# A Regular, Hydrophobically Modified Polyampholyte as Novel Pour Point Depressant

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**ABSTRACT:** A new regular polyampholyte, namely poly(N,N-diallyl-N-octadecylamine-*alt*-(maleic acid)), was studied as an additive to crude oil. The amphiphilic polyampholyte proved to be an efficient pour point depressant, to inhibit the deposition of wax, and to improve the viscosity of waxy crude oil from the Akshabulak oilfield (Western Kazakhstan). On optimizing the concentration of the polymer, both the kinematical viscosity and the pour point of waxy crude oils were found to be strongly decreased. The morphology of the paraffin aggregates formed was compared before and after heat treatment of the waxy crude oils, in the presence and the absence of the polymer. The rheological characteristics of the waxy crude oil were markedly improved, in particular, by decreasing the plastic viscosity and the yield stress values upon addition the polymer. The inhibition of wax deposits in the presence of the amphiphilic polyampholyte was interpreted in terms of its interference with the wax crystallization process because of the formation of inverse micellar structures. Although the interaction of the cationic and the anionic groups on the polymer backbone stabilizes the smaller size of the aggregates, the hydrophobic side chains of the polymer provide nucleation sites and cocrystallize with the paraffins, thus modifying the paraffin crystal structure. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2101–2108, 2005

**Key words:** Akshabulak crude oil; regular polyampholyte; pour point depressant; paraffin aggregates

## INTRODUCTION

Hydrophobically modified polyampholytes have unique structures and properties because of the presence of hydrophobic "tails" and hydrophilic, strongly interacting zwitterionic "heads."[1–3] Laschewsky and coworkers[4–11] reported on the synthesis and characterization of such zwitterionic polysoaps, which combine the features of polyzwitterions and micellar polymers. According to the variation of the polymer geometry, "head-type," "mid-tail-type," and "tail-end-type" zwitterionic polysoaps can be produced. The unusual low viscosities of zwitterionic polysoaps in water are attributed to intramolecular aggregation of the hydrophobic side chains, keeping the hydrodynamic radius small.[5,6] DSC and X-ray studies of the amphiphilic polyampholytes revealed the formation of superstructures in the bulk.[6,7,9,11] The combination of electrostatic attractions between the cationic moieties (typically ammonium groups) and the anionic groups (typically sulfonate and carboxylate groups) with hydrophobic interactions between the long flexible side chains are the driving force of superstructure formation.[7,11]

Although well-defined homopolymers were preferred in the above-described and related model studies,[12] the underlying need for the synthesis of new monomers, when polymer properties must be adjusted, is not practical for most applications. Therefore, more convenient approaches have been developed, in particular, the free-radical copolymerization of zwitterionic and hydrophobic monomers.[13–19] For instance, acrylamide-based hydrophobically modified polysulfo- and carbobetaines containing N-butylphenylacrylamide and varying amounts of 3-(2-acrylamido-2-methylpropanedimethylammonio)-1-propanesulfonate (AMPDAPS) or 4-(2-acrylamido-2-methylpropyldimethylammonio)butanoate (AMPDAB), respectively, were synthesized by micellar copolymerization.[20] The amount of AMPDAPS or AMPDAB in the terpolymers varied from low (5 mol %) to high (25 mol %). An alternative convenient route to hydrophobically modified polyampholytes is offered by the chemical modification of polymers, enabling variable strategies.[21–25] However, the simplicity of these two strategies is counterbalanced by the less-defined molecular structure of the resulting products. An attractive compromise between these two extremes is offered by the alternating

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copolymerization of appropriate monomer pairs, to incorporate anionic moieties, cationic moieties, and hydrophobic groups into the same polymer in a regular way.[26]

Hydrophobically associating polyampholytes may be effective viscosity enhancers in high salinity media, as they combine the properties of hydrophobically modified neutral polymers and polyampholytes.[27,28] The viscosity of hydrophobically modified polyampholytes increases much faster than that for the unmodified because of intermolecular association of hydrophobic parts. This would make them useful in applications where thickeners are required in brine solution, as for example, in sewage treatment, flocculation, and oil recovery processes. Another perspective application area of hydrophobic polyampholytes is their use as pour point depressants (PPDs) of oil.[29] The PPDs are specially designed substances to change the rheology of the crude oil and to ease the flow problems in pipelines affected by deposition of wax.[30] The use of PPDs to change wax appearance temperature, power point, and viscosity of crude oils is well known in the literature, and various types of (co)polymers such as ethylene–vinylacetate copolymers, vinylacetate–olefin copolymers, alkyl esters of styrene and maleic acid copolymers, polyalkyl(meth)acrylates, alkyl phenols, and $\alpha$-olefin copolymers have been described.[15,31–38] Manka and Ziegler[37] discussed what factors affect the performance of crude wax-control additives and what contributes to crude oil specificity.

