

# Synthesis and structural study of new copolymers, based on acrylamide and N-acryloyl acids, with persistent drag reduction activity

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Syntheses of acryloyl amino acid monomers, some of which were optically active, have been carried out. These compounds have been copolymerized with acrylamide and characterized. The polymers prepared from optically active monomers form a compact structure in solution. Aqueous solutions of these macromolecules were then tested to assess their drag reduction effect under turbulent flow conditions. For this series of macromolecules, including partially hydrolysed polyacrylamide, a particular persistent activity is observed, which is similar to the behaviour of natural products and different from the drag reduction activity of polyethyleneoxide (PEO) and polyacrylamide (PAM).

It is shown that the particular main chain structure induced by the chiral monomers is not responsible for this persistence. Moreover, relationships between the polymer structure and drag reduction properties enabled us to propose a mechanism which emphasises the role of the branch chain and the terminal charge. This persistent drag reduction activity is also linked with a critical energy level. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polymers; drag reduction; N-acryloyl amino acid)

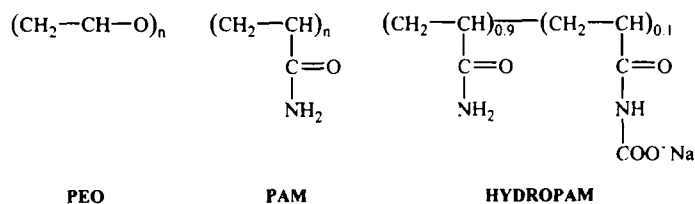
## INTRODUCTION

Over the last 20 years there has been a growing interest in polyacrylamides derivatives<sup>1</sup>. Significant commercial and scientific advances have been made, particularly in water-soluble applications such as water treatment, mining and paper manufacture. However, the main potential application which has been explored extensively is in enhanced oil recovery. In fluids flow, energy losses occur due to the frictional resistance. In order to increase the velocity and to minimize the acoustic emissions, it is of interest to reduce the friction coefficient. Among the different solutions proposed, drag reduction and flow modification by polymer

still no universally accepted model which explains the mechanism of this phenomenon and outstanding questions still remain.

In this regard, an innovative research was undertaken to understand the way in which the polymer molecules behave to reduce the friction, taking into account the chemical aspect of drag reduction. Three types of structures were investigated, namely polyethyleneoxide (PEO), polyacrylamide (PAM) and PAM derivatives.

PEO<sup>5</sup> is a non-ionic linear polymer without any side chain. PAM<sup>6</sup> is also unchanged, but with a pendant group including a polar terminal functional group.



additives were first pointed out by Toms<sup>2</sup> in the 1940s on the basis of the efficiency shown by polymethylmethacrylate in chlorobenzene.

Since then, numerous studies<sup>3,4</sup> have contributed to the understanding of the influence of some polymer parameters (molecular weight, hydrodynamic volume, solvent interactions) on drag reduction properties. However, there is

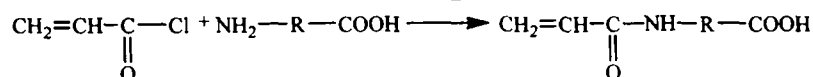
The last series concerns charged copolymers based on acrylamide and acrylamide derivatives. Of these the partially hydrolysed polyacrylamide (HYDROPAM) is a commercial product. The others were prepared from the acrylamide and N-acryloyl amino acids, including chiral compounds. They are poly[acrylamide-co-N-acryloyl (X)] where X stands for the amino acid. Particular attention was directed to the influence of polymer structure induced by the optically active moiety on drag reduction properties.

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EXPERIMENTAL

Monomers synthesis

The N-acryloyl amino acid monomers were synthesized according to a nucleophilic substitution between an amino acid and acryloyl chloride. The reagents were obtained from Aldrich. The reaction can occur either in aqueous solution<sup>7,8</sup> or in organic medium<sup>9</sup>.



The aqueous route was particularly studied and improved<sup>10-13</sup>.

Some monomers were optically active due to the chiral amino acid. The optical rotation was assessed using a Bergson polarimeter having a 3 cm cell.

