Polymers
for Enhanced Oil Recovery
Make your EOR operations more economic with Aspiro™ Polymers

Mobility control is one of the most important concepts in any enhanced oil recovery process. Polymers are added to the water phase to increase its viscosity and reduce water permeability and thus decrease its mobility. To choose the best polymer for your conditions several factors have to be taken into account:

- Reservoir permeability and oil viscosity largely determine the choice in molecular weight of a suitable polymer.
- Reservoir temperature and brine composition have major influence on polymer stability and solubility under given conditions.
- Polymer injectivity, propagation profile, and retention behavior need to be considered to identify the most efficient solutions for your field.

The Aspiro™ Polymer product range

BASF offers a variety of different Aspiro™ Polymers which can be used to match diverse crude oils and particularly diverse field conditions.

<table>
<thead>
<tr>
<th>Aspiro™ Polymer</th>
<th>Type</th>
<th>Monomer Components</th>
<th>Application</th>
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<tr>
<td>P 42XX range</td>
<td>Copolymer</td>
<td>Acrylamide-Sodium Acrylate</td>
<td>$T &lt; 80 , ^\circ C;, \text{low salinity;},\text{medium hardness}$</td>
</tr>
<tr>
<td>P 54XX range</td>
<td>Copolymer</td>
<td>Acrylamide – ATBS*</td>
<td>$T &lt; 95 , ^\circ C;, \text{all salinities}$</td>
</tr>
<tr>
<td>P 66XX range</td>
<td>Associative Polymer</td>
<td>Acrylamide – ATBS* – Hydrophobic Monomer</td>
<td>$T &lt; 95 , ^\circ C;, \text{all salinities;},\text{high resistance factor in reservoir esp. in high salinity, high temp. conditions}$</td>
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<td>Associative Polymer</td>
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<td>$T &lt; 80 , ^\circ C;, \text{low salinity;},\text{high resistance factor}$</td>
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* ATBS: 2-Acrylamido-tertiary-butyl sulfonic acid
Standard hydrolyzed polyacrylamide (HPAM) is the most widely used polymer in enhanced oil recovery applications. HPAM can be obtained either by post hydrolysis of acrylamide homopolymers or by copolymerization of acrylamide and sodium acrylate. Advantages and disadvantages of the different products are summarized here.

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<th>Standard</th>
<th>Sulfonated</th>
<th>Associative</th>
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<td>Aspiro™ P 4211</td>
<td>Aspiro™ P 5411</td>
<td>Aspiro™ P 6631</td>
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<td>Aspiro™ P 4261</td>
<td>Aspiro™ P 5451 X</td>
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**Advantages**

- High molecular weight;
- High viscosifying power

**Disadvantages**

- Low calcium tolerance;
- Shear sensitive

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**Posthydrolyzed PAM**

- Better calcium tolerance;
- Improved shear stability;
- Improved dissolution

**Copolymer**

- Lower viscosifying power
BASF offers a range of copolymers that have a more narrow molecular weight and anionicity distribution as well as excellent solubility (e.g. Aspiro™ P 4251). For copolymers, anionicity in general has a strong impact on the overall solubility and adsorption performance of the polymer.

While high anionicity is advantageous to achieve low adsorption on sandstone rock, the solubility of the polymer is impaired in particular in saline brines.

With increasing temperature lower anionicity products should be chosen since hydrolysis of acrylamide moieties will increase anionicity further. This, however, might cause precipitation when the polymer propagates in the reservoir.

The viscosifying power of a copolymer is mainly impacted by the molecular weight of the polymer. High molecular weights result in high viscosifying power. However, this results in a pronounced susceptibility against mechanical degradation.

