

New Polymers for EOR – A Laboratory Study

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Abstract: Comb polymer and hydrophobic associative polymer have been recently proposed as new flooding agents. Comb polymer is high salinity and temperature resistant, while both associative polymer and comb polymer solutions can be prepared in produced water, without requiring any further precaution. Besides, as demonstrated in this paper, these polymers exhibit higher viscosity than polyacrylamide; This paper describes a laboratory study conducted on these polymers. The solution properties of these two different types of polymer solutions depend on mid-range association between or within polymer molecules. Rheological measurements indicate that: (1) the rigidity of the main chain of a comb shape polymer is strengthened by the stereo and electric repulsions between short side branches along the main chains. The resulting polymer structure is similar to an elastic “ willow ”. (2) In solution, the hydrophobic associative polymer molecules, with relatively weak links between hydrophobic chains, can be compared to a “necklace” in which polymer molecules can easily interchange their position and are weakly elastic. In solution, the molecules of the comb polymer possess high viscoelasticity and good viscosifying ability at low shear rate due to their specific chain structure. Comparative core tests, conducted under the same conditions with several polymers, reveal that the highest oil displacement recovery is obtained with the comb shape polymer, while the hydrophobic associating polymer requires the polymer concentration to be higher than the critical associating concentration in order to get a very viscous fluid with a high oil displacement efficiency. There are two stages in the hydrophobic associating process: in the first stage, the association is mainly intramolecular and the increase in viscosity is slow; in the second stage, the association is mainly intermolecular and affects the structure of associated polymer chains, resulting in a fast increase of the viscosity. A critical associating concentration (CAC) can be associated to each of these two steps.

Key words: *Polymer Flooding; Viscosity; Oil Displacement Efficiency; Viscoelasticity; Comb polymer; Hydrophobic Associative Polymer*

Polymers have been successfully used for long time in EOR as flooding agent. In this respect, the most widespread technique is based on partly hydrolyzed polyacrylamide (HPAM), [1-3] which is a low price polymer with good viscosifying properties, and well-known physicochemical characteristics. The implementation of HPAM flooding is easy and can improve significantly the oil recovery rate under standard reservoir conditions. Nevertheless, until recently most of the polymer techniques suffer from strict temperature and salinity limitations, and oil recovery specialists focused their research on new temperature and salt-resistant polymers.

The followed research directions investigated gave rise to three different families of new polymers: □ comb polymer (CP), □ hydrophobic associative polymer (HAP), □ amphoteric polymer. Polymers from the same family possess similar structure and properties. Comb polymer, for instance is resistant to high temperature and high salinity and therefore can be used in high salinity high temperature reservoirs as a flooding or profile control agent^[4]. The viscosifying effect of comb polymer in production water is 40% higher than that of a high molecular weight HPAM prepared with the same water under the same conditions. On the other hand, the hydrophobic associative polymer requires the polymer concentration to be higher than a critical value in order to exhibit a thickening behavior: hydrophobic branches tends to form intramolecular and intermolecular associations creating a three dimensional network in solution.^[5]

As the structures of the new polymers described above are completely different from standard HPAM, three different polymers provided by oilfield operators were evaluated through viscoelastic measurement and oil displacement experiments. Our evaluation approach considers not only the technical efficiency of the oil displacement agent but also the economics of the project.

1 Experimental section

1.1 Materials

Polymer samples were provided by the oilfields when available. Table 1 gathered the characteristics of the polymer powders. The HPAM sample is used as a reference and is of common use in Chinese oilfield.

Table 1 characteristics of the polymer samples

Ref. n°	Sample	Origin	solid content □	Molecular Weight ×10 ⁴	Degree of hydrolysis □	Remark
1	MO-4000	Mitsubishi	92.4	1988	24.6	HPAM
2	KYPAM-2	Beijing Hengju	89.64	/	25.68	CP
3	DH-1	Daqing oilfield	90	/	/	HAP
4	DH-2	Daqing oilfield	90	/	29.92	HAP