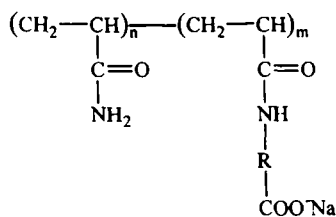
All the monomers were purified and analysed by NMR and FTIR. NMR spectra were carried out on a Bruker AC-200 machine operating at 50.3 Mhz and FTIR spectra were acquired with a Ati Unicam spectrophotometer.

The main results are gathered in Table 1 (experimental or characterization details are reported elsewhere<sup>14</sup>).

Copolymers synthesis

The commercial polymers PEO and PAM are obtained from Aldrich and the hydrolysed PAM is obtained from Floerger.

The N-acryloyl amino acid monomers were copolymerized with acrylamide at different feed compositions. Experiments were carried out in basic aqueous solution so that the N-acryloyl amino acid converts into a sodium salt. Therefore, the structure of the final product is composed of a main linear chain and a branch chain ending with a charged group:



The radical copolymerization were performed using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as initiator at 0.1 mol% rate. The solution containing initiator and monomers was degassed and heated to 40°C. The final polymer from high viscosity solution was precipitated in acetone solvent and dried. The procedure details are described elsewhere<sup>15</sup>). The initial compositions of copolymers were varied and the conversion rates reached were 100%.

Copolymer characterization

The copolymers obtained were subjected to light scattering measurements in order to determine their molecular weight and radius of gyration. All light scattering experiments were carried out in a 0.5 M NaCl solution on a Brookhaven BI8000 photogoniometer composed of a Spectra Physics laser argon source (λ = 514 nm), an optical

system, a quartz cylinder cell and a multi-angle measuring instrument.

Viscosity measurements

Water-soluble polymer solutions often have special viscometric properties. The polymers were then dissolved in 0.5 M NaCl solution and tested with a Low Shear 30 viscosimeter designed to determine low viscosities and operating at very low shear rates. Relative viscosities were assessed with a system MS 412/8S, composed of two conic concentric cylinders. The intrinsic viscosities were calculated according to the Huggins<sup>16</sup> equation:

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C, \quad \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} \quad (1)$$

where the constant k' is a function of the polymer-solvent interactions and of the solvent nature, η the relative solution viscosity, η<sub>0</sub> the solvent viscosity and C the polymer concentration.

Drag reduction measurements

Drag reduction tests have been conducted using a new device<sup>17</sup> to measure the hydrodynamic friction under turbulent flow conditions. It consists of two concentric cylinders, the outer one of which rotates. The device includes on-line experimental data acquisition and processing facilities which provide rapid and accurate assessment of a large number of tests carried out over widely varying time periods. The drag reduction corresponds to the lowering of the torque value due to the introduction of the additive in the medium. 'Drag reduction coefficient' represents the ratio of this difference over the value of the torque due to the solvent (N<sub>s</sub>):

$$DR (\%) = \frac{N_s - N}{N_s} \times 100 \quad (2)$$

The experiments were carried out by adding the polymer powder to the solvent at a concentration of 5-30 ppm. The Reynolds number was about 50 000 with a well-established<sup>18</sup> turbulent flow, and the shear rate was about 10<sup>-3</sup> s<sup>-1</sup>.

Table 1 Syntheses results and characterization of N-acryloyl amino acid monomers

N-acryloyl	R	Yield (%)	Melting point (°C)	Optical rotation (°·cm <sup>3</sup> ·g <sup>-1</sup> )
Glycine	CH <sub>2</sub>	50	132	—
β-Alanine	CH <sub>2</sub> -CH <sub>2</sub>	50	93	—
DL-Alanine	CH(CH <sub>3</sub> )	70	129	—
L-Alanine	CH(CH <sub>3</sub> )	70	163	- 102.5
L-Valine	CH(IPr)	72	121	- 38.7
L-Phenylalanine	CH(CH <sub>2</sub> φ)	85	128	+ 50.3

## RESULTS AND DISCUSSION

## Structure parameters

Among the parameters which affect drag reduction properties, the molecular weight is one of the most important and must be high enough in order to reach interesting level of drag reduction. The molecular weights calculated for the studied copolymers (Table 2) were checked to be high enough in that they are above  $10^6 \text{ g mol}^{-1}$ . Moreover, they are independent of N-acryloyl amino acid monomer proportion, which means that the comonomer do not induce kinetic variation of the constant of polymerization (Table 3).