Taking the different product requirements into account the Aspiro™ Polymer range covers different anionicities and molecular weights for varying field conditions with the viscosifying performance being shown in Fig. 2 – 5.
Aspiro™ P 4251 exhibits a good viscosity performance at relatively low concentrations (Fig. 2). Viscosity remains constant even when calcium content is increased substantially (Fig. 3). This versatile applicable polymer is able to cover a wide range of salinities and temperatures while maintaining good solubility (Fig. 3 and 4).
Fig. 4: **Bulk viscosity scan of Aspiro™ P 4251 at 20 °C in brines with different salinities**

![Graph showing bulk viscosity of Aspiro™ P 4251 at 20 °C in brines with different salinities. The x-axis represents polymer concentration (ppm) ranging from 0 to 2,500, and the y-axis represents viscosity in cPs ranging from 0 to 90. Four lines represent different TDS concentrations: 70 ppm TDS, 4,300 ppm TDS, 10,700 ppm TDS, and 21,250 ppm TDS.](image)

- **70 ppm TDS**
- **4,300 ppm TDS**
- **10,700 ppm TDS**
- **21,250 ppm TDS**

Brookfield LV with UL Adapter

T = 20 °C

Brine: TDS in ppm as indicated

Fig. 5: **Bulk viscosity scan of Aspiro™ P 4251 in a saline brine at different temperatures**

![Graph showing bulk viscosity of Aspiro™ P 4251 in a saline brine at different temperatures. The x-axis represents polymer concentration (ppm) ranging from 0 to 2,500, and the y-axis represents viscosity in cPs ranging from 0 to 60. Five lines represent different temperatures: 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, and 70 °C.](image)

- **20 °C**
- **30 °C**
- **40 °C**
- **50 °C**
- **60 °C**
- **70 °C**

Brookfield LV with UL Adapter

T = as indicated

Brine: 42,400 ppm TDS with 6,033 ppm divalents
High salinity conditions

When long term stability in highly saline brines at moderate to high temperatures is required, the stability of standard polyacrylamide sodium acrylate copolymers (Aspiro™ P 42XX series) against hydrolysis and degradation might not be sufficient. In this case BASF offers the range of sulfonated polymers (Aspiro™ P 54XX).

This polymer class is known to be less sensitive to high temperature, high salinity conditions. Fig. 6. depicts an improved viscosity performance of Aspiro™ P 5411 in the presence of divalent ions. While standard HPAM loses 69% in viscosity with increasing content of calcium ions, the more stable Aspiro™ P 5411 loses only 56% in viscosity. It is worth noting that the molecular weight of Aspiro™ P 5411 is lower than that of Aspiro™ P 4251.

Fig. 6: Improved viscosifying stability of sulfonated HPAM in presence of divalent ions

![Graph showing improved viscosity performance of Aspiro™ P 5411 compared to standard HPAM]
We support you to be more successful with our associative polymer technology.

BASF has developed another range of commercial polymers based on associative technology which offers several application improvements over standard HPAM:

- significantly lower polymer consumption
- excellent mobility control
- improved sweep efficiency

Associative polymers are hydrophobically modified, but still water soluble polymers. Compared to standard HPAM, small amounts of hydrophobic groups are incorporated in the polymer backbone in addition to the well-known monomer components acrylamide and sodium acrylate. The hydrophobic side groups of different polymer molecules interact with each other and thereby generate additional viscosity by forming a polymer network (see Fig. 7). Since the viscosity of this polymer network is significantly larger than that of independent, individual polymer chains, associative polymers in general are able to deliver superior viscosifying power than standard HPAM of a similar molecular weight.

All Aspiro™ P 6XX associative polymers have shown excellent solubility and filterability in various brines. The dissolution characteristics are excellent and very similar to standard HPAM. Aspiro™ P 62XX polymers are designed for mild field conditions. These polymers yield high mobility reduction at a significantly lower dose level compared to standard HPAM. Aspiro™ P 66XX polymers have been developed for use in harsh conditions. Their distinct performance profile is based on a unique, thermally stable hydrophobic component. The hydrophobe-hydrophobe interaction becomes even stronger with increasing temperature. A major advantage of this thermo-associative effect is, that the initial viscosity is maintained or even increased over a wide temperature range. In contrast to this, standard polyacrylamides significantly lose viscosifying power with increasing temperature (see Fig. 9).
Associative polymers – performance evaluation

Unique rheology profile of associative polymers in porous media

The rheology behavior of associative polymers in porous media flow is significantly different from that of standard HPAM. While standard polyacrylamides exhibit a linear increase of the resistance factor with increasing bulk viscosity of the polymer / brine solution, associative polymers show an exponential increase of the in-situ viscosity (see Fig. 9). Thus, the performance of associative polymers can be hardly assessed from measuring bulk rheology. It is decisive for associative polymers to perform porous media flow experiments in order to assess their true performance. We recommend to perform coreflood experiments – preferably in the presence of oil.