Most recently, new regular amphiphilic polyampholytes bearing hexyl, dodecyl, and octadecyl side chains were reported, which were synthesized by alternating copolymerization of maleic acid and $N$-alkyl-diallylamines.[39] These copolymers disposed in a well-defined structure are readily accessible from low-cost starting materials and are hydrolysis resistant. Although these copolymers are soluble in aqueous base for short-to-medium alkyl chains, forming micellar aggregates, the copolymer derived from $N$-octadecyl-diallylamine is no more water-soluble but exhibits a weak affinity to hydrocarbons such as toluene.[39] In the context of the successful use of some hydrophobically modified polyampholytes in our previous work,[15] we investigated the usefulness of the new copolymer as additive for crude oil, in particular as PPD.

This paper presents the results of our study for crude oil samples originating from the Akshabulak oil field (Western Kazakhstan). The Akshabulak crude oil, due to high content of heavy paraffins, looses its fluidity at +21°C. Therefore, the reduction of the pour point, the suppression of paraffin deposits, and an improvement of oil fluidity are very important.

## EXPERIMENTAL

The synthesis of the copolymer is reported in Ref. 39. The FTIR spectrum in solid state was recorded by a PerkinElmer Spectrum GX. Chromatographic analysis of the Akshabulak crude oil and paraffins was carried out using AutoSystem XL gas chromatograph (PerkinElmer, Wellesley, MA) according to ASTM D2887 standards.

For preparation of the samples PPD-1–PPD-6, an appropriate amount of poly[($N,N$-diallyl-$N$-octadecylamine-$alt$-(maleic acid)] (50–300 ppm) was dissolved in isopropanol at 80°C and vigorously stirred for 1 min. The polymer solution was added to the Akshabulak crude oil at 60°C. The oil was then thermostated for 30 min and cooled at a rate of 35–40°C/h.

Pour points were measured according to ASTM D97 and ASTM D5853 standards, in a chamber equipped by a refrigerator (model SDM-530, S.D.M. Lin-Tech, Germany) at 0°C, −17°C, and −34°C.

Kinematic viscosity was measured by thermostated Ubbelohde viscometer with appropriate capillary constant in the temperature range from 10°C to 60°C, according to ASTM D445–96 standard. Before starting of the measurement, the oil sample was thermally equilibrated for 20 min.

Paraffin morphology was determined with a polarized microscope connected with a video camera (VC 301, Linkam Hotstage; Linkam Scientific Instruments, The Netherlands). A special software used allowed to view the image of paraffin crystals on the computer display as a micrographs. Oil samples were heated up to 30°C on a heat table (Model TMS 94, Linkam Scientific Instruments), and cooled at a rate of 1°C/min until the first paraffin crystals appeared.

Inhibition of wax deposition was tested on a "Cold Finger" that models the process of wax precipitation within an oil pipeline (Fig. 1). About 350 mL of Akshabulak oil was placed inside a double-walled steel cylinder and thermostated (thermostat Julabo F12, Julabo Labortechnik GMBH, Germany) at 30°C for 15 min. Then, a steel finger at 0°C was placed into the warm oil. After 4 h, the finger was taken out and placed into acetone to remove residual adhering oil. Finally, the remaining wax deposit was thoroughly removed from the cold finger and weighed.

The apparent viscosity ($\eta$) and shear rate ($\tau$) were measured with a computer-controlled Brookfield rheometer (EuroPhysics Rheo 2000; Brookfield Viscometers Ltd., UK) combined with thermostated "cylinder-to-cylinder" measurement system—MK-CC45 (MS-CC45, Brookfield Viscometers Ltd.). Temperature, shear rate ($D$), and frequency were controlled by the software "RHEO 2000 (2.6)." The measurements were carried out at constant shear rate (5 s$^{-1}$), changing the temperature linearly (cooling rate is 30°C/h), as well as at constant temperature changing the shear
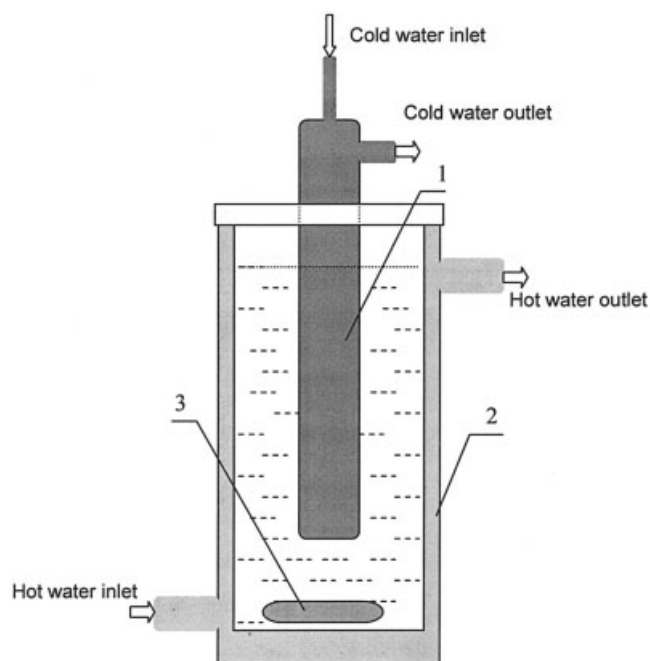
**Figure 1** Cold finger for the measurement of paraffin deposition. 1: cold finger (with the temperature 0°C), 2: thermostated bath, 3: magnetic stirrer.