The radius of gyration are also quite high due to the presence of ionic monomer. However, these values show that the organized structure induced by the optical activity of N-acryloyl(L)alanine leads to a more compact coil in solution for similar molecular weights.

Expansion coefficient which represents the ratio of the actual dimension of the chain to its unperturbed one is also determined (Table 3). It is seen to depend on the polymer composition and the chain becomes more expanded when the content of ionic monomer increases. This effect is similar to that caused by charge repulsion in hydrolysed polyacrylamide.

Particular attention is paid to the optical rotation  $[\alpha]$  of these products. In fact, the optical activity of a macromolecular skeleton is due to both an 'atomic' optical activity caused by the spatial disposition of the four asymmetric centre groups and a 'conformational' optical activity caused by the resulting conformation of the main chain atoms:

$$[\alpha] = [\alpha^*] + [\alpha^c] \quad (3)$$

$[\alpha^*]$  corresponds to the chiral group optical rotation

given by

$$[\alpha^*] = f_A \cdot [\alpha_1^*] \quad (4)$$

where  $f_A$  is the N-acryloyl amino acid proportion in the copolymer and  $[\alpha_1^*]$  is the optical activity caused by 1 g of monomer (specific optical activity).

$[\alpha^c]$  can be evaluated according to the Brewster<sup>19</sup> method which takes into account the optical polarizability of the main chain units:

$$[\alpha^c] = (1 - \exp(-f_A \cdot k)) \cdot [\alpha_1^c] \quad (5)$$

where  $k$  is the number of segments perturbed by the conformation of another segment. Consequently,  $[\alpha]$  can be determined from equation (3) as

$$[\alpha] = f_A \cdot [\alpha_1^*] + (1 - \exp(-f_A \cdot k)) \cdot [\alpha_1^c] \quad (6)$$

The resulting calculated values are close to the experimental ones and are reported in Table 4. The values of both parameters  $[\alpha_1^*]$  and  $[\alpha_1^c]$  are given in Table 5. It appears that the atomic optical activity is not very different from the N-acryloyl monomer value obtained in Table 1. The conformation aspect represented by  $[\alpha_1^c]$  underlines an evolution linked with the amino acid size and enables one to conclude that the chiral group of the side chain is responsible for a left helix coiled conformation.

## Drag reduction

The drag reduction profile against time (Figure 1) can be divided into three parts. At zero time, the additive is introduced as a powder and the step of solvation corresponds to part A, which is governed by the particle size of the powder. Maximum drag reduction is reached at point B ( $DR_{max}$ ). Then the activity decreases in step C and after a 72 h running test, was defined 'intrinsic drag

**Table 2** Intrinsic viscosity and hydrodynamic volume of four studied polymers

Polymer	$[\eta]_0 (\text{dl g}^{-1})$	Molecular weight ( $10^6 \text{ D}$ )	Hydrodynamic volume ( $\text{dl mol}^{-1}$ )
PEO	12.1	4	48.4
PAM	5.7	4	22.8
Hydrolysed PAM	28.2	8	225.6
Poly[acrylamide-co-N acryloyl(L)valine] [90/10]	8.6	2.8	24.08

**Table 3** Molecular weights, radius of gyration, refractive index increment and molecular expansion coefficient for poly[acrylamide-co-N-acryloyl(X)]sodium salt

