEO 1000 95 : 5 (2), for illustration purposes. It can be seen that the higher the concentration of PAAM-g-PEO 1000 95 : 5 (2), the better the drag-reduction performance is. In general, the other polymers showed the same performance with increasing concentration in the range studied. The influence of the polymer concentration parameter on drag-reduction is frequently reported in the literature.<sup>3</sup> Besides this, another result here in agreement with the literature<sup>3,8,27,28</sup> is that, the drag-reduction is more pronounced in regions with higher Reynolds number, that is, regions of greater turbulence, no matter what the polymer solution.

Table II also presents the drag-reduction percentage results for the aqueous copolymer solutions only at a concentration of 0.10 g/L and with Reynolds number of 7000. For purposes of correlation, the

TABLE II  
Mass Composition and Average Numerical Molar Mass of the Copolymers and Drag-Reduction Percentage of Their Aqueous Solutions at 0.1 g/L

#	Polymer (%) <sup>a</sup>	MM <sup>b</sup> of PO (g/mol)	PAAM : PO <sup>c</sup> composition	$\langle M_n \rangle$ (g/mol)	% DR Re = 7000
1	PAAM-g-PEO (1.5%)	1,000	87 : 13	62,000	33.1
2			96 : 4	96,000	35.5
3	PAAM-g-PEO (1.3%)		90 : 10	140,000	43.9
4	PAAM-g-PEO (0.5%) (1)		95 : 5	103,000	30.1
5	PAAM-g-PEO (0.5%) (2)		95 : 5	135,000	50.5
6	PAAM-g-PEO (0.5%) (3)		89 : 11	132,000	44.4
7	PAAM-g-PEO (0.5%) (4)		96 : 4	39,000	32.7
8	PAAM-g-PEO (0.5%) (5)		95 : 5	113,000	47.9
9	PAAM-g-PEO (0.5%)		62 : 38	83,000	16.7
10	PAAM-g-PEO (0.3%)		88 : 12	183,000	35.9
11	PAAM-g-PEO (1.3%)	600	84 : 16	35,000	16.2
12			95 : 5	49,000	40.0
13	PAAM-g-PEO (0.3%)		>1% de PO	210,000	64.9
14	PAAM-g-PPO (0.3%)	1,000	75 : 25	<sup>d</sup>	12.3
15			84 : 16	169,000	44.4
16			83 : 17	187,000	44.7
17			89 : 11	189,000	48.5
18			96 : 4	197,000	22.7
19			95 : 5	202,000	39.4
20	PAAM-g-PPO (0.4%)	300	72 : 28	84,000	45.3
21			76 : 24	142,000	56.0
22			92 : 8	146,000	44.9
23	PAAM-g-PPO (0.3%)		74 : 26	136,000	50.9
24			86 : 14	118,000	33.9
25			89 : 11	278,000	52.7
26			84 : 16	182,000	34.6
27			78 : 22	115,000	68.1 <sup>e</sup>
28	PAAM	–	–	182,000	44.8

<sup>a</sup> Initiator composition in wt % in relation to the acrylamide.

<sup>b</sup> MM = molar mass.

<sup>c</sup> AAM = acrylamide, PAAM = polyacrylamide, PO = poly(alkylene oxide).

<sup>d</sup> Not calculated.

<sup>e</sup> Result obtained without duplication.

mass compositions of the copolymers are once again highlighted in this table.

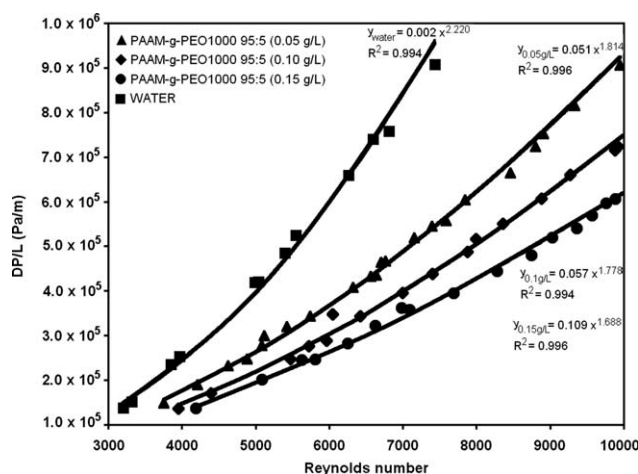
A general evaluation of the results shows that the drag-reduction performance varied as a function of the molar mass, as expected, as well as of the chemical constitution and the composition of the copolymers. Good performances were obtained regardless of the hydrophilicity of the grafted chain in the hydrophilic chain of the PAAM. This can be seen in the values of ~ 50% both for sample #5 and for sample #23, which respectively contain graft chains of PEO (hydrophilic) and PPO (hydrophobic).