rate (from 0 to 100 $s^{-1}$). The plastic viscosity ($\eta$) and the yield stress ($\tau_0$) were obtained using the Newton model $r = k_1 \times D$ (where $k_1$ is the Newtonian viscosity, $D$ is the shear rate) and the Hershel–Balkly equation $\tau = \tau_0 + \eta \times D^n$ (where $\tau_0$ is the yield stress, $\eta$ is the plastic viscosity, $n$ is the non-Newtonian coefficient).

## RESULTS AND DISCUSSION

Although polyampholytes mostly dissolve well, in few, protic solvents, such as trifluoroethanol or formamide,[4,6] the regular copolymer structure with the long alkyl side chains enables the dispersion of poly(N,N-diallyl-N-octadecylamine-*alt*-(maleic acid)) in the crude oil. This finding is an agreement with the ability to swell the bulk polymer with toluene.[39] Presumably, the dispersion of the copolymer in the oil is due to the formation of inverse micellar structures; the octadecyl chains shielding the zwitterionic groups from the environment so that clustering with subsequent phase separation is prevented. The presence of both hydrophobic and hydrophilic groups is easily recognized in the FTIR spectrum of the polymer (Fig. 2). It exhibits intensive symmetrical and antisymmetrical vibrations of CH groups at 2923 and 2852 $cm^{-1}$ from the octadecyl groups. The rocking vibration of $CH_2$ groups appears at 712 $cm^{-1}$ and corroborates the presence of long paraffin moieties. The intensive band at 1725 $cm^{-1}$ belongs to carbonyl group of maleic acid. Additionally, a weak mode of the carboxylate ion appears at 1542 $cm^{-1}$. The poorly resolved signals at
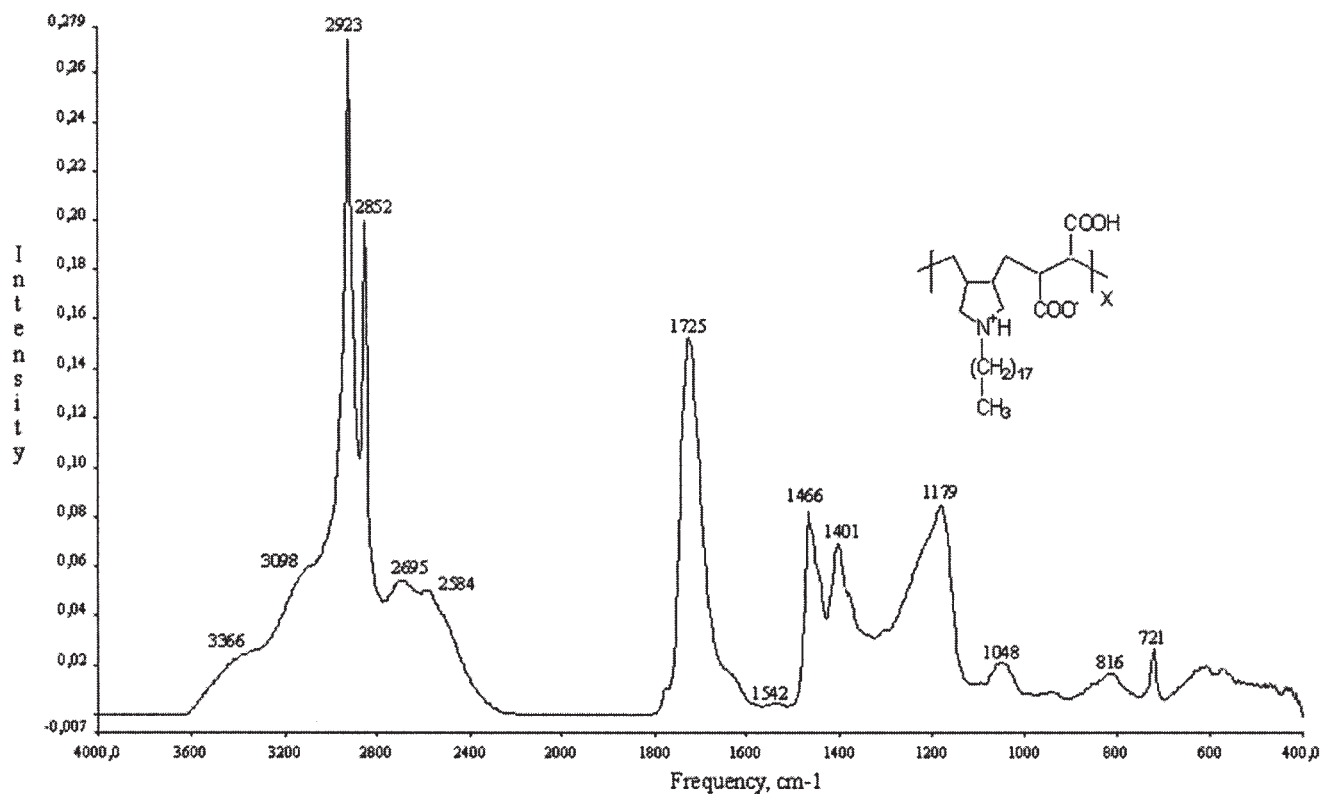