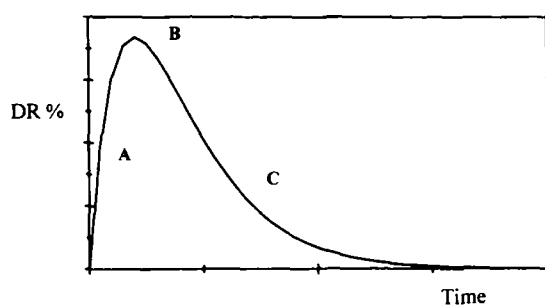
X	X (%)	Melting point $\times 10^{-6}$ (D)	$R_G$ (nm)	$\frac{dn}{dc}$ ( $\text{g ml}^{-1}$ )	$\alpha$
(D.) Alanine	10	2.96	126.1	0.161	5.2
	25	2.54	124.6	0.150	6.0
	40	2.79	128.1	0.145	6.4
	60	4.06	139.4	0.140	6.2
	75	2.40	127.3	0.165	7.8
	90	1.89	111.2	0.154	8.0
(L.) Alanine	100	2.00	115.7	0.162	8.4
	10	5.22	85.3	0.125	2.7
	25	2.40	81.2	0.140	4.1
	40	1.36	78.0	0.171	5.5

**Table 4** Optical activity of synthesized poly[acrylamide-co-N-acryloyl(X)]

X	Y	$[\alpha]_{25}^D$ ( $^{\circ}\text{cm}^3\text{g}^{-1}\text{dm}^{-1}$ )	
		(Experiment)	(Calculated)
Alanine	5	-4.4	-4.8
	10	-10.4	-9.3
	25	-20.9	-22.1
	40	-35.3	-34.6
	60	-41.9	
	75	-53.5	
Valine	100	-53.5	
	10	-7.0	-6.8
	25	-12.3	-13.2
	40	-20.2	-19.2
	60	-26.9	-27.2
	75	-19.7	
Phenylalanine	90	-21.3	
	100	-18.6	
	10	-2.1	-3.8
	25	0.2	0.4
	40	11.1	8.1
	60	20.5	19.2
	75	27.9	
	90	17.9	
	100	21.5	

**Table 5** Optical activity results for poly[acrylamide-co-N acryloyl(X)]

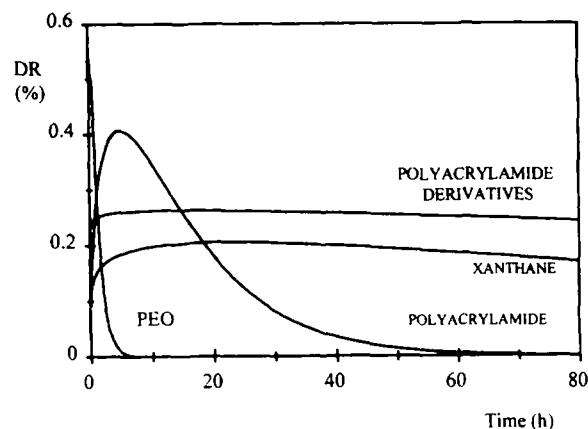
X	$[\alpha]_1^A$	$[\alpha]_1^B$
(L) Alanine	-82.5	-1.6
(L) Valine	-40.0	-3.2
(L) Phenylalanine	+57.2	-15.1



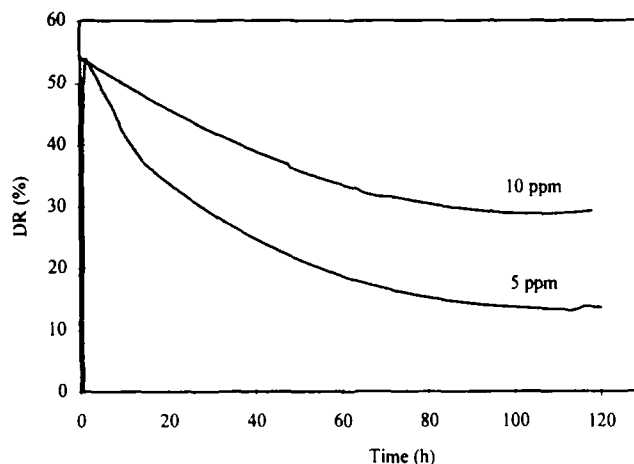
**Figure 1** Drag reduction profile against time

reduction' which depends on the nature of the macromolecule.