1.2 Methods

1.2.1 Viscosity measurements

Polymer solutions were prepared with water from Jin 16 unit, Liaohe oilfield. The water had the following characteristics: Salinity 3770 mg/L, hardness 218mg/L, type NaHCO₃. The temperature of the experiment was that of Liaohe Oilfield reservoir (56□). The variations of viscosity of the polymer solution with polymer concentration and shear rate were evaluated with the *RS150* rheometer and Brookfield viscometer.^[6]

In order to determine which kind of instrument was more suitable for the viscosity measurement of polymer solution, we measured the evolution of apparent viscosity of HAP solution with polymer concentration, using both the *RS150* rheometer and the Brookfield viscometer with the U.L. adapter at the same shear rate. For a purpose of comparison we also measured the apparent viscosity of HPAM (MO-4000). Results were plotted on figure 1. Values measured for the HPAM sample with the two apparatus were almost identical. This coincidence of the curves remained true for the HAP sample (DH-2), but only at low concentration. When the polymer concentration exceeded 1000mg/L the two curves diverge, the values measured with the viscometer being higher. This discrepancy was most likely due to a shift of the rotation axis of the Brookfield viscometer at high hydrophobic associative polymer (HAP) concentration. The viscometer measured a shear stress produced by the viscous fluid and also the stress caused by the eccentric rotation of the spindle, thus overestimating the apparent viscosity of the polymer solution. This displacement could be at least partly explained by the fact that the hydrophobic associative polymer (HAP) was partly unsolvable in water. Thus, the polymer solution must be considered as a dispersion, and at high polymer concentration, when the non-water phase proportion had markedly increased, the non-homogeneous fluid induced the eccentric rotation of the U.L. adapter. As for the rheometer, the cell was directly connected to the rotor and the axis of rotation was rigid. The eccentric rotation of the spindle would not happened at all in the rheometer.

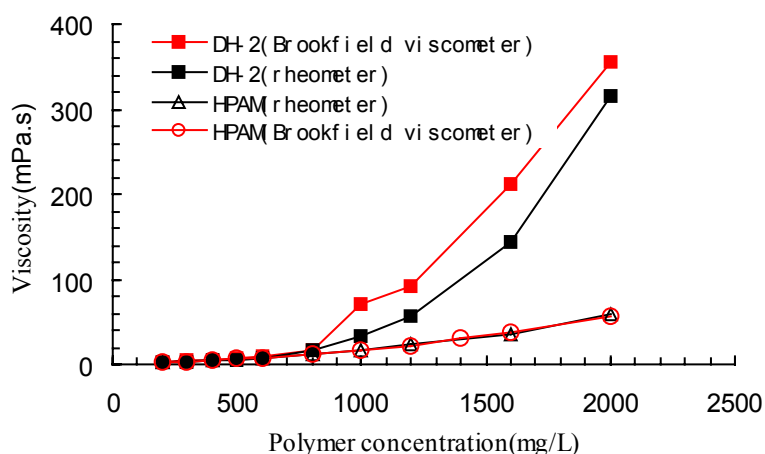


Fig.1: The influence of hydrophobic polymer concentration on viscosity measurements

1.2.2 Oil displacement experiments

Oil displacement experiments were conducted in consolidated quartz sand packs. We carefully selected

cores with similar petrophysical properties. The cores were 8 cm long with a diameter of 2.54cm and an average gas permeability of $1.20 (\pm 0.05) \mu\text{m}^2$. The fluids used were from Jin 16 unit, Liaohe oilfield. In laboratory conditions the viscosity of the crude oil is 68mPa.s, its density 0.931g/cm^3 .

The experimental procedure was the following:

Prior to injection the core was first vacuum-pumped for three hours and then saturated with reservoir water filtrated through $0.45 \mu\text{m}$ filters. The core porosity was calculated and the permeability was derived from pressure measurements at several water injection rates. Temperature was set to 56°C (Jin 16 unit reservoir temperature) and the annulus pressure was always 0.5MPa higher than the maximum injection pressure. Injection speed was 0.3mL/min (equivalent to 0.879m/d, Darcy speed).

Afterwards, the core was flushed with:

- (1) oil until a steady state corresponding to S_{wi} was reached (irreducible water saturation, about 20%).
- (1) water until a state corresponding to S_{or} was reached (the oil recovery rate was around $55 \pm 3\%$).
- (3) A slug of 0.1% polymer solution (0.1-0.3PV) followed by a water injection until no oil produced.