To better explore the information obtained, the groups were separately analyzed below. This analysis shows that much of what has been published on the subject was also observed in this study, evidencing the reliability of our results. However, some new aspects are also present here.

With respect to the influence of the molar mass, as expected a higher molar mass clearly enhanced the copolymer's performance. However, this correlation is only valid when analyzing copolymers with the same structure, as showed in Figure 3(a). Copoly-

mers #2, #5, #7, and #8 have a PAAM-g-PEO 1000 structure (compositions ~ 95 : 5), and their performances vary essentially with their molar mass. Likewise, copolymers #12 and #13 have a PAAM-g-PEO 600 structure (compositions ~ 95 : 5) and their performances also vary essentially with their molar mass. The same occurs with the copolymers containing PPO300 as graft chain (compositions ~ 75 : 25) (#20 and #21), as shown in Figure 3(b). If these three copolymer families are mutually compared in terms of the influence of molar mass, no satisfactory correlation is observed. For example, samples #2, #12, and #20 have increasing molar mass in the order #12 < #20 < #2 and their performances, expressed as drag-reduction percentage, follow a different rising order: #2 < #12 < #20. Hence the statement that "the drag-reduction increases with increasing molar mass of the polymer" is only valid for comparisons within a single family of copolymers with the same architecture and composition. In reality, the molar mass is only one of the factors that affect drag-reduction, acting together with other factors.

Despite the need for more %DR results from testing copolymers with other molar mass values,

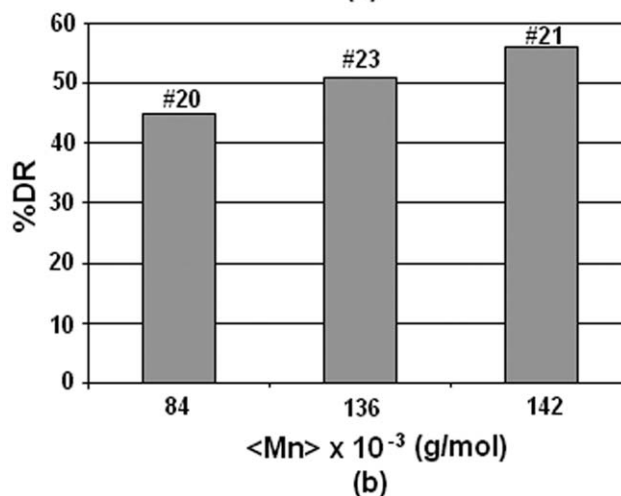
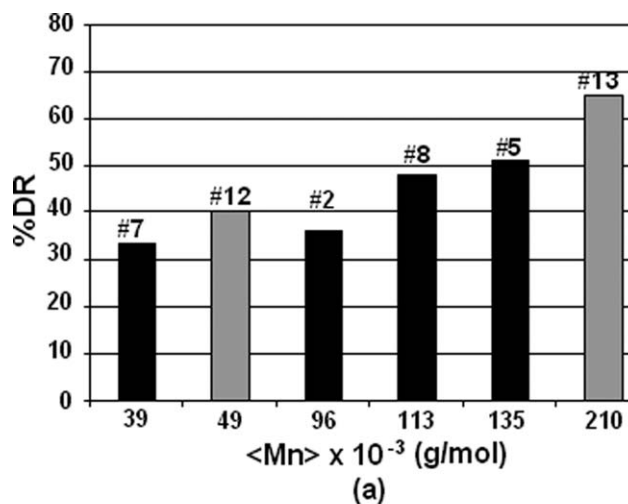


**Figure 2** Load loss curve per capillary length (DP/L) as a function of the Reynolds number (Re) for the aqueous solution, at 0.1 g/L, of PAAM-g-PEO1000 95 : 5 (# 5).

besides more specific tests, the results obtained for the systems evaluated here fit the theory of Brostow et al.<sup>4</sup> well regarding the solvation number, when analyzing a family of copolymers with the same chemical nature: types of mers and type and length of the graft chain.