**Figure 2** FTIR spectrum of solid poly[(N,N-diallyl-N-octadecylamine-*alt*-(maleic acid))].
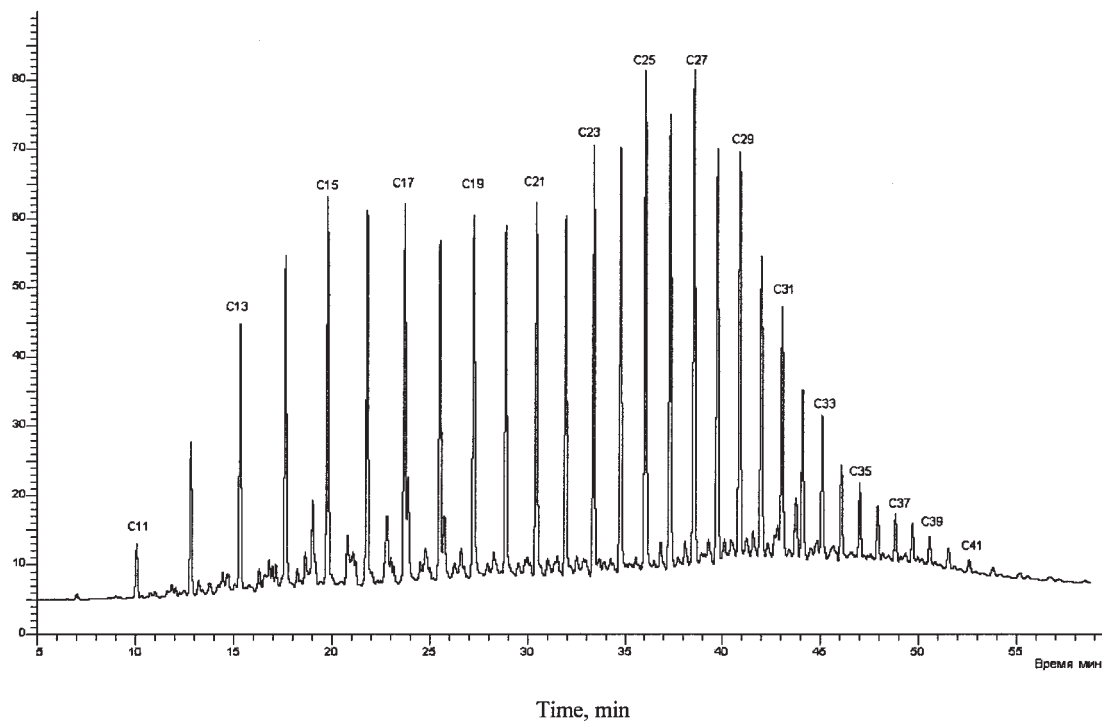
**Figure 3** Chromatograms of paraffins extracted from the Akshabulak oil field (Western Kazakhstan).

2695 and 2584 cm$^{-1}$, on the shoulder of the alkyl bands, indicate the presence of protonated amines and reflect the zwitterionic character of the polyampholyte structure.