The oil displacement efficiency was determined by analyzing the fluid production.

2 Results and Discussion

2.1 Viscosifying ability

The viscosity of the two different types of new polymers is compared to that of HPAM at 56°C under a shear-rate value of 8s^{-1} and for polymer concentration ranging from 200mg/L to 2000mg/L (see figure 2).

The viscosity of the comb polymer is 1.6 to 1.8 higher than that of HPAM (MO-4000) for the entire range of concentration explored. This can be easily explained by the specific structure of the comb polymer: the polymer molecule tends to stretch due to the steric and electric repulsions between the side branch groups along the main chain, increasing both the viscosity and the stability of the polymer solution. Therefore the solution is also much more resistant to high salinity or high temperature.

The behavior of one of the hydrophobic associative polymer solution (DH-1) depends strongly on the polymer concentration (see figure 2): at low concentration (below 600mg/L) the viscosifying ability of this polymer is lower than that of the HPAM (MO-4000), the viscosity is very much like that of a low-molecular weigh HPAM.

For higher values of the polymer concentration the increase in viscosity is much faster, and when the concentration reaches 1700mg/L, the viscosity curve of the associative polymer is above the HPAM viscosity curve. This thickening behavior is readily explain by the mechanism of polymer association: above a critical associating concentration (CAC), polymer molecules tends to associate each other by their hydrophobic groups, eventually building up a three-dimensional network which considerably increases the viscosity of solution.

The viscosity of the other of the hydrophobic associative polymer solution (DH-2) shows the same trend as the DH-1. This curve and the HPAM viscosity curve intersect for a polymer concentration around 1000mg/L, indicating a critical associating concentration higher than that of the hydrophobic associative polymer.

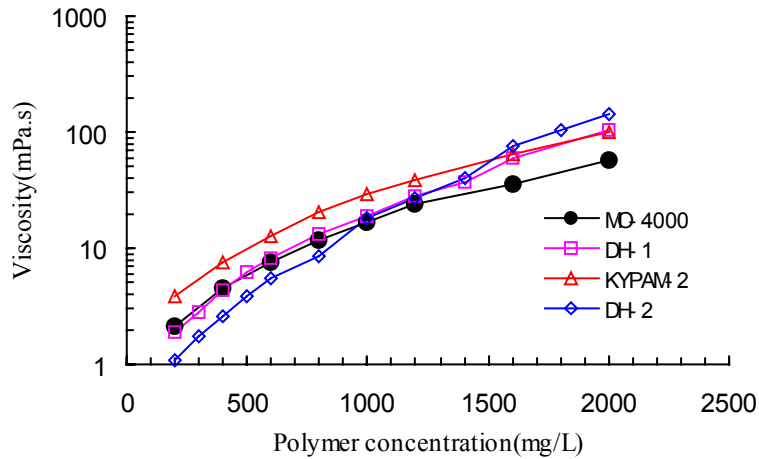


Fig.2: Effect of polymer concentration on viscosity for different polymer solutions (56j æ

2.2 Rheological behavior

The evolutions of the viscosity with the shear rate are plotted on figure 3. Polymer concentration was 0.2%. The comb polymer and the HPAM exhibit a same shear-thinning or pseudoplastic behavior, the viscosity decreasing regularly when increasing the shear rate. Although the HAP can also be viewed as shear thinning fluids, however the slope of the viscosity curve is much smaller for the two later polymer solutions. The propensity of polymer molecules to aggregate in solution — the polymer concentration is above the critical associating concentration — shifts the behavior toward that of a shear-thickening fluid.