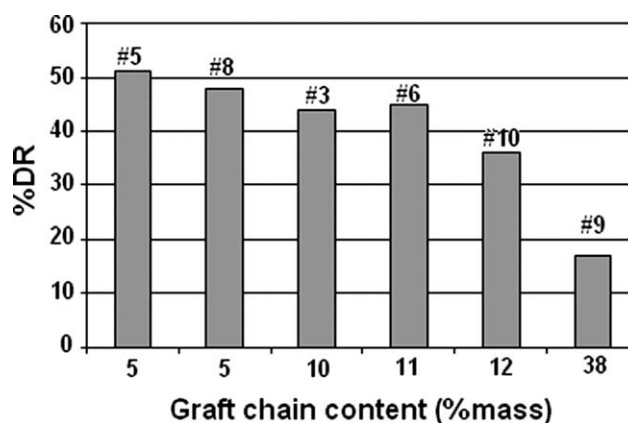
As mentioned earlier, besides the molar mass, the presence of side chains with different structures also is investigated in this study. The molecules difference in terms of hydrophilicity was chosen, as it provides different molecule conformations in solution.<sup>29</sup> A separate evaluation of the drag-reduction percentages within the PAAM-g-PEO family and within the PAAM-g-PPO family, seeking to correlate the drag-reduction with the content and length of the side chains, shows different behaviors in function of the type of grafted chain used: hydrophilic (PEO) or hydrophobic (PPO). The hydrophilicity of the polymer is related to the hydrophilicity of the respective monomers, when comparing similar molar mass ( $3 \times 10^2$ – $10^3$  g/mol). So, ethylene oxide, that presents a higher solubility parameter ( $\delta = 21.55 \text{ MPa}^{1/2}$ )<sup>30</sup> than propylene oxide ( $\delta = 18.71 \text{ MPa}^{1/2}$ ),<sup>30</sup> will produce a more hydrophilic polymer chain.

An evaluation of the PAAM-g-PEO molecules shows that the increasing in PEO length (# 12 < # 7) and PEO content (# 5 < # 10), within the range analyzed, appears to favor a relatively more “open” conformation, due to the high solubility of the PEO chains in water. This likely contributes to reduce the %DR. Copolymers #12 and #7 have similar graft chain contents and molar masses, and the drag-reduction percentage is higher for the sample with a shorter pendant chains. With respect to the influence of the variation of the graft chains’ content, it can be seen in Figure 4, for the copolymers with graft chains of PEO1000, that as decreasing graft chain content is observed the reduction of %DR. Copoly-



**Figure 3** Drag-reduction percentage in function of molar mass of the copolymers: (a) PAAM-g-PEO (~ 95 : 5) with PEO length of 1000 g/mol in black and 600 g/mol in gray; (b) PAAM-g-PPO 300 (~ 75 : 25). The samples related to # are listed in Table II.

mer # 5 (5% graft), although having a lower molar mass than copolymer # 10 (12% graft), produces much better drag-reduction. It seems that similar



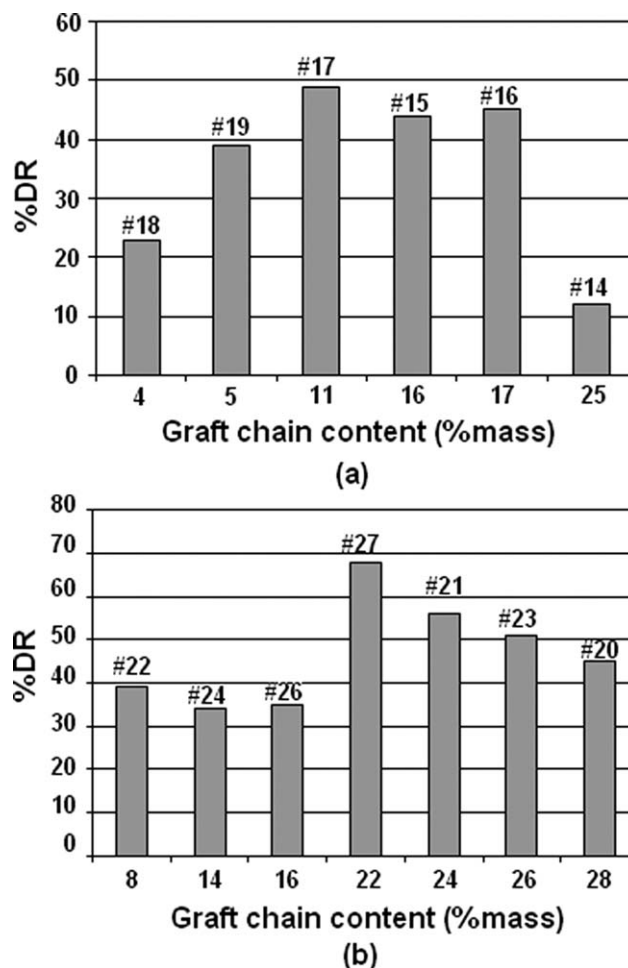
**Figure 4** Drag-reduction percentage in function of graft chain content of the copolymer PAAM-g-PEO1000.

behavior occurs for the copolymers with graft chains of PEO 600: copolymer # 12 (5% graft) has a higher drag-reduction percentage (40.0%) than copolymer # 11 (16% graft) (16.2%), even though they have similar molar masses ( $\sim 40,000$  g/mol).

It can thus be concluded that in the case of copolymers with PEO (hydrophilic) grafts, within the content and chain length ranges analyzed shorter pendant chains in lower content likely allow a conformation that, when submitted to flow, making them more favorable as drag-reducing agents.

The molecules with graft chains of PPO (# 21) performed well, even though they had a tendency to present a smaller hydrodynamic volume, in relation to the homopolymer chains of PAAM (# 28) with similar molar mass, due to the unfavorable solvation conditions for the hydrophobic segments in the aqueous medium. This disagrees with other findings in the literature,<sup>13</sup> where worse drag-reduction percentages have been observed for less favorable solvent medium conditions. According to the literature, different solvent conditions tend to influence the performance of a single structure due to its solubility in a particular solvent, and consequently its hydrodynamic volume. Here we evaluate the drag-reduction effect of different structures in a single solvent (water). This result suggests that besides a molecule's hydrodynamic volume, its conformation under flow is a relevant parameter that can influence its drag-reduction performance. This conformation can be associated with the theory of solvation number, so finding the ideal conformation might be possible by evaluating the solvation number, as suggested by Brostow et al.<sup>4</sup>

With respect to the influence of the content and length of the graft chains in the case of the PAAM-g-PPO copolymers, we only observed differences regarding the variation of content, not the chain length, within the range studied. In this case, there appears to be an optimum incorporation content to attain the best drag-reduction, as showed in Figure 5(a,b), respectively, for PAAM-g-PPO1000 and PAAM-g-PPO300. However, this optimal content varies in function of the length of the graft chain: in the PAAM-g-PPO 1000 series, the maximum content reached was at  $\sim 11\%$  of grafts, whereas for the PAAM-g-PPO300 series, this maximum content was observed at  $\sim 22\%$  of grafts. This behavior may be related to the hydrophilicity of the structure analyzed, suggesting that the copolymer's solubility is also a factor that influences its drag-reduction performance. This observation once again leads to the possibility that there is an ideal conformation, which provides the best performance. However, additional investigations are necessary, using broader ranges of graft chain lengths and contents in the copolymer, to find a closer relationship between these contributions.



**Figure 5** Drag-reduction percentage in function of graft chain content of the copolymer PAAM-g-PPO, presenting graft chain molar mass of (a) 1000 and (b) 300.

## CONCLUSIONS

Based on the systematic study carried out for synthetic PAAM-g-polyoxide polymers, it is possible to suggest that any type of molecule, either water-soluble or organophilic, natural or synthetic, can be modified with hydrophilic or hydrophobic side chains to obtain a product that performs well in reducing drag in a determined type of fluid. The choice of the type of modification of hydrophilic polymers should be associated with the facility of the industrial process to obtain each type, considering the following observations: (1) modification grafting side chains that are also hydrophilic should be done with low content and short pendant chain; (2) the more hydrophobic side chains should have a composition with a smaller proportion the longer the length of the pendant chain is, to produce the best solvation conditions. The choice of the additive to be synthesized for a specific purpose should also consider its compatibility with the fluid, cost, toxicity, and biodegradability. It is important to stress



that the parameters investigated in this study are limited to the ranges tested.