The phase stability of crude oils is dependent on a multitude of factors, including temperature, pressure, and component fractions, especially long chain paraffin and polar asphaltene fractions.[40] Paraffins precipitate out of the crude oil during pipeline transportation because of solubility limits, and form paraffin–oil deposits on the pipe walls. To overcome this problem, heating, dilution with lighter stocks, and preferentially wax-control additives are applied. The typical concentration of PPDs to be added depends on crude oil characteristics and is varied between 50 and 5000 ppm. The interaction between the PPD and paraffin in the crude oils is crucial, and the additives work best when they are matched to the paraffin distribution in the crude oil.[37] Chromatograms of the Akshabulak crude oil together with paraffins and asphaltenes content, as well as physicochemical and rheological characteristics, are shown in Figure 3 and Table I.

To investigate the usefulness of the new hydrophobically modified polyampholyte, it was added to the crude oil in amounts from 50 to 300 ppm, and the results were compared with one of the commercial additive "DMN-2005" (Russia) that is applied for improvement of the fluidity of the waxy crude oils of Western Kazakhstan. The influence of polymer concentration on the kinematic viscosity and pour point of the Akshabulak crude oil are summarized in Table

II. As shown in Table II, the heat treatment decreases both the kinematic viscosity and pour point temperature. However, the improvement is only temporary, and after some time the pour point temperature and kinematic viscosity restore. In contrast, the reduction of the kinematic viscosity and the pour point temperature due to the addition of the polymer is permanent. An effective concentration of 100–150 ppm of the polyampholyte is needed to decrease the pour point temperature down to 3°C, while 50 ppm is sufficient to obtain a markedly improved viscosity. The commercial additive DMN-2005 in the same concentration decreases the pour point temperature of the Akshabulak crude oil down to 9°C.

**TABLE I**
**Distribution of Hydrocarbons and Paraffins, Content of Asphaltenes and Rheological and Physicochemical Properties of Akshabulak Crude Oil**

| | |
|---|---|
| Hydrocarbons and paraffins (wt. %) | |
| $C_4$–$C_8$ | 1.12 |
| $C_9$–$C_{14}$ | 24.55 |
| $C_{15}$–$C_{19}$ | 29.61 |
| $C_{20}$–$C_{29}$ | 37.2 |
| $C_{30}$–$C_{44}$ | 6.4 |
| Asphaltenes (wt. %) | 0.58 |
| Physicochemical and rheological characteristics | |
| Density (kg/m$^3$) | 812 |
| Kinematic viscosity at 20 °C (cSt) | 7.73 |
| Kinematic viscosity at 50 °C (cSt) | 3.57 |
| Pour point according to ASTM D 5853 | 21 |

**TABLE II**
**Kinematic Viscosity and Pour Point Temperature of the Akshabulak Crude Oil in the Absence and Presence of PPDs**

| Sample | Kinematic viscosity (mm²/s) of oil samples at various temperatures (°C) | | | | | | | Pour point (°C) |
|---|---|---|---|---|---|---|---|---|
| | 20 | 25 | 30 | 35 | 40 | 45 | 50 | |
| Crude oil | 12.7 | 9.7 | 7.03 | 5.9 | 4.8 | 4.3 | 3.8 | 21 |
| Heat-treated crude oil | 11.0 | 8.3 | 6.3 | 5.0 | 4.4 | 3.9 | 3.6 | 9 |
| PPD-1 (50 ppm) | 10.7 | 8.2 | 6.2 | 5.0 | 4.5 | 4.0 | 3.6 | 6 |
| PPD-2 (100 ppm) | 7.7 | 6.8 | 5.9 | 5.0 | 4.3 | 3.9 | 3.5 | 3 |
| PPD-3 (150 ppm) | 9.9 | 7.7 | 6.0 | 4.9 | 4.4 | 4.0 | 3.3 | 3 |
| PPD-4 (200 ppm) | 11.1 | 8.2 | 6.1 | 4.9 | 4.5 | 4.0 | 3.5 | 6 |
| PPD-5 (250 ppm) | 11.3 | 8.3 | 6.1 | 5.0 | 4.6 | 4.1 | 3.5 | 6 |
| PPD-6 (300 ppm) | 11.7 | 8.6 | 6.2 | 4.9 | 4.5 | 4.1 | 3.6 | 6 |
| "DMN-2005" (100 ppm) | 7.6 | 6.9 | 6.1 | 5.0 | 4.3 | 4.0 | 3.4 | 9 |