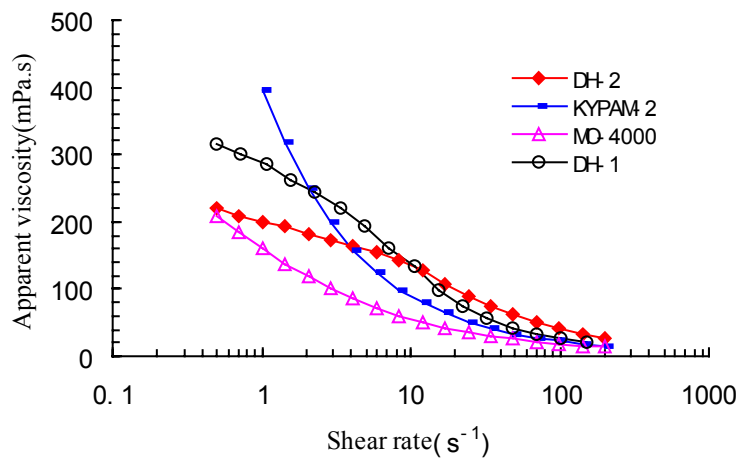


Fig.3: Influence of the shear-rate on the viscosity of 0.2% polymer solutions

During field test the polymer solution will be submitted to high shear rate in the near well-bore area — values higher than 20s^{-1} are commonly accepted — and lower shear-rate in the reservoir. A "good" polymer would be easy to inject deep inside the reservoir, therefore hydrophobic association is detrimental to the injectivity of the polymer solution. As an illustration we can compare viscosity values at 99s^{-1} in figure 3: $40.6\text{ mPa}\cdot\text{s}$ for the HAP (DH-2) and nearly the half ($22.9\text{ mPa}\cdot\text{s}$) for the comb polymer (KYPAM-2). The HAP will require an injection pressure almost twice as high as the comb polymer. Moreover, injection of the HAP could result in damaging the near-well bore. Inside the reservoir -under low shear rate — the comb polymer solution will exhibit a higher viscosity than the other polymers, leading to a better improvement of the mobility ratio.

Shown in Figure 4 are the variation of G' with the frequency for the four polymer solutions tested (polymer concentration is 0.2 mg/L). G' is the storage modulus or elastic modulus, it reflects the elasticity of the fluid.

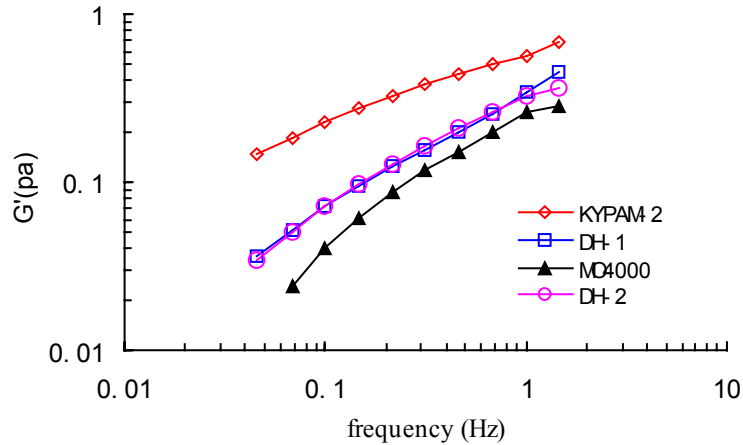


Fig.4: The relationship between G' and frequency for 0.2% polymer solutions

As made clear by figure 4, the elastic modulus is increasing with the frequency. The lowest values of G' correspond to the HPAM. At high flow rate the comb polymer exhibits the highest value of G' compared to other polymer solutions — $G'_{(\square, \text{KYPAM-2})} \approx 3G'_{(\circ, \text{DH-2})}$. Neither this phenomena is reversed if the frequency is lowered. On the contrary, the gap between the curves increases at low frequency — $G'_{(\square, \text{KYPAM-2})} \approx 6G'_{(\circ, \text{DH-2})}$. Such a behavior contrasts strongly with what we have observed on figure 3 where at low shear rate — low frequency — the HAP is more viscous than the comb polymer, for the same polymer concentration. Much of the explanation rests in the weakness of the hydrophobic association: viscosity is a "macro" value, high values for the hydrophobic polymer accounts for the three-dimensional network built up by the polymer molecules while low G' reflects the fact that the hydrophobic bond is weak. We can illustrate this behavior by comparing the weak hydrophobic aggregate to a "necklace" in which each bead can move and easily change its position while the overall structure remains. On the opposite, the comb polymer main chain has a strong rigidity due to the electrostatic and steric repulsion between the side branch groups, where the molecule structure is very much like some elastic "willow". As a consequence of its rigidity, the comb polymer exhibits the highest G' values among the four polymers considered in this study. According to the results of the micromodel experiments by Wang Demin & al,^[7] polymer viscoelasticity can be directly related to an enhancement of the microscopic oil displacement efficiency; therefore, we can reasonably assume that the best polymer choice would be the comb polymer.