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## References

1. Cho, S.; Tae, C.; Zaheeruddin, M. *Energy Conversion Manage* 2006, 48, 913.
2. Suksamranchit, S.; Sirivat, A. *Chem Eng J* 2006, 128, 11.
3. Suksamranchit, S.; Sirivat, A.; Jamieson, A. M. *Colloid Interface Sci* 2005, 294, 212.
4. Brostow, W.; Majumdar, S.; Singh, R. P. *Macromol Rapid Commun* 1999, 20, 144.
5. Brostow, W.; Lobland, H. E. H.; Reddy, T.; Singh, R. P.; White, L. *J Mater Res* 2007, 22, 56.
6. Zhang, Y.; Schmidt, J.; Talmon, Y.; Zakin, J. L. *J Colloid Interface Sci* 2005, 286, 696.
7. Li, F.; Kawaguchi, Y.; Yu, B.; Wei, J.; Hishida, K. *Int J Heat Mass Transfer* 2007, 51, 835.
8. Li, C.; Sureshkumar, R.; Khomami, B. *J Non-Newtonian Fluid Mech* 2005, 140, 23.
9. Martins, A. L.; Massarani, G.; Waldmann, A. T. A.; Costa, F. G. *Avaliação da invasão de fluidos de perfuração em rochas reservatório de petróleo; ENEMP: São Carlos*, 2002.
10. Ferreira, M. V. D. *Seminários de Mestrado, IMA/UFRJ: Rio de Janeiro*, 2003; p 51.
11. Cowan, M. E.; Garner, C.; Hester, R. D.; McCormick, C. L. *J Appl Polym Sci* 2001, 82, 1222.
12. Camail, M.; Magaillan, A.; Maesano, J. C.; Thuret, S.; Vernet, J. L. *Polymer* 1998, 39, 3187.
13. Bizotto, V.; Sabadini, E. In *Redução de atrito hidrodinâmico por agentes poliméricos e a cinética de degradação molecular; 4º PDPETRO: Campinas*, 2007.
14. Nakken, T.; Tande, M.; Nystron, B. *Eur Polym J* 2004, 40, 181.
15. Brostow, W. *J Ind Eng Chem* 2008, 14, 409.
16. Muller, A. J.; Garcés, Y.; Torres, M.; Scharifker, B.; Sáez, A. E. *Colloid Polym Sci* 2003, 281, 73.
17. Argillier, J. F.; Audibert, A.; Lecourtier, J.; Moan, M.; Rousseau, L. *Colloids Surf* 1996, 113, 247.
18. Lucas, E. F.; Mansur, C. R. E.; Spinelli, L.; Queirós, Y. G. C. *Pure Appl Chem* 2009, 81, 473.
19. Ghannam, M. T.; Esmail, M. N. *J Appl Polym Sci* 1998, 69, 1587.
20. Ghannam, M. T. *J Appl Polym Sci* 1999, 72, 1905.
21. Lucas, E. F.; Oliveira, C. M. F. *Polym Bull* 1990, 24, 363.
22. Lucas, E. F.; Silva, C. X.; Pereira, G. P. *Polym Bull* 1997, 39, 73.
23. Figueiredo, M. S.; Almeida, L. C.; Costa, F. G.; Clarisse, M. D.; Lopes, L.; Leal, R.; Martins, A. R.; Lucas, E. F. *Macromol Symp* 2006, 245, 260.
24. Guimaraes, M. J. O. C.; Gomes, A. S.; Coutinho, F. M. B. *J Polym Sci Pol Chem* 1986, 24, 2131.
25. Demirdal, A. K. *Experimental Investigation of Friction Pressure Reducers for Improved Drilling Hydraulics*, Ms Thesis, University of Tulsa, 2002.
26. Lozano, J. *TUDRP/ACTS Advisory Board Meeting, Tulsa-Oklahoma*, May 2005.
27. Miska, J.; Mik, V. *Chem Eng Process* 2004, 43, 1495.
28. Miska, J.; Zakin, J. L. *Ind Eng Chem* 1997, 36, 5483.
29. Mansur, C. R. E.; Spinelli, L. S.; Oliveira, C. M. F.; González, G.; Lucas, E. F. *J Appl Polym Sci* 1998, 69, 2459.
30. Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook; 2nd ed.; CRC Press* 2007: New York, Appendix A.