To understand the effect of the polymer, the morphology of the paraffin crystals formed in the waxy crude oil before and after heat treatment, with and without added PPD, was studied by microscopy. Representative micrographs are shown in Figures 4(a–d). The structure of paraffin in untreated waxy crude oil represents a three-dimensional network [Fig. 4(a)]. However, after the heat treatment, the paraffin aggregates are bigger in size [Fig. 4(b)]. The appearance of platelike paraffin aggregates is probably due to the adsorption of paraffin molecules on the surface of asphaltenes and resins.[41] It was observed for a model paraffin–oil system that the presence of asphaltenes in small proportions (~0.1 wt %) hinders the paraffin gelation,[40] whereas the presence of higher amounts of asphaltenes resulted in macroscopic phase separation:
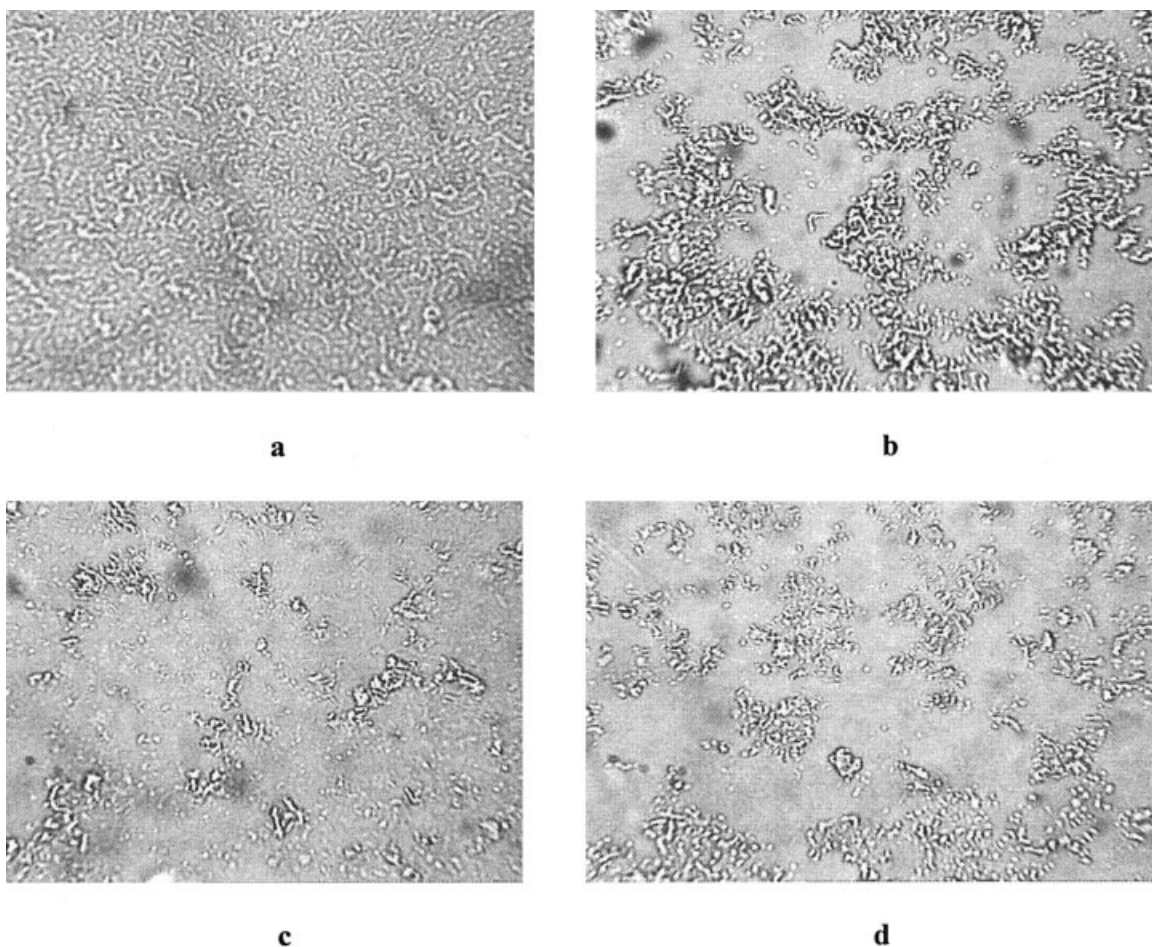


**Figure 4** Morphology of crude oil before (a) and after heating and cooling (b), treated with 100 ppm PPD-2 (c) and 150 ppm PPD-3 (d) at 0 °C.

**TABLE III**
**The Quantity of Wax Precipitates and Wax Inhibition Degree of Crude Oil After Heat Treatment and in the Presence of PPD-2 and Commercial "DMN-2005" (Russia)**

| Akshabulak oil sample | Precipitated wax amount (g) | Inhibition degree of wax precipitation (%) |
|---|---|---|
| Crude oil | 6.9 | — |
| Heat-treated oil | 4.3 | 37.7 |
| Addition of PPD-2 | | |
| (100 ppm) | 3.1 | 55.1 |
| "DMN-2005" | | |
| (100 ppm) | 3.0 | 56.5 |

a deposit consisting of asphaltenes and paraffins separated out of the liquid. Since the Akshabulak crude oil contains 0.58 wt % of asphaltenes, it is likely that asphaltene–paraffin complexes are responsible for formation of big aggregates after the heat treatment. In comparison, the aggregates found in the presence of PPD-2 and PPD-3 are much smaller. As shown in Figures 4(c,d), the sizes of agglomerates upon addition of PPD-2 and PPD-3 are different. Paraffin aggregates in the sample PPD-2 are smaller than that of aggregates in sample PPD-3. This means that the polymer additive with concentration of 100 ppm most effectively influences the morphology of the paraffins. This is presumably due to the preferential adsorption of the high molecular weight paraffin fractions on the surface of amphoteric macromolecules mediated by the long alkyl groups. The corona of the inverse micelles made of octadecyl chains immobilizes the paraffins, and thus prevents them from forming a continuous three-dimensional network. This results in a large free space, which is available for the liquid fraction of the crude oil to flow freely. The zwitterionic part of the macromolecules is dissimilar to the wax crystals and blocks the extensive growth of wax matrices. As a result, the pour point is reduced and the rheological properties are improved.

Table III lists the quantity of wax deposited and the degree of inhibition of wax deposits in crude oil. Wax deposits are reduced by 55.1% in the presence of PPD-2 and this amount is comparable with commercial DMN-2005. The deposits are also notably lower than that for heat-treated oil.

The results of the rheological experiments follow the same pattern. The shear stress versus shear rate curves at 10°C and at −5°C are exhibited in Figures 5 and 6, for the crude oil before and after heat treatment or in the presence of polymer additive, respectively. The addition of polymer decreases the value of shear stress by a factor of >2 in comparison with the crude oil, e.g., the rheological characteristics of the crude oil are significantly improved. These results are in good
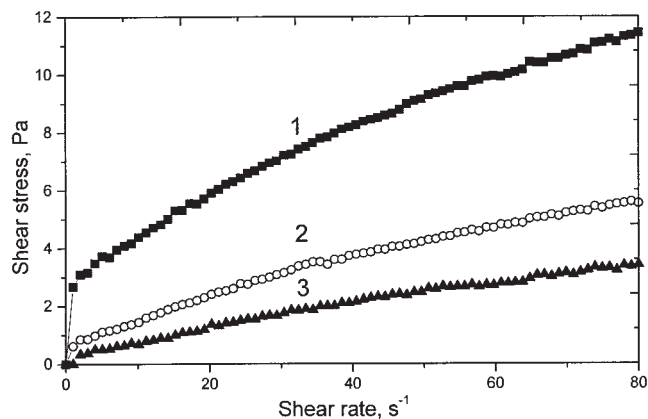


**Figure 5** Dependence of shear stress on the shear rate at 10°C for crude oil before (curve 1), after heat treatment (curve 2), and in the presence of 100 ppm of PPD-2 (curve 3).

agreement with data on the plastic viscosity and yield stress shown in Table IV and in Figures 7 and 8.

Concerning the paraffin adsorption on the macromolecular chains, one can outline the existence of supramolecular structure of polyampholyte. A supramolecular structure of polyampholyte in oil environment represents reverse micelles consisting of hydrophilic core (zwitterionic part) surrounded by hydrophobic edge (octadecyl group). The PPD mechanism suggests the adsorption of paraffin molecules on the surface of hydrophobic micelles inhibiting the formation of large wax crystal matrix and hindering the gelation mechanism. Thus, the hydrophobically modified polyampholyte based on poly(*N,N*-diallyl-*N*-octadecylamine-*alt*-(maleic acid)) acts both as wax deposition inhibitor and as PPD. Its efficiency is comparable with commercial polymers that are commonly used as wax-control additives. Though the octadecyl groups in polyampholyte side chains fit more or less to the paraffin distribution of the Akshabulak crude oil, the PPD
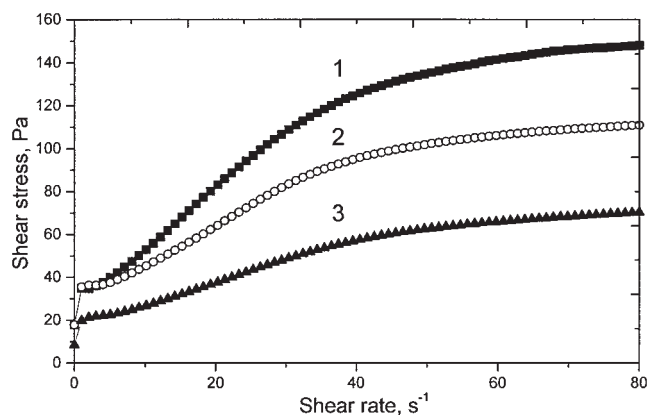


**Figure 6** Dependence of shear stress on the shear rate at –5°C for crude oil before (curve 1), after heat treatment (curve 2), and in the presence of 100 ppm of PPD-2 (curve 3).