2.3 Temperature stability

Viscosity values of polymer solution (polymer concentration is 0.1%), at temperature ranging from 32°C to 75°C are plotted in figure 5. This figure makes clear that viscosity values decrease with temperature.

At low temperature the highest values are given by the two associative polymers (DH-2 and DH-1), but their decrease rate is much faster than HPAM (MO-4000) and KYPAM-2. There are two main causes for such a rapid fall down:

(1) With the increase of temperature the polymer conformation changes are much faster; making the association between hydrophobic side-branch group more difficult. Besides, the Brownian motion of the particles increases with the temperature, weakening the 3D-network built up by the associative polymer molecules.

(2) With the increase of temperature the degree of dissociation of the water molecules also increases, thus there are more ions dissolved in solution, those ions are detrimental to the intermolecular hydrophobic association. Consequently intramolecular associations prevail, leading to a rapid decrease of the thickening efficiency of the polymer.

This phenomenon is currently being further investigated. Nevertheless, the present study demonstrates conclusively that the hydrophobic associative property of those two polymers is not good enough to resist to a standard average reservoir temperature — At temperatures higher than 60°C their viscosity values are lower than that of HPAM. The viscosity of KYPAM-2, on the contrary, remains higher than that of HPAM, with the ratio between the two viscosity increasing: from 1.52 at 32°C to 1.65 at 75°C. The slope of the two curves are very much alike. From the above, we can infer that the thickening mechanisms of KYPAM are more akin to that of HPAM, with a better resistance to temperature than the three other polymers.

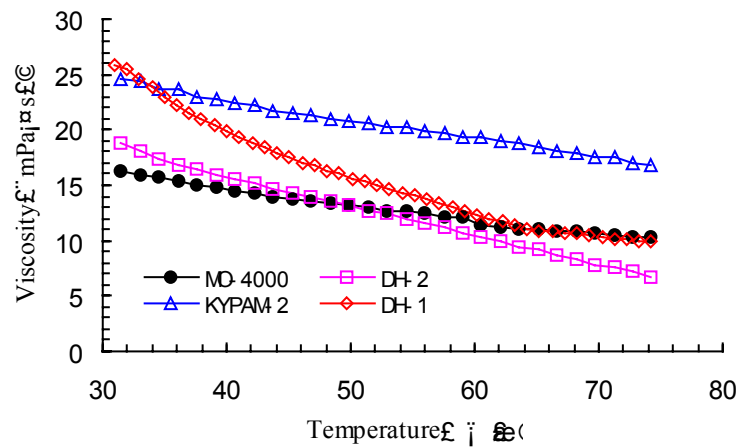


Fig.5: Relationships between viscosity of 0.1% polymer solutions and temperature

2.4 Oil displacement efficiency

We injected a slug of polymer solution in a core at S_{or} and then displaced it with water.

Results from the series of experiments are summarized in table 2: in the left-and column of table 2 are the amount of polymer solution injected in pore volumes (PV). The other columns contain the value of the oil displacement efficiencies for the four polymer solutions tested. The polymer concentration is 0.1%. Comparing all the polymers solutions efficiency when injecting 0.3PV of solutions shows clearly that KYPAM-2 is the most efficient polymer with an oil recovery efficiency about 12.1% (see also figure 6). In comparison, the oil recovery efficiency of MO-4000 is only 5.61%. When injecting 0.2 PV the oil recovery efficiency of KYPAM-2 drop down to 5.24% while that MO-4000 falls to 2.81%. All other things being equals, in laboratory, the injection of a given amount of KYPAM-2 leads to an oil recovery efficiency more than twice higher than a standard HPAM, while oil displacement mechanisms are similar for these two kinds of polymers.