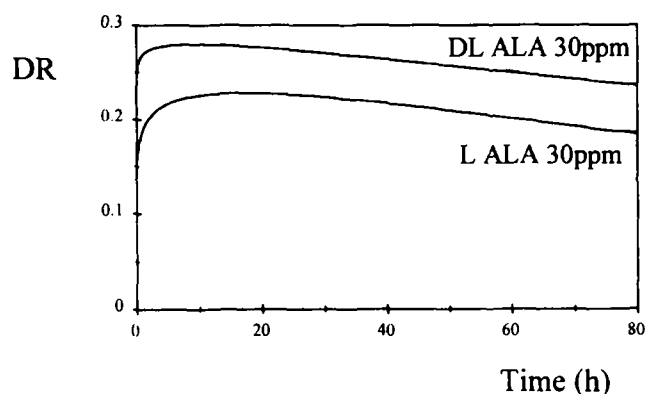
The general drag reduction behaviour of the three series is exhibited in *Figure 2*. The instantaneous drag reduction efficiency of PEO is higher, but its activity decreases sharply falling to zero after a few hours. The other non-ionic macromolecule PAM shows almost the same behaviour: in that its activity is reduced to zero after several days, depending on the concentration. The ionic macromolecule additives show a small drop during the first few days and subsequently evolves to a plateau. Therefore this kind of macromolecule can be said to present a persistent activity similar to the natural polysaccharides, such as xanthan gum.



**Figure 2** Drag reduction behaviour of different products



**Figure 3** Partially hydrolysed PAM drag reduction

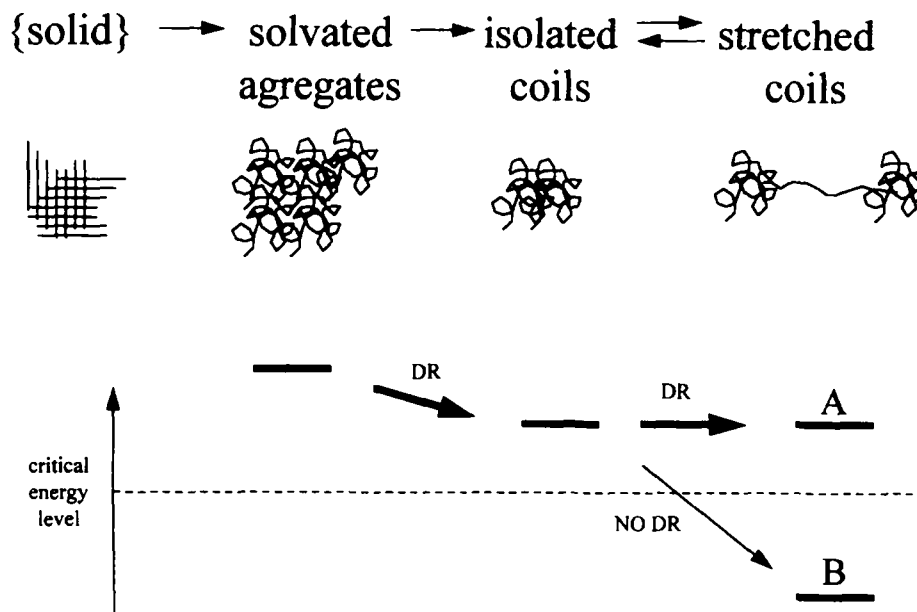


**Figure 4** Drag reduction activity of poly [acrylamide-co-N-acryloyl(-DL)alanine sodium salt] [90/10] and poly [acrylamide-co-N-acryloyl(L)alanine sodium salt] [90/10]

To relate these properties to the molecular parameters, the hydrodynamic volumes of the four compounds are compared in *Table 2*. While the hydrodynamic value is of the same order for PEO, PAM and poly[acrylamide-co-N-acryloyl(L)valine] (90/10), their drag reduction properties are quite different. In fact, poly[acrylamide-co-N-acryloyl(L)valine] (90/10) exhibit persistent activity, which means that the behaviour in drag reduction is not only linked to the conformation of the isolated macromolecule, but also

**Table 6** Drag reduction results of two studied polymers

Polymer	Concentration(ppm)	$DR_{max}$	$DR$ (24 h)	$DR$ (48 h)	$DR$ (72 h)
PAM	100	27.6%	6.0%	4.2%	2.4%
Poly[acrylamide-co-N acryloyl(L-valine)] [90/10]	15	25.0%	18%	17.4%	17.2%


**Figure 5** Drag reduction mechanism.

to their association in solutions. This mechanism is well known, and the decrease of efficiency is caused by the desegregation of macromolecular clusters. Moreover, the rates of desegregation are different due to competition between polymer-polymer and polymer-solvent interactions. This phenomenon explains the difficulty in obtaining reproducible results when the measurements are made using concentrated solutions.

Other tests were conducted on partially hydrolysed PAM at two different concentrations (5 and 10 ppm) and are reported *Figure 3*. In fact, the drag reduction curves with the presence of a plateau shows that after some time (several hours) stability is reached. As the tests are carried out at low concentration, the activity corresponding to the plateau cannot be linked to the desaggregation of clusters. Therefore, we assume that isolated molecules are responsible for this persistent activity.

Another explanation of this unusual activity could be the effect of chiral structure provided by the optical activity of some of the synthesized monomers (*Figure 4*). The level of activity for macromolecules prepared from racemic and levogyre compounds are compared. The level of the plateau for the more compact molecule is about 20% lower even though its molecular weight is almost twice as high (*Table 2*).

#### Proposed mechanism

This study led to a possible mechanism which would explain the observed persistent drag reduction properties of polyacrylamide derivatives and the activity of PEO and PAM, by taking into account the molecular parameters.

The first step of this scheme, as shown in *Figure 5*, is that the solvation of the solid and no drag reduction occurs at this point.

The second step concerns isolated coils which are extracted from aggregates. The extraction phenomenon dissipate energy which can decrease the power of the eddies and thus, drag reduction is observed.

The last step is linked with the stretching of parts of chains of macromolecules. The isolated coils obtained before the third step are of two kinds. The first series (A) includes polymer molecules, the stretching energy of which is above the critical energy level and large enough to produce drag reduction, when intramolecular interactions are broken. This is the persistent effect relative to ionic PAM derivatives. However, some difference can be underlined in relation to their molecular structure. In fact, in the case of spatial organization of the optically active macromolecule, we assume that the stretching of some parts of the chain is not possible because intramolecular interaction are too strong. For this reason, a greater drag reduction efficiency is reached for less compact macromolecules.

The second series (B) concerns most of the drag reducers polymers for which the number of intramolecular interaction is not large enough. This is the case of small macromolecules and of large ones such as PEO and PAM which are non-ionic. Thus the energy level reached during the stretching does not lead to a drag reduction effect.

Moreover, to explain the previous mechanism, at no point did we take into account phenomenon of macromolecular degradation. Two reasons for this can be given:

- First, Kulicke and Bouldin<sup>20</sup> studied the shear stability of polymer solutions showing that mechanical chain scission takes place when a critical shear rate is reached. With a  $10^3 \text{ s}^{-1}$  shear rate, the experimental conditions of our experiments prevents this degradation phenomenon.

- Then, this is confirmed by the results obtained on PAM and poly[acrylamide-co-N-acryloyl(L)valine] [90/10]. In fact, the structure difference between these two polymers comes from the 10%mol of the acryloyl valine monomer. However, their drag reduction behaviours (Table 6) are not similar in so far as the activity of the PAM decreases quickly whereas the other copolymer presents persistent activity. So if macromolecular degradation occurred, drag-reduction properties of both polymers would be similar.

## CONCLUSION

From this study, the main emphasis of which was on the relationships between copolymer structure and drag reduction properties, the following ideas about the friction resistance mechanism can be suggested:

- It is thought that it involves a reversible change of the macromolecule structure from a 'compact' configuration to an elongated form under a gradient effect. The polymers therefore are able to absorb energy and to subsequently release it.
- The structure induced by the chiral compounds (the local organization of the four groups linked to the asymmetric centre and the global chain organization, similar to a left helix-coiled conformation) cannot be the explanation of the particular observed properties.
- In contrast, the branch chain and the side chain charge contribute to favour intramolecular interactions which could explain the persistent activity.

A study is being carried out with a range of non-chiral polymers in order to show to what extent these two factors influence drag reduction performance.

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