**TABLE IV**
**Rheological Data Calculated According to the Hershel-Balkli-Type Model**

| Oil sample | $T$ (°C) | Yield stress (Pa) | Plastic viscosity (Pa s) |
|---|---|---|---|
| Crude oil | 15 | 0.06 | 0.35 |
| | 10 | 1.87 | 0.63 |
| | 5 | 5.83 | 1.30 |
| | 0 | 10.23 | 5.74 |
| | −5 | 23.18 | 21.92 |
| Heat-treated oil | 15 | 0 | 0.07 |
| | 10 | 0.13 | 0.33 |
| | 5 | 2.97 | 0.70 |
| | 0 | 5.53 | 4.35 |
| | −5 | 10.21 | 14.46 |
| 100 ppm of PPD-2 is added | 15 | 0 | 0.08 |
| | 10 | 0 | 0.15 |
| | 5 | 0.30 | 0.61 |
| | 0 | 4.21 | 1.09 |
| | −5 | 7.35 | 7.34 |
| 100 ppm of "DMN-2005" (Russia) is added | 15 | 0 | 0.07 |
| | 10 | 0 | 0.13 |
| | 5 | 0.57 | 0.71 |
| | 0 | 4.24 | 0.98 |
| | −5 | 7.25 | 7.61 |

might be further optimized by increasing the length of the side chains somewhat.

## CONCLUSIONS

The new regular hydrophobically modified polyampholyte poly(*N,N*-diallyl-*N*-octadecylamine-*alt*-(maleic acid)) was shown to act as efficient PPD for crude oil of the Akshabulak oil field. The effective concentration of PPD to inhibit the wax deposition, to de-
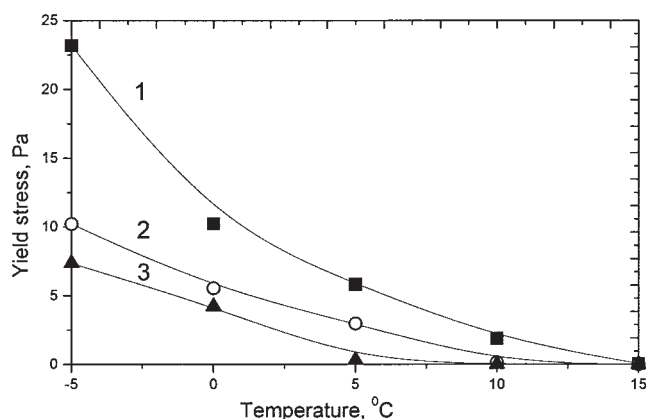


**Figure 7** Dependence of yield stress on temperature for the crude oil before (curve 1), after heat treatment (curve 2), and in the presence of 100 ppm of PPD-2 (curve 3).
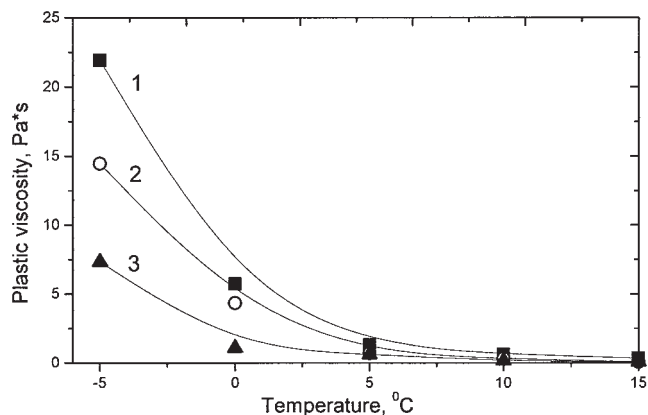


**Figure 8** Dependence of the plastic viscosity on temperature for the crude oil before (curve 1), and after heat treatment (curve 2), and in the presence of 100 ppm of PPD-2 (curve 3).

crease of the pour point temperature, and to improve the rheological characteristics of crude oils was found to be 100–150 ppm. The paraffin aggregates before and after heat treatment present a three-dimensional network and platelike structures, respectively. In the presence of the new PPD, the amount of paraffin crystals is drastically reduced, and the size of the aggregates becomes much smaller than that after heat treatment. The efficiency of the hydrophobically modified polyampholyte is attributed to the presence of both long hydrophobic chains and strongly interacting zwitterionic moieties in the polymer. In the oil environment, the polymer is assumed to form inverse micellar aggregates, in which the octadecyl groups of the shell adsorb the paraffin molecules and cocrystallize with them, while the zwitterionic parts prevent the further growth of the paraffin crystals.

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