When injecting 0.3PV of DH-1 polymer at 0.1% the recovery efficiency is 10.72%, higher than that of HPAM, but decreasing the injected volume to 0.2PV leads to a fast decrease and the recovery efficiency is only 1.69% (see table 2 forth column from the left). This accounts for the polymer concentration to reach a critical concentration before the hydrophobic association occurs giving the polymer high recovery efficiency. If the concentration in the core is lower than the critical associating concentration, the oil displacement can be a complete failure. The mechanism of oil recovery by hydrophobic associative polymer is fundamentally different than that of HPAM.

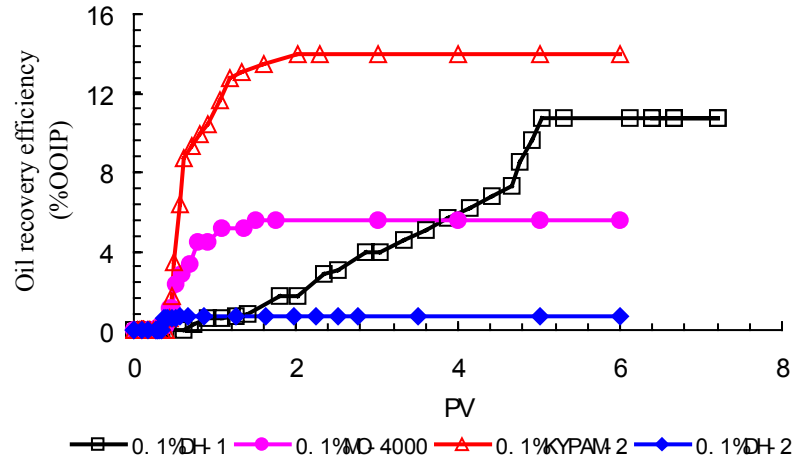


Fig.6: Displacement efficiency when injecting 0.3PV of 0.1%polymer solution

Table 2: Oil displacement efficiency of 0.1% polymer solutions for different sizes of polymer slug

PV	MO-4000	KYPAM-2	DH-1	DH-2
0.2	2.81	5.24	1.69	/
0.3	5.61	12.1	10.72	0.67
0.4	/	/	/	2.82
0.5	/	/	/	4.65
0.7	/	/	/	8.14

We can see from figure 6 or table 2 that the recovery efficiency of the hydrophobic associative polymer DH-2 is 0.67% when injecting 0.3 PV. We successively tried to inject bigger amount of polymer suspension (see table2), which logically results in increasing the recovery efficiency, but without observing any striking improvement. It is therefore reasonable to think that the hydrophobic association process didn't occur inside the core.

2.5 Critical associating concentration for Hydrophobic associative polymer

According to a report by Feng Yujun & al, ^[8] a common hydrophobic associative polymer would have a critical associating concentration (CAC) around 0.2%. Nonetheless, considering the mechanisms of hydrophobic association, there should be two critical associating concentrations:

(1) At concentration lower than the first critical associating concentration (CAC) the hydrophobic association is insignificant. The viscosity increases slowly with the polymer concentration.

(2) When the polymer concentration exceeds the first critical associating concentration (CAC) intramolecular and intermolecular associations occur. Intermolecular association tends to increase the viscosity of the solution, while intramolecular tends to decrease it (by reducing the volume of the molecule). Due to intermolecular association the viscosity increases faster than in the first part of the curve.

(3) Equilibrium for intramolecular association is reached when the polymer concentration exceeds the second critical associating concentration (CAC). Increasing the concentration only increases the ratio of the intermolecular association to the intramolecular association. The viscosity of the solution increases even faster than before.

According to the above remark, we should observe three slopes on the viscosity plot of the two hydrophobic associative polymers DH-1 and DH-2. Experimental curves at 56°C are shown on figure7a and 7b. With the help of linear regression we can calculate the actual values of the critical associating concentrations.

For DH-1: first CAC 766mg/L, second CAC 1908mg/L.

For DH-2: first CAC 1167mg/L, second CAC 2155mg/L.

These values make clear that what Feng Yujun calls the CAC (0.2%) is in fact the second critical associating concentration. When we performed oil displacement experiments, the polymer concentration was 0.1%, lower than the second CAC. An observed increase in oil recovery can therefore only be credited to the fact that the injected concentration exceeds the first CAC.

For DH-2, the polymer concentration in our experiment is even lower than its first CAC so that no substantial improvement in the recovery is observed.

For field use, in order to limit the cost of the polymer flood and to insure a good injectivity, the HPAM polymer concentration generally ranges from 100ppm to 1000mg/L. In contrast, when injecting HAP, for a successful field test, the operator must ensure that the injection concentration remains always higher than the CAC.

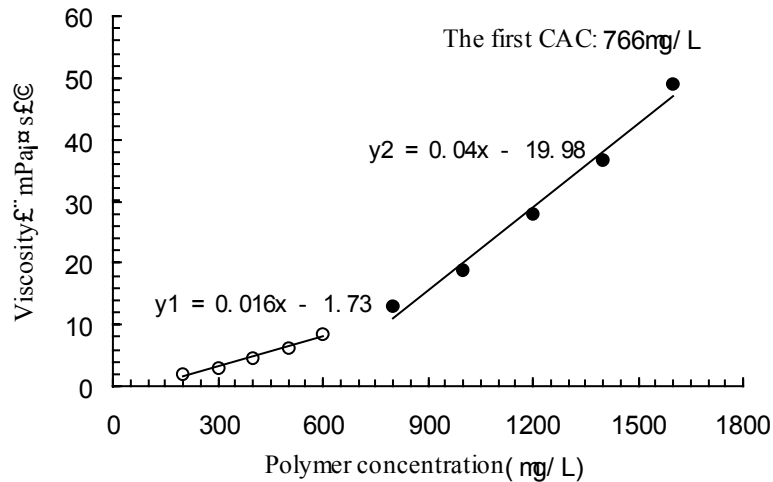


Fig.7a: The first CAC of DH-1

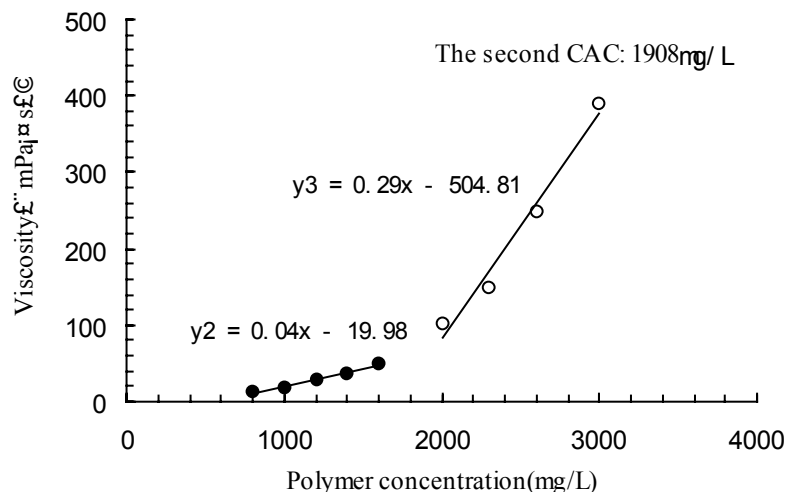


Fig.7b: The second CAC of DH-1

3 Conclusion

- (1) Comb polymer has a structure similar to HPAM. Its specificity lies in the electric and steric repulsions between pendant chains that confer a high rigidity to the backbone or main chain. The elasticity of this polymer can be compared to that of "willow". Compared to HPAM, it exhibits a better temperature and salinity resistance. At concentration higher than the CAC, the hydrophobic groups of the associative polymer tends to associate each other building up a three-dimensional network which strongly increases the viscosity of the polymer solution. The associative bond is weak, leading to a structure comparable to a "necklace".
- (2) All things being equal, the comb polymer, due to its high elasticity, exhibits an oil displacement efficiency higher than the other polymers studied. In contrast, the hydrophobic associative polymer requires the polymer concentration to be higher than the CAC to show a noticeable oil displacement efficiency. if the polymer concentration decreases lower than the CAC, the thickening ability of the polymer is low and oil displacement efficiency rapidly falls down. The concentration criterion is a strong limitation for the field use of hydrophobic associative polymers.

- (3) The hydrophobic association process can be divided in two steps: in the first one intramolecular bonds are predominant and there is a slight upward trend in the viscosity curve; in the second one intermolecular bonds are dominant leading to a rapid increase of the viscosity with the polymer concentration. At each step we associate a CAC.

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