Fig. 9: Coreflood experiments on polymers with rel. associative content ranging from 0 to 2

Anton Paar Physica MCR301, cone plate geometry; shear rate 10 s⁻¹
T = 20 °C
Brine: 10,000 ppm TDS, no divalents
Polymer concentration: 1,000 ppm
Serial dual-core set-up: length 7 cm each, Bentheimer sandstone
Brine injection starting @ 1 ml/min with rate steps up to 50 ml/min
How to evaluate associative polymers?

While the resistance factor and the network strength generated for associative polymers strongly depend on temperature and salinity conditions, further key performance parameters like injectivity, propagation profile, and retention are impacted also by these parameters. We adjust the chemistry of our Aspiro™ Polymers in order to cope with technical requirements over a broad range of field conditions.

Aspiro™ P 6201 is our associative polymer for low temperature, low salinity applications. As can be seen in Fig. 10–12 it shows good injectivity, excellent propagation, as well as low adsorption under the conditions stated. Aspiro™ P 6631 provides improved temperature stability as well as excellent salt tolerance – it is therefore designed for more challenging field conditions under which high to very high resistance factors can be achieved.

**Injectivity**

- Good injectivity
- $p_{\text{max}} = 1$ – $5$ PV
- $p_{\text{plateau}} = 5$ – $20$ PV

Flooding experiment with serial dual-core set-up: length 7 cm each, Bentheimer sandstone; polymer concentration: 750 ppm, temperature: 50°C; brine: 16,500 TDS with 1,000 ppm divalents; brine injection: 1 ml/min

**Propagation**

- $d_{p1}$
- $d_{p5}$
- $d_{p2}$
- $d_{p6}$
- $d_{p3}$
- $d_{p7}$
- $d_{p4}$

Coreflood with oil, Core: Bentheimer Sandstone; brine: 20,000 TDS; temperature: 29°C; waterflood until Sor; Polymer injection 1 ft/day (1 PV); Polymer concentration 1,000 ppm; post water flush 4 PV
Adsorption

- TOC 1
- TOC 2
- TON 1
- Tracer 2
- Tracer 1
- TON 2

Adsorption: 33 µg/g of rock
Inaccessible pore volume (IPV): 0.25
Polymer concentration 750 ppm; brine 16,000 ppm TDS; 1,000 ppm divalents; Bentheimer sandstone core (12 inches); flooding until Sor and injection of polymer, three pressure tabs along the core; determination of adsorption via effluent analysis regarding polymer concentration by total organic carbon (TOC) and total organic nitrogen (TN) relative to initiated polymer concentration

Fig. 12: Low adsorption for Aspiro™ P 6201

**Selecting the right product for your field**

Due to excellent compatibility of our associative polymers with BASF Aspiro™ Surfactants, our products are in general a great choice for alkaline-surfactant-polymer or surfactant-polymer projects.

Each polymer flooding project is different and requires a variety of different disciplines to be involved. Especially the number of variables involved in the design of a polymer project can make the undertaking a quite complex scenario in which many parameters have to be considered, e.g. monomer selection, polymer structure, dissolution techniques, injection systems, injection water, product logistics, supply chain aspects and many more. BASF provides a wide range of expertise to make your operations more successful. Our dedicated teams are well prepared to support you to identify the best solutions that fit your company requirements and your reservoir conditions. We are experts in delivering large quantities of product around the world and ensure reliable supply with the scale to grow your business.
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