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Polymer Depressor Additives: Synthesis, Microstructure, Efficiency

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Abstract—Depressor additives, an important class of functional polymers widely used in petrochemistry, are discussed. The consideration is based on the comparison of the synthetic approaches to the basic structural classes of polymer depressor additives and the characteristics of different polymers. The mechanisms of the depressor additive action related to their molecular structure and the advanced lines in the chemistry of polymers demonstrating the depressor effects are analyzed. In the bibliography of the review, the most important publications within the last 15 years are presented.

INTRODUCTION

Both crude oil and a number of the petroleum products (diesel fuel, kerosene, oils, and lubricants) are composed of multiple paraffin fractions with a wide molecular mass distribution and different molecular structures (acyclic hydrocarbons of normal and isomeric structure, paraffins proper; alicyclic hydrocarbons with extended alkyl fragments, which are named ceresines in the petroleum industry). Depending on the product type and the technology of its purification, the paraffin content can be as high as 30% [1, 2]; thus, petroleum is subdivided into low-paraffin (concentration of paraffins below 1.5 wt %), middle-paraffin (1.5–6.0 wt %), and paraffin petroleum (above 6.0 wt %) [3].

High-paraffin hydrocarbons are characteristic of the loss of viscoelastic properties at cooling. The fluidity loss is usually due to the crystallization of paraffins with formation of gels consisting of large-sized concretions of microcrystals (Fig. 1a). The paraffin crystallization results in the formation of sediments on the pipeline walls, in the clogging of fuel filters, and in the problems on functioning of fuel pumps (Fig. 1b) [4]. The paraffin sediments formed in transport of oil never consist of 100% paraffins. Usually, they are mixtures of paraffins (up to 70 wt %), resins and asphaltenes (up to 40 wt %), silica, and other mineral sediments, as well as water. In the petroleum industry of Russia, such sediments are designated by the abbreviation ARPS (asphalt-resin-paraffin sediments). In spite of the complex character of the ARPS composition; in most cases, they are formed because of easy paraffin sedimentation.

As a basic characteristic of crude oil and petroleum products, which reflects a lower relatively comfort temperature of their transport and operation, fluidity loss temperature $T_{f.l.}$ is used [5]. This characteristic applied to fuels is supplemented with an important performance parameter—filterability loss temperature $T_{ft.l.}$ determined according to the unified international standard.

For solving technical problems of oil production and transport of oil and petroleum products arising at reduced temperatures, special polymer additives are used [3, 6–9]. These additives are irreplaceable in marine oil production as well as in transport of heavy high-paraffin petroleum. The application of polymer additives providing transport of oil and petroleum products is a current problem for countries with a cold climate and extended communications. The consumption of these agents grows constantly and the prospects of the world market of these products for 2020 are estimated at 1.4 billion US dollars [10].

These agents act via different mechanisms. Some compounds reduce the fluidity loss temperature and may be considered as depressor additives (DA). It is important that the lowering of $T_{f.l}$ results both in prevention of formation of paraffin crystals (compounds with similar properties are named paraffin sedimentation inhibitors PSI) and in modification of paraffin crystals through variations in their morphology and surface properties so that the crystals do not stick together, giving paraffin gels (this group of compounds constitutes modifiers of paraffin crystals) [3, 7]. In addition to the modifiers of paraffin crystals, low-molecular-mass organic compounds and polymers acting as detergents and dispersants are also used
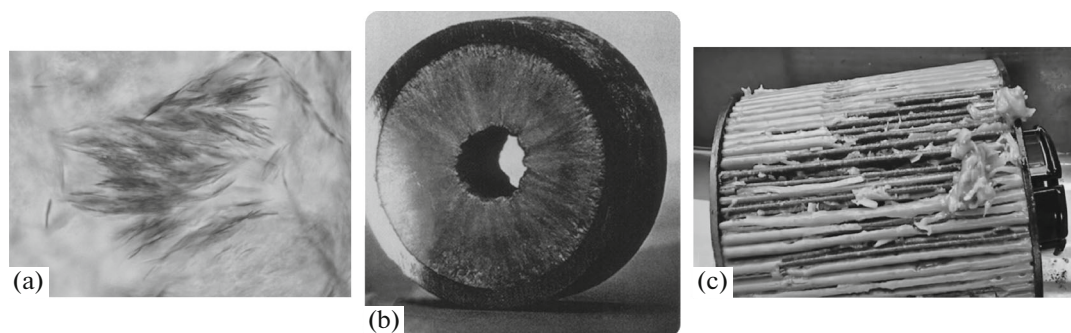
Fig. 1. Microcrystals of paraffin (a), paraffination of oil pipe (b), and automobile fuel filter (c).

[11]. Applied to the transport of heavy oil, in many cases, the term "depressor" implies a decrease in the oil viscosity independently of the process mechanism rather than a drop of gelation temperature. In the current review on heavy oil transport [12], depressor additives affecting the process of paraffin sedimentation and agents reducing hydraulic resistance are discussed separately.

The complex composition of petroleum suggests a fully empirical approach to the development of PSI: the same additives may demonstrate the opposite effects in the samples of oil and petroleum products. Moreover, the same polymer compounds (depending on oil composition) can affect its fluidity via different mechanisms. This is the reason that the title of this review reflects the unique characteristic of the polymer additives, namely, their depressor properties. However, the additives considered in this work can influence the process of formation of paraffin sediments via various mechanisms.

The mechanisms of the depressor action are related to their effects on the process of the paraffin crystallization. The specific structural feature of DA macromolecules (modifiers of the paraffin crystals) is the combination of long linear saturated hydrocarbon chains and polar functional groups or branched hydrocarbon fragments [13]. Because of the structural similarity of paraffins and linear saturated fragments, on the surface of the paraffin crystal nuclei, the coordination of DA macromolecules is observed. Further paraffin crystal growth is hindered by the presence of polar groups or branched fragments of macromolecules [14−16]. As a result, the crystallization of paraffin begins at a lower temperature or proceeds through formation of fine aggregates consisting of a stable crystalline modification of paraffin [17]. The paraffin crystallization in the form of the most stable crystalline phase prevents to a great extent the sticking together of crystals formed by the mesophase in the course of crystallization (aging) of a paraffin gel. These additives really act as dispersants. However, the formation of stable paraffin dispersions becomes possible owing to modification of the paraffin crystals, which differentiates them from the common surfactants used also in oil transport.

Thus, in the absence of DA, paraffins are crystallized with formation of platelike crystals easily sticking together to give bulky agglomerates, and in the presence of DA, the crystallization of paraffin results in dispersions of fine uniform crystals (Fig. 2). Some depressor additives do not reduce the turbidity temperature, but owing to formation of mobile suspensions of small crystals, the filterability loss temperature decreases significantly.

The mechanism of action of paraffin sedimentation inhibitors, which reduce $T_{f.l.}$ significantly, is unclear. It is believed that the retardation or prevention of paraffin crystal growth is attained by means of modification of the surface of nuclei (this mechanism is similar to the mechanism of action of modifiers). However, this effect is qualitatively different: in the presence of inhibitors, the crystallization begins at substantially lower temperatures. This uncertainty of the mechanisms of action determines the use of a general term "depressor additives" for designation of functional polymers intended for providing oil transport.

When analyzing the behavior of hydrocarbon mixtures containing DA, the effects of deformation history should be taken into account. This aspect of the problem was investigated previously [19] by following the changes in the morphology of paraffin particles during rheological tests in a rotating vessel at high rotation velocities (up to 400 s^{-1}). It was found that the primary fine paraffin particles form agglomerates upon long-time treatment, which results in an increase in $T_{f.l.}$ The solution flow rate also has an effect on the rate of paraffin sedimentation [20, 21]. A significant error in estimation of the real depressor effect, which is often ignored by researchers, is determined by the tendency of paraffin solutions in hydrocarbons to supercooling, especially for solutions in aromatic hydrocarbons. The correct method for $T_{f.l.}$ determination taking into account the possible supercooling was developed quite recently [22].
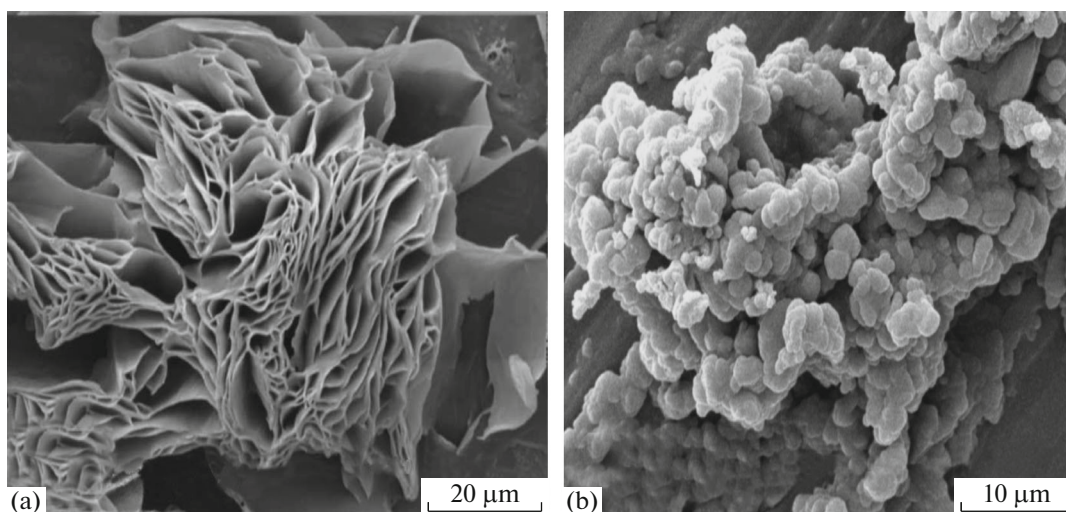
Fig. 2. SEM images of paraffin crystals formed in the absence (a) and in the presence of ethylene−vinyl acetate copolymer as depressor (b) [18].

The depressor effect of different additives manifests itself in changes in the physical characteristics of oil and petroleum products and was studied by various physicochemical methods (Table 1). The methods allow one to perform a qualitative and/or comparative evaluation of the DA efficiency, but the final conclusion on the prospects for the practical use can be made only from the results of range tests at different temperatures for a specific sample of petroleum or petroleum product.

The effect of DA on heavy oil may be explained by the influence on the process of paraffin crystallization, but the effects due to the DA coordination with asphaltenes [23, 24] as well as surface active properties of DA molecules (effect of "lubrication") show themselves in parallel [25]. Moreover, DAs are often combined with detergents and dispersants. The additives of these types, on one hand, modify the pipe surface, hindering paraffin sedimentation, and, on the other hand (which is more important) favor the formation and retention of fine dispersions of paraffin crystals in addition to the DA action [11].

The influence of the nature and the component ratio of petroleum on the efficiency of different DA and the qualitative and quantitative composition of paraffin sediments and ARPS depending on the chemical nature of depressor additives, temperature, and flow rate recently have been under thorough investigation in parallel with the synthesis of new-type additives and the study of their action on the viscosity of petroleum and petroleum products and fluidity loss and filterability loss temperatures. The crystallization of even two- or three-component paraffin mixtures is a complex process often dependent on multidirectional factors [26]. For multicomponent model mixtures and real petroleum samples, the p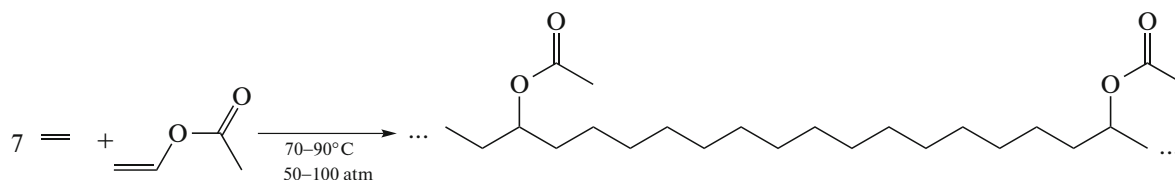roblem becomes much more difficult [27−30]. At the present stage, such problems are solved fully empirically: the creation of a valuable "work" model (perhaps, with determination of quantitative structure−property dependences) may be considered as a current problem of modern applied chemistry.

The detailed analysis of the mechanism of DA action is beyond the scope of this review, and the mentioned polymers predominantly demonstrate the properties of modifiers of paraffin crystals. The aim of this review was to consider the basic structural classes of depressor additives (both widely used and offering

Table 1. Key properties of petroleum and petroleum products changing under the action of DA as well as methods used for evaluating these variations

Property	Method
Paraffin sedimentation	"Cold rod" method, cooling disk
Morphology of paraffins	Scanning electron microscopy, optical microscopy, polarized light microscopy
Molecular structure of paraffins	Diffraction methods
Turbidity temperature (petroleum products) or crystallization onset temperature (petroleum)	Polarized-light microscopy, DSC, visual observation, viscometry
Fluidity loss temperature or solidification temperature	Visual observation
Fluidity at different temperatures	Viscometric determination of dynamic viscosity η, shear stress τ

promise) in terms of the efficiency of application in transport of oil and petroleum products. Special attention is paid to the problems of depressor synthesis, microstructure, and efficiency. In the descriptive part of the review, the current tasks and promising lines of investigation of the modification of DA of different types and the creation of new groups of these important functional materials for the modern petroleum industry were formulated.

ETHYLENE–VINYL ACETATE COPOLYMERS

Ethylene–vinyl acetate copolymer (EVA), a large-tonnage commercial polymer widely used as a structural material, plasticizer, and a base for adhesive emulsions also finds application as a depressor agent. The method of EVA production is based on the radical copolymerization of ethylene and vinyl acetate at moderately elevated temperature (up to 90°C) and pressure ≥50 atm:

$$7 = \quad + \quad \xrightarrow[50-100 \text{ atm}]{70-90°C}$$

EVA macromolecule is a linear molecule of PE with hydrogen atoms partially replaced by acetoxy groups. EVA has a history of investigation and practical use of more than fifty years [31]; now it finds wide application both in the transport of light oil and petroleum products [32, 33] and in the transport of heavy oil [15, 34] because of extremely low cost.

During the synthesis of EVA intended for use as DA, the ratio of comonomers should be controlled thoroughly. It was found experimentally that a polymer with high randomness and a strictly determined ratio of $-CH_2CH_2-$ and $-CH_2CHOAc-$ units has the best depressor characteristics. For high-paraffin petroleum products, for example, the optimum content of vinyl acetate is approximately 30 wt %, which corresponds to the molar ratio of comonomers [ethylene] : [vinyl acetate] ~ 7; for transport of diesel fuel, somewhat lower ratios of about 6 are admissible [15]. The effect of molecular mass and polydispersity index of EVA on the depressor properties in oil was studied previously [35]. In this case, it was found that the best characteristics are shown by a polymer with M_n ~ 1.0 × 10^4, and polydispersity has almost no effect on the efficiency.

The mechanism of EVA action in hydrocarbon solutions of paraffins is realized via coordination of the oleophilic fragment of the polymer molecule on the paraffin surface at the early stage of crystallization [36]. This results in the formation of fine crystals less prone to agglomeration; this effect was observed experimentally as early as 1979 [37]. The process of paraffin crystallization in the presence of EVA was considered in detail with the use of quantum-chemical calculations (MM, $T_{f.l.}$) in 2004 [38]. Within seven years, a simple and rational method of the experimental evaluation of the minimum effective dosage of EVA for oil with various qualitative and quantitative contents of paraffins was developed [39].

The depressor effect of EVA depends substantially on the type of hydrocarbon to which a DA is added [40]. Some brands of diesel fuel [41] require as low as 200–300 ppm EVA to reduce $T_{f.l.}$ by 10°C. However, for crude oil, the depressor effect of 10°C is attained at a significantly high EVA content on the order of 500–1000 ppm [39]. For asphaltene-containing oil [34], the situation is more complex: as asphaltenes themselves demonstrate weak depressor properties relative to paraffins, for similar mixtures, M_n values of EVA should be chosen so that the copolymer provides efficient cocrystallization with paraffin. As a whole, the presence of asphaltenes in petroleum reduces the EVA efficiency markedly [42]. The detailed study of the influence of the EVA concentration on the physical and rheological properties of oil at different pressures was carried out in 2012 [43]. It was found that, at the EVA concentration of ~100–200 ppm, $T_{f.l.}$ and the enthalpy of crystallization of paraffin oil decrease efficiently; the data obtained at atmospheric pressure may be extrapolated for more severe conditions of oil production and transport at high pressure.

An important factor influencing the EVA efficiency is the composition of the paraffin fraction of oil: the depressor effect of EVA increases with the average number of carbon atoms in the paraffin molecule [44]. In the latter work, it was noted that even minimum additives of EVA result in the morphology of the formed paraffin crystals changing from platelike to more compact spherical. These changes are reflected in the SEM data shown in Fig. 2 [18].

The thorough study of the paraffin crystallization from solutions containing EVA (28 wt % vinyl acetate, M_w = 1.08 × 10^4) showed that, depending on solvent and molecular mass characteristics of paraffin, EVA can demonstrate both mechanisms of depressor effect: either as a nucleator for stable fine paraffin crystals or as an inhibitor of crystal growth [45]. In the presence of EVA, the choice of solvent for preparation and addition of the polymer dispersion is of importance [39]; the use of mixtures of polar (acetone) and aromatic (xylene) solvents enhances the depressor effi-
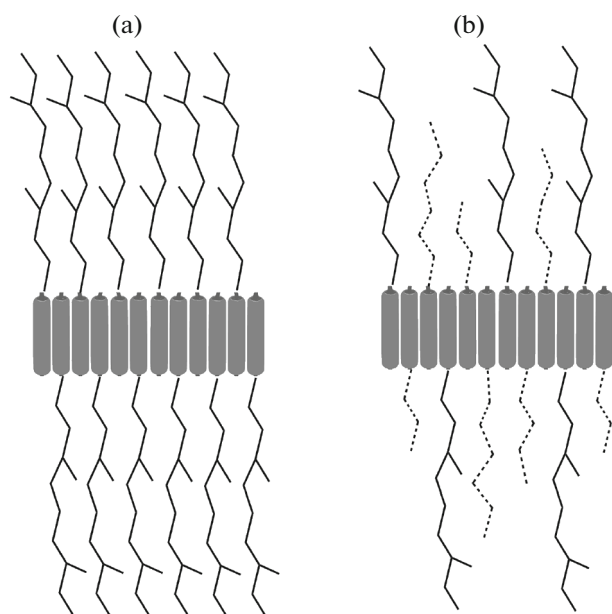
(a) (b)

Fig. 3. Crystallization of PE−PEP (a) and cocrystallization of PE−PEP with paraffin (b).

ciency significantly. As additives enhancing the depressor effect of EVA, nonionic surfactants, such as oxyethylated higher alcohols [46] as well as ethylene oxide−propylene oxide copolymers modified by phenols or amines, are employed [47].

The works on the structural modification of EVA are relatively few in number. The theoretical and experimental study of the mechanism of interaction between the paraffin crystals and EVA as well as its derivatives with propylene and butene units was performed [48]. It was found that EVA modified by propylene has a higher efficiency compared to the copolymer containing ethylene alone. It was proposed to use a copolymer obtained via radical polymerization of EVA ($M_w = 1.34 \times 10^5$, ethylene content of 76 wt %) and some monomers, such as hexadecyl acrylate, octadecyl acrylate, or acrylate prepared from C_{18}−C_{20}−C_{22} alcohols taken in the ratio of 1 : 4 to allyl alcohol as a universal depressor additive [49]. Polymers prepared via acylation of the product of EVA hydrolysis by higher carboxylic acid chlorides were studied also [50]. Finally, a complex study of the effect of degree of hydrolysis of ester bonds in EVA on the depressor characteristics of polymer was carried out recently [51]. It was established that the depressor characteristics of hydrolyzed PVA involving CH−OH fragments instead of CH−OAc units substantially exceed the corresponding value for pure EVA.

In addition to EVA, the depressor effect of vinyl acetate−styrene copolymer was studied. Because of a low reactivity of vinyl acetate relative to styrene, the copolymer was synthesized via dispersion radical copolymerization with the parallel introduction of comonomers, whereas 1-dodecanethiol was used as a chain transfer agent [52]. The depressor characteristics of this copolymer were significantly lower, but it showed a high efficiency as an agent reducing hydraulic resistance for asphaltene-containing heavy oil.

POLYETHYLENE−POLY(ETHYLENE-PROPYLENE)

Copolymer containing extended polyethylene and ethylene-propylene blocks with pronounced depressor properties is available to the same extent. The synthesis of this copolymer was performed with the use of the "living" successive anionic polymerization of butadiene-1,3 and isoprene followed by hydrogenation [53]:
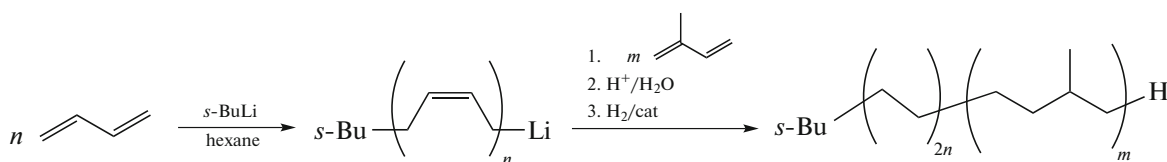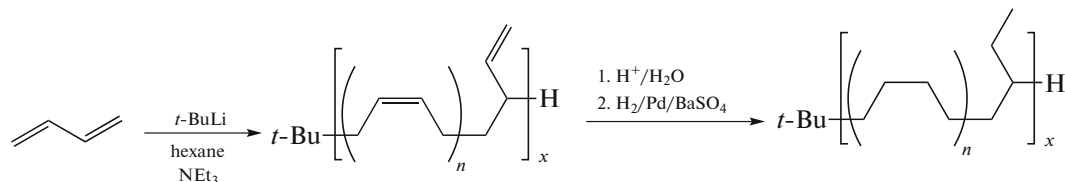

The obtained block copolymers demonstrate a high efficiency as initiators of crystallization (nucleators) controlling the size of paraffin particles formed in diesel fuels [54, 55].

Owing to the presence of extended polyethylene fragments, the copolymer itself is prone to formation of platelike agglomerates, which have no tendency to aggregation because of their ethylene-propylene "tails" (Fig. 3) [54]. In the presence of paraffin, the polyethylene fragments act as effectors of crystallization forming the plate structures. Ethylene−propylene fragments prevent the sticking together of these structures as before, resulting in stabilization of fine dispersions of paraffins in the stable crystalline form [56, 57]. PE−poly(ethylene-propylene) (PEP) rank below other even more available depressor additives (EVA, poly(ethylene-butene)) in efficiency and are no longer used as individual DA. At present PE−PEP are used as regulators of viscosity of lubrication oils and fuels, and the depressor effect of these polymers is considered as a useful additional function.

POLY(ETHYLENE-BUTENE)

Depressor additives of this group attracted the interest of researchers owing to their structural similarity to PE−PEP, significantly higher solubility in hydrocarbons, and the synthetic availability. First poly(ethylene-butene) (PEB) was prepared via nonselective polymerization of butadiene-1,3 with formation of products of 1,4- and 1,2-addition followed by their hydrogenation [26, 58]:

The ratio of 1,4- and 1,2-addition products was varied by changing the ratio of the components of the reaction medium, such as *n*-hexane and triethylamine. The study of the molecular structure of ethylene−butene block copolymers and their interaction with paraffins showed that these copolymers (like PE−PEP) form plate agglomerates as well, and their sticking together is hindered by the branchings in molecule [59, 60]. The depressor effect of PEB manifests itself via the mechanism analogous to the mechanism of PE−PEP action; the basic function of PEB consists in changing the paraffin crystal shape by "programming" of the crystallization morphology [58]. The multilevel character of the architecture of crystallites formed by paraffins in the presence of PEB was established [61]. The basic function of PEB as a modifier of the crystal shape is also corroborated by the results of studying the paraffin crystallization with the use of the DSC method [62].

The influence of PEB on the morphology of paraffin particles results in a drop of shear stress in the paraffin gels [26, 63, 64]. The depressor properties of PEB are affected by the content of 1,2-butylene units in the polymer: at the ratio of 1,2-butylene and ethylene units about 1 : 10, the maximum depressor efficiency is observed [26]. When studying the depressor properties of PEB, one should take into account that the above polymer has virtually no effect on the turbidity temperature and a weak effect on the fluidity loss temperature determined by the standard "test tube" method. At the same time, PEB is responsible for a significant decrease in the filterability loss temperature of diesel fuel.

Functionalized PEB containing −CH$_2$CH$_2$OH, −CH$_2$SCH$_2$COOH, and phenyl fragments instead of a portion of ethyl substituents were described [65].

These polymers exhibit no marked improvement of the depressor properties justifying the complication of the structure.

The simple molecular structure of PEB and its analogs as well as the possibility of realizing alternative synthetic approaches to these polymers based on the random copolymerization of ethylene with alpha olefins allows one to consider PEB and its analogs as efficient and available DA. The investigation of the applicability of PEB and its analogs to heavy oil transport appears to have considerable promise.

MALEIC ANHYDRIDE−α-OLEFIN COPOLYMERS

Depressor additives on the basis of maleic anhydride copolymers with olefins (MAC) like EVA fall in the group of amphiphilic copolymers containing extended hydrocarbon fragments in side chains. In the synthesis of these copolymers, the radical polymerization is used profitably, since maleic anhydride is copolymerized rather easily with different unsaturated hydrocarbons. In this case, copolymers with the maleic anhydride : olefin ratio of 1 : 1 are frequently formed. With allowance for this fact and for an extremely low reactivity or its absence in the case of maleic anhydride and olefin taken individually under the copolymerization conditions used [66, 67], for these copolymers, an alternating structure was suggested. At present, copolymers of maleic anhydride with ethylene, isobutylene, styrene, and linear α-olefins are well known [68−82]. Recently, copolymers of maleic anhydride with vinylidene dimers of olefins and the products of their modification were synthesized [83]:

R = H, n-Alkyl, R' = H
R = R' = Me
R = Ph, R' = H, Me
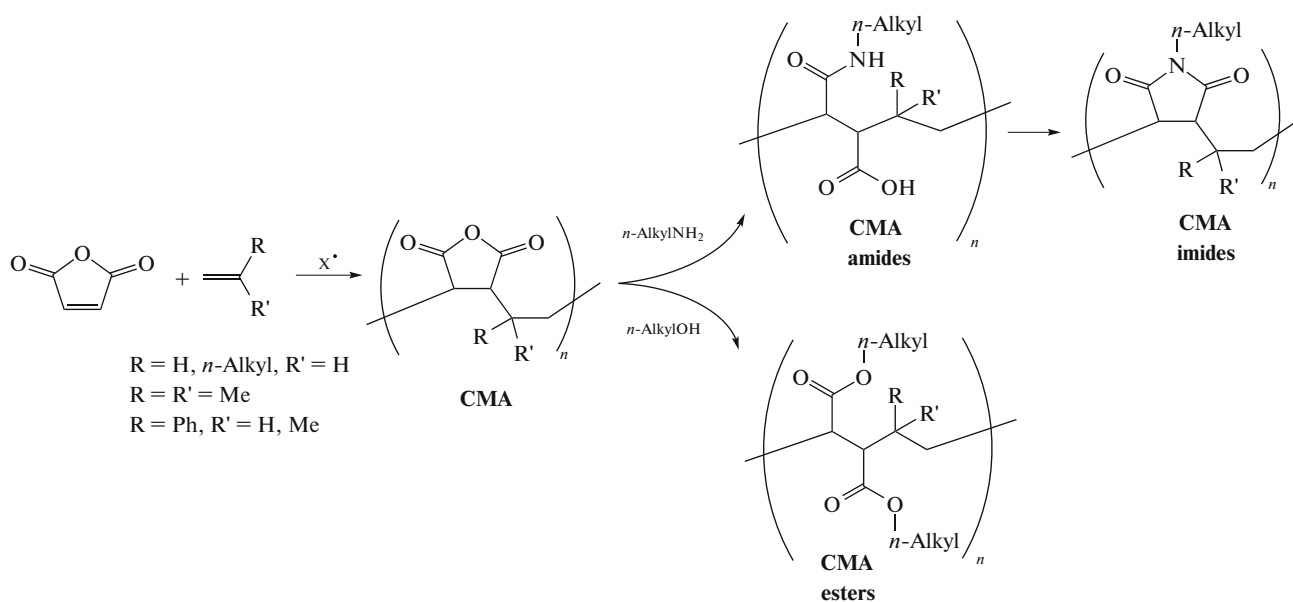
The alternating nature of MAC was correctly confirmed for copolymers with isobutylene and styrene. Copolymers with α-olefins are usually considered as alternating compounds (with allowance for the proved comonomer ratio of 1 : 1), but in some works [84, 85], a varied ratio of comonomers is allowed. On synthesis of MAC, simple and efficient methods are usually employed: the initiation with AIBN or benzoyl peroxide and the reaction proceeding at moderate temperatures (80–120°C) in solution, which makes it possible to attain conversions as high as 80% and above within several hours. The molecular masses of the reaction products usually range from several thousand to several tens of thousands of dalton.

MACs, as such, have a low efficiency when used as depressor additives. Efficient DA were synthesized from MAC via interaction with higher aliphatic amines [80, 86–90] or alcohols [85, 88, 91–93]. The modification of MAC is carried out, as a rule, via heating of copolymer with amine or alcohol at ~130–150°C over many hours; in the reaction with alcohols, acid catalysis is applied. Amides formed in the reaction with amines can further form cyclic imides and the degree of such "imidization" influences the depressor characteristics of copolymers [94, 95]. The formation of diamides during modification of MAC was shown [96] and the effect of this process on the depressor characteristics of polymers was confirmed. The depressor properties of modified MACs have been under investigation since the 1970s [97]. Over this period, hundreds of experiments on the synthesis of copolymers were performed, their depressor characteristics both in model hydrocarbons and diesel fuel and in middle and even heavy petroleum products and in petroleum were studied. Great interest in copolymers of maleic anhydride with α-olefins comes not only from a clearly pronounced depressor effect,

which is demonstrated by even relatively simple and synthetically available polymers of this class. Supposedly, the main reason is the easy modification of MAC owing to the presence of the anhydride fragment; the suitable methods of this modification not explicitly reduced to addition of alcohol or amine.

Almost all researchers of the depressor efficiency of MAC are in agreement on the nature of the influence of the hydrocarbon fragment length on the characteristics of polymers. It was established experimentally that the high depressor characteristics are typical of MAC derivatives involving extended alkyl fragments in side chains (C_{16} and above). The mechanism of depressor action of modified MACs is dictated by their molecular structure and generally is analogous to the mechanism of the action of other depressors (modifiers of paraffins). The extended alkyl fragments of modified MAC are incorporated into the structure of the crystal packing of paraffin nuclei (Fig. 4), with the polar fragments of MAC forming a steric barrier, which prevents the sticking of the paraffin layers and crystallization. Thus, MAC can act as inhibitors of paraffin crystallization [98].

When crystallization occurs in the presence of MAC, rhomb-shaped fine crystallites are formed. The efficiency of such effect of MAC depends on the nature of the side radical R in the polymer and the n-alkyl fragment in a modifier (amine or alcohol). Both fragments must be rather extended, which is corroborated by a number of experiments on the comparative evaluation of the depressor efficiency of modified MACs. For example, the influence of the length of radical R and n-alkyl fragment in an amine modifier on the efficiency of MAC was studied, and it was found that the maximum depressor effect is demonstrated by the derivatives of octadecene and 1-octadecylamine (as compared to dodecene and 1-dodecyl-
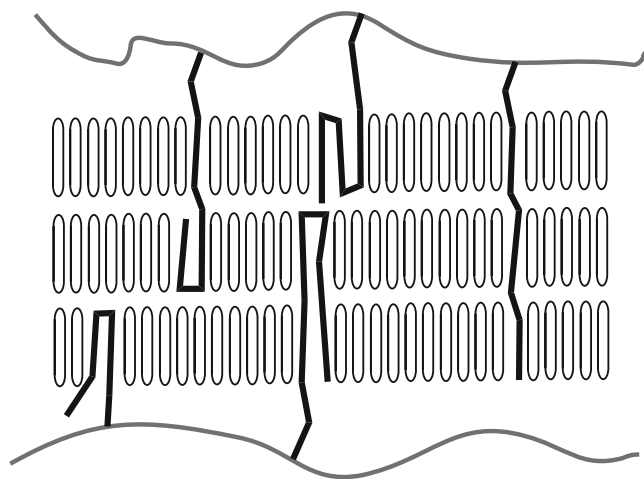
Fig. 4. Interaction of paraffin molecules with modified MAC during formation of crystals.

amine) [86]. The analogous result was obtained elsewhere [65]. The maximum depressor efficiency of this copolymer is also confirmed by the results of studying the properties of paraffins, which are formed in the presence of amine-modified MACs [99]. Figure 5 shows diffraction patterns and microphotographs of paraffin crystallites formed in the presence of polymers of three types, the products of modification of a copolymer of maleic anhydride with 1-octadecene under the action of *n*-dodecylamine, *n*-tetradecylamine, and *n*-octadecylamine [99]. It follows from Fig. 5 that the copolymer of maleic anhydride with 1-octadecene modified by *n*-octadecylamine in amounts of 500 ppm changes the morphology of paraffin crystals completely unlike the derivatives of lower amines, which show an insufficient efficiency even at a twofold higher concentration.

The data on the synthesis and depressor characteristics of different maleic anhydride−olefin copolymers are summarized in Table 2. The comparison of these data is difficult, since in most cases DA were studied when applied to concrete samples of oil. In model experiments on the comparative study of the basic classes of DA (EVA, PEB, and MAC), it was shown that their efficiency increases in the series PEB < EVA < MAC [64]. Styrene−maleic anhydride copolymers have somewhat lower characteristics as compared with the copolymers of long-chain linear olefins [94, 100, 101].

The effect of depressors based on maleic anhydride copolymers may be observed visually when analyzing the shape of paraffin crystals formed in the absence
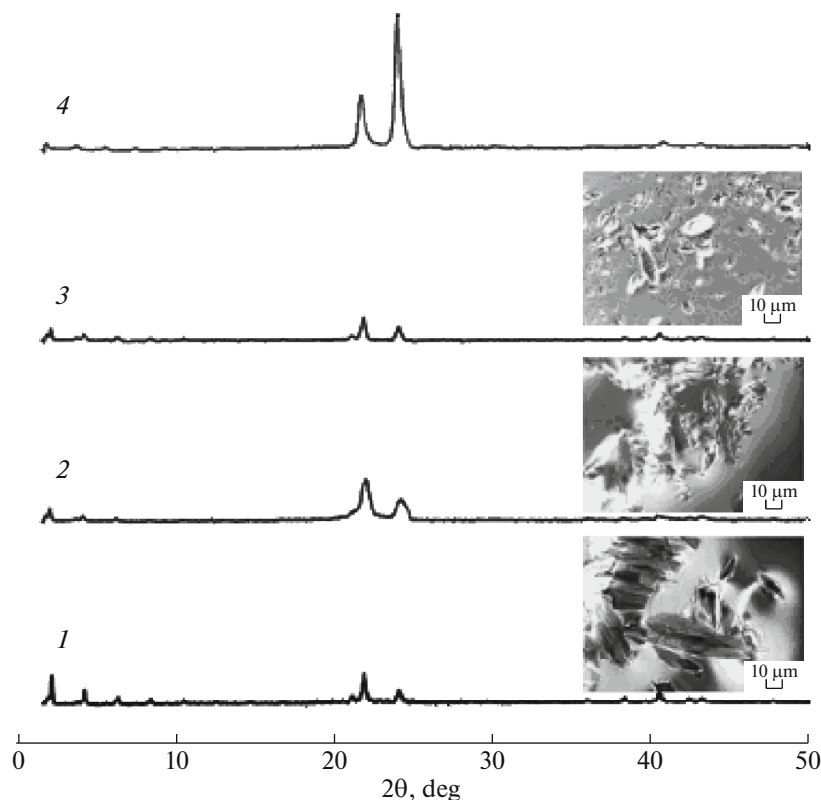

Fig. 5. The effect of alkyl group length on characteristics of $C_{36}H_{74}$ crystals formed in the presence of maleic anhydride−1-octadecene copolymers modified by *n*-alkylamines RNH_2 [99]: (*1*) R = *n*-$C_{12}H_{25}$, 1000 ppm; (*2*) R = *n*-$C_{14}H_{29}$, 1000 ppm; (*3*) R = *n*-$C_{18}H_{37}$, 500 ppm; and (*4*) R = *n*-$C_{18}H_{37}$, 5000 ppm.

Table 2. Synthesis, composition, and depressor characteristics of modified maleic anhydride−olefin copolymers

Comonomer	Modifier	Depressor efficiency			Reference
		object	$\Delta T_{\text{f.l.}}$	concentration, ppm	
$C_{18}H_{37}$	n-$C_{12}H_{25}OH$	Petroleum $T_{\text{f.l.}}$ 27°C	0	1000	[85]
			0	4000	
$C_{18}H_{37}$	n-$C_{16}H_{33}OH$		12	1000	[85]
			24	4000	
$C_{18}H_{37}$	n-$C_{22}H_{45}OH$		12	1000	[85]
			18	4000	
Styrene	n-$C_{18}H_{37}OH$	Petroleum $T_{\text{f.l.}}$ 27°C	30	10000	[100]
$C_{18}H_{37}$	n-$C_{18}H_{37}NH_2$	Petroleum $T_{\text{f.l.}}$ 27°C	7*	5000	[102]
$C_{18}H_{37}$	Aniline		10*	5000	[102]
$C_{18}H_{37}$	1-Naphthylamine		6*	5000	[102]
$C_{18}H_{37}$	n-$C_{18}H_{37}NH_2$	Petroleum $T_{\text{f.l.}}$ 62°C	9	5000	[82]
Styrene	n-$C_{18}H_{37}NH_2$	4% $C_{24}H_{50}$ in decane	4	1000	[103]
$C_{18}H_{37}$	2-Aminobenzimidazole	Petroleum $T_{\text{f.l.}}$52°C	14*	5000	[104]
$C_{18}H_{37}$ + styrene	n-$C_{18}H_{37}NH_2$	Petroleum, 80% decrease in shear stress at temperature close to $T_{\text{f.l.}}$			[89]
$C_{10}H_{21}$	n-$C_8H_{17}NH_2$	Model solutions	10*	<1000	[90]

*DSC data, change in phase transition temperature.

and in the presence of DA. Figure 6 shows microphotographs of $C_{36}H_{74}$ crystals formed in solutions with various MACs [82].

It was shown [65] that the modification by MAC can be realized via addition of comonomers (for example, styrene) followed by their functionalization (sulfonation); however, this does not result in principal improvements of depressor characteristics and viscosity parameters of oil containing a DA modified in such a manner. The study of the shear stress in heavy asphaltene oil in the presence of octadecene−styrene−maleic anhydride copolymers (modified with octadecylamine) showed the opposite character of the effects of aromatic fragments in the polymer: an increase in the styrene content led to a deterioration of the depressor properties relative to paraffins; however, this negative effect was compensated by a drop of shear stress in high-asphaltene oils [87]. The presence of asphaltenes made any study with the use of MAC much more complicated, since asphaltenes as such are capable of the reaction with polymers involving anhydride and carboxylate fragments [80]. It is believed that an experiment is the criterion of the applicability of a particular copolymer as a depressor in the presence of asphaltene.

In the recent work [102], the synthesis and depressor properties of MACs containing aromatic amines are discussed. Such polymers are capable both of coordination with a paraffin (owing to the presence of extended alkyl fragments) and of interaction with asphaltenes because of the presence of polar and aromatic groups, which must lead to a substantial gain in the efficiency. However, the significant improvement of the depressor characteristics of polymers was observed only for a copolymer with aniline. These investigations were continued [105] for the purpose of determining the effect of the length of alkyl fragment between nitrogen atom and aromatic ring on the depressor properties of polymers. It was found that the polymers with long alkyl fragments are capable both of more efficient dispersion of asphaltene and of cocrystallization with paraffins.

COPOLYMERS OF MALEIC ANHYDRIDE AND FUMARIC ACID ESTERS WITH COMONOMERS DIFFERENT FROM α-OLEFINS

Copolymers with higher acrylates are among the promising groups of DA involving maleic anhydride and monomers different from α-olefins [106−109]. The synthesis of these products is also carried out via
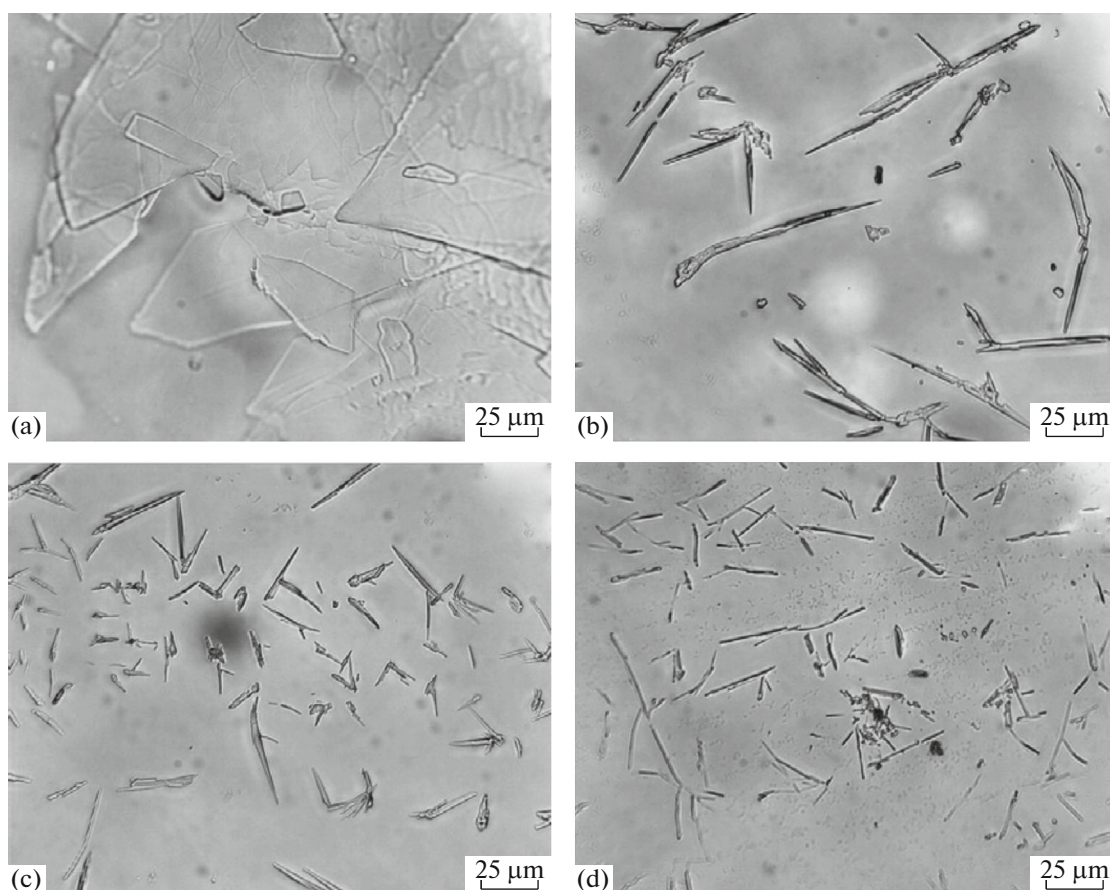
Fig. 6. The influence of MAC on the morphology of crystals of model paraffin oil: (a) $C_{36}H_{74}$, (b−d) $C_{36}H_{74}$ + 0.1% MAC with increasing content of octadecylamine in copolymers [82].

radical copolymerization in the presence of thermal initiators. For example, the synthesis of such copolymers by interaction of maleic anhydride with acrylates and methacrylates (100°C, toluene, benzoyl peroxide) and their modification through reaction with n-$C_{18}H_{37}NH_2$ at 80−90°C were described [109]. The resulting products were investigated as depressors and agents reducing hydraulic resistance of high-paraffin oil ($T_{f.l.}$ > 50°C); in this case, a marked reduction of $T_{f.l.}$ and viscosity at concentrations of 200−1000 ppm was observed. The analogous copolymers were obtained and studied as depressors of crude oil with $T_{f.l.}$ ≈ 20°C. It was shown that, even at a concentration of 100 ppm, these additives decrease $T_{f.l.}$ by 10−15°C [110]. The application of n-butylamine instead of n-$C_{18}H_{37}NH_2$ for modification of copolymer resulted regularly in an abrupt deterioration of the depressor properties [111]. Similar to maleic anhydride−α-olefin copolymers, copolymers of maleic anhydride with higher acrylates unmodified by amines or alcohols showed a moderate depressor effect [112, 113].

Copolymers of vinyl acetate with higher diesters of fumaric acid ROOCCH=CHCOOR were also studied as depressors [114, 115]. It was found that the effective concentration of DA at which the rate of crystal formation from a weakly supersaturated solution of paraffin $C_{32}H_{66}$ reduces to zero depends strongly on the length of alkyl substituent R: the optimum value ranges from C_{18} to C_{22}, and the effective concentration of polymer for C_{12} is three orders of magnitude higher than the effective concentration for C_{20}.

Copolymers of maleic anhydride with higher esters of cinnamic acid modified by n-octadecylamine were studied as well [116]. The depressor effect of these copolymers in heavy oil ($T_{f.l.}$ ≈ 35°C) was 2−15°C at concentration of 100 ppm and attained 33°C for concentration as high as 1000 ppm. The efficiency of polymers increased with the length of alkyl fragment in esters (from C_8 to C_{22}). Copolymers of maleic anhydride with oleic acid esters demonstrate very mediocre depressor characteristics [117]. Copolymers of maleic anhydride−linoleic acid esters modified by octadecanol exhibited a substantial depressor effect for heavy oil at concentration of 1000 ppm and above [118].

It is evident that maleic anhydride−vinyl acetate copolymers even modified by higher alcohols have mediocre depressor characteristics [119−121].
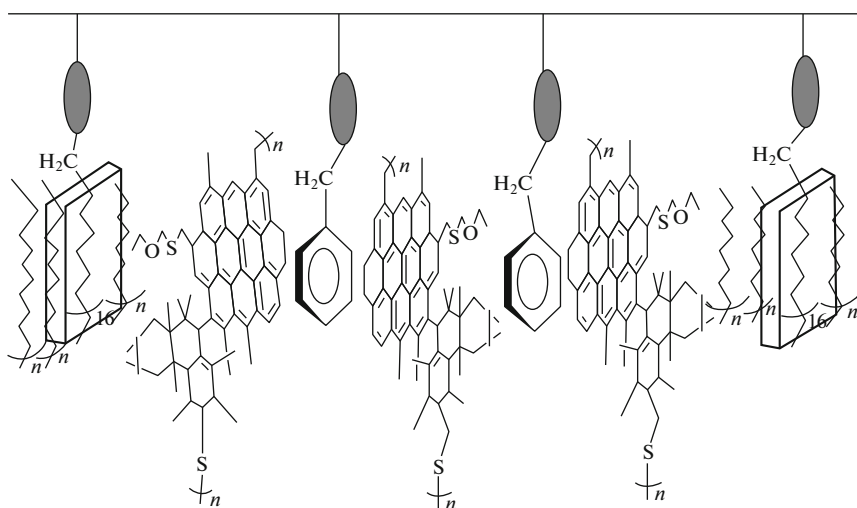
Fig. 7. Combined action of DA based on octadecyl acrylate and maleic anhydride treated with benzyl alcohol [126].

The investigation of a terpolymer of maleic anhydride, styrene, and octadecyl acrylate corroborated its high efficiency when used as a depressor for crude oil [122]. It was also shown that the depressor effect of the synthesized maleic anhydride—vinyl acetate—higher acrylate terpolymer was as low as 10°C at concentration of ~500 ppm [123]. The efficiency of similar terpolymers is also low relative to reduction of the limit filterability temperature [124]. The synthesis of a series of copolymers and terpolymers based on maleic anhydride is described in [125−127]:
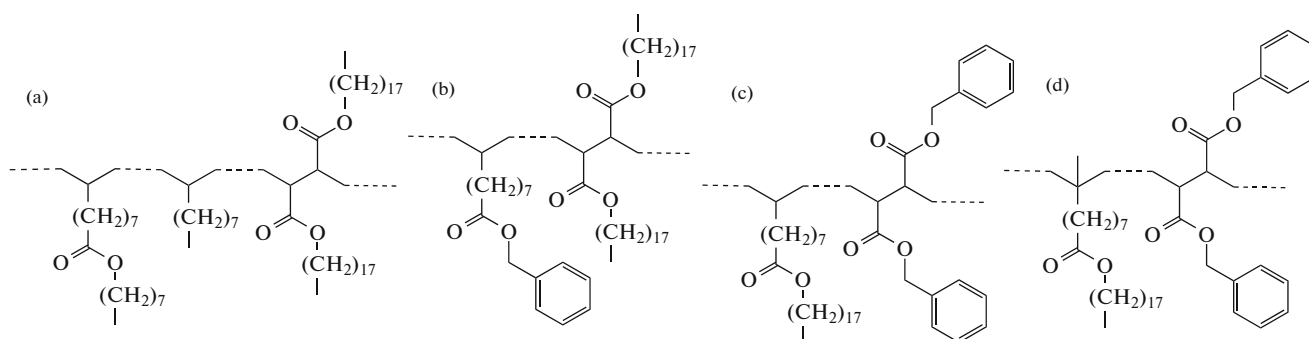

Among the polymers given above, the best depressor properties for high-paraffin asphaltene oil were shown by polymer (c). Its structure provides the complex action of DA both on paraffins and on asphaltene components of oil (Fig. 7). The synthesis of complex copolymers of maleic anhydride was described with the example of polymers containing branched alkyl and alkenyl fragments in the structure of alcohols used in reaction of anhydride ring opening [92, 128]. These compounds proved also to be efficient depressors for oil, which allowed one to make a conclusion on the principal possibility of creation of a "universal" additive for reducing hydraulic resistance on flow of oil and petroleum products with the structure favoring the interaction with paraffins and asphaltenes. This interaction 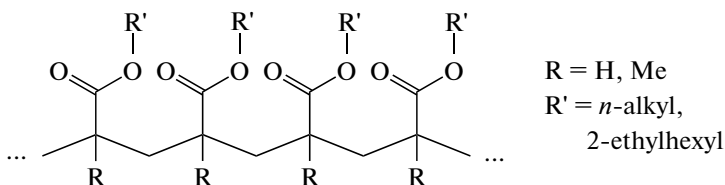must result in a marked depressor effect as well as in a drop of viscosity owing to prevention of formation of asphaltene agglomerates.

Terpolymers obtained from maleic anhydride, acrylates C_{14}−C_{18}, and acrylic acid morpholide followed by treatment with $C_{18}H_{37}NH_2$ (M_w = (1.5−2.0) × 10^4) were studied as DA for diesel fuels [129]. It was found that these polymers reduce the turbidity temperature and viscosity of diesel fuel; however, the filterability loss temperature does not decrease significantly (the best result is equal to −6°C for concentration of 500 ppm). The attempts to obtain four-component copolymers on the basis of maleic anhydride, olefins, vinyl acetate, and styrene resulted in inaccurately determined products with very mediocre characteristics [93].

Polybetains based on the products of copolymerization of diallyl(octadecyl)amine with maleic anhydride [130] showed a high efficiency as DA for crude petroleum owing to the presence of long *n*-alkyl and bipolar fragments in the macromolecular structure:

HOOC
COO$^{\ominus}$
NH$^{\oplus}$
C$_{18}$H$_{37}$
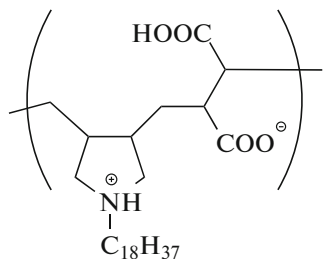
Apart from maleic anhydride polymers, some low-molecular-mass derivatives may be used as depressors. For example, with the use of ene reaction between higher (C$_{30}$ and above) α-olefins and maleic anhydride, alkenylsuccinic anhydride was obtained, which was subsequently fed into the condensation reaction with pentaerythritol and higher aliphatic acids. The resulting product demonstrated clearly pronounced depressor properties, in spite of relatively low molecular mass ($M_n \sim 3.0 \times 10^3$) [97].

POLYACRYLATES

In some reviews (for example, [7]), only EVA, PE–PEP, PEB, and MAC are considered as the basic classes of DA. However, as known, polymer esters of acrylic and methacrylic acids find a wide application as efficient depressor additives:
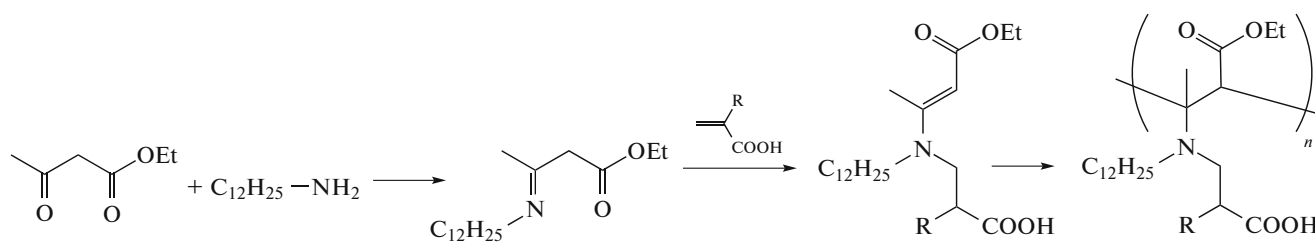
R = H, Me
R' = *n*-alkyl,
2-ethylhexyl

In synthesis of polyacrylates, radical copolymerization is predominantly used both in the organic phase and in the dispersion medium with thermal and chemical initiators (redox pairs). The experimental and theoretical studies of the mechanism of depressor action of polyacrylates based on alcohols C$_{18}$–C$_{24}$ [131, 132] showed that their addition leads to a partial transformation of the formed paraffin crystallites from the orthorhombic to more low-melting hexagonal form. At the same time, there is an alternative point of view on the depressor properties of acrylates that the DA changes the character of the paraffin particle growth, which becomes uniform in all directions. This results in formation of a number of spherical and relatively small particles hindering the transport to a lesser extent and being less prone to formation of paraffin sediments on the pipeline walls [133].

The first work on the depressor activity of polyacrylates was published in 1949 [134]. Initially, polyacrylic esters of higher alcohols soluble in hydrocarbons were considered as efficient depressor additives to fuels and oils and the first patents were dedicated to this area of application [135]. Polymers based on acrylic esters of alcohols C$_{18}$–C$_{30}$ were proposed as depressors for petroleum in the 1970s [136, 137]. The literature on the synthesis of polyacrylates is quite extensive and there are many patents. It was shown that the depressor efficiency of polyacrylates increases with the content of higher alcohols (C$_{22}$ and above) [136, 138–147]. The simple synthetic procedure and moderately high efficiency make polyacrylates promising as DA, but they are unsuitable as depressors of hydrocarbons involving heavy paraffins (C$_{35}$ and over) [148]. Their use as DA for diesel fuel is fully justified: copolymers of higher acrylates with methyl methacrylate demonstrated a high depressor effect in the standard fuel with the fluidity loss temperature equal to 0°C, reducing $T_{f.l.}$ by 20°C even at concentration of 50 ppm [149].

The efficiency of polymethacrylates as depressors for crude oil was studied [150] and it was shown that the depressor effect correlates with the length of the alcohol alkyl fragment and reaches the maximum values for poly(methacrylic esters) of *n*-alkanols C$_{18}$–C$_{24}$. The reduction of the fluidity temperature of moderately viscous paraffin oil ($T_{f.l.} \approx 10–20$°C) by 10°C or more required the addition of polyacrylate in amounts of ~500 ppm. The use of polyacrylates as depressor additives to lubricating oils is described in an RF patent [151]. The effect of polyacrylates and polyacrylate-based copolymers on the thickening temperature of mineral oils ($T_{f.l.} = -3$ and -6°C) was discussed, and it was shown that $T_{f.l.}$ decreased by 10°C at the DA concentration of ~5000 ppm [152].

Besides polyacrylates, various copolymers of acrylic and methacrylic esters of higher alcohols were synthesized and studied. For example, it was proposed to use acrylic esters of alcohols C$_{20}$–C$_{22}$ with 4-vinylpyridine having $M_n = (4.0–6.0) \times 10^4$ as depressors [153]. It was shown that the depressor efficiency of such copolymers is substantially higher than the corresponding efficiency of "pure" polyacrylates [154]. The

synthesis of copolymers of acrylates with acrylamides was described, and it was shown that these products have mediocre depressor characteristics [155].

The efficiency of acrylate copolymers with acrylic acid, styrene, and *N*-vinylpyrrolidone was studied; it was found that copolymers based on acrylates C_{20} have the maximum efficiency [156]. Another work is dedicated to the polymer products with a similar structure [157].

OTHER STRUCTURAL CLASSES OF DEPRESSOR ADDITIVES

Polyolefins are soluble polymers of higher α-olefins having pronounced depressor properties. At the present time, the investigations in the field of polyolefin DA are of a fragmentary character [158], in spite of the evident promise of these polymers and their synthetic availability.

Acyclic polybetains obtained according to the scheme [159]

and involving rather long hydrophobic fragments $C_{12}H_{25}$, at concentration above 100 ppm, effectively reduce the thickening temperature of paraffin oil (to 18°C) and decrease shear stress by several times. For providing heavy oil transport, it is necessary to use higher concentrations of betains—1000 ppm.

As for depressors on the basis of vegetable raw material, the use of renewable raw material is one of the main lines of advanced applied research. Naturally, the glycerides of higher carboxylic acids (especially, unsaturated acids) may be proposed as the promising initial compounds for DA synthesis. The synthesis of the products of interaction of polyethylene polyamine with rapeseed oil (polyaminoamides) and their application as DA were considered [160]:
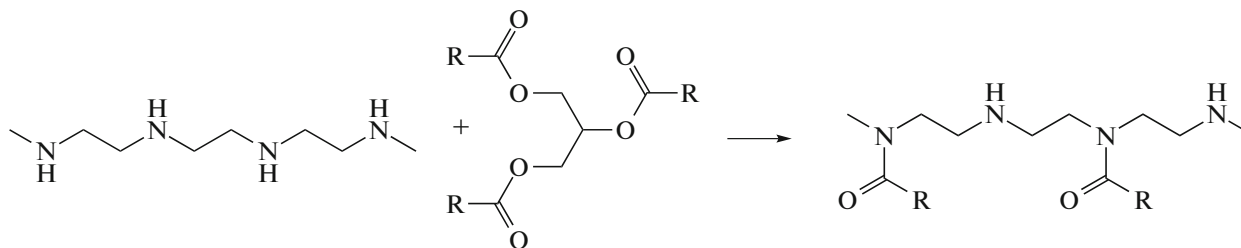
Polyaminoamides demonstrate a high efficiency as inhibitors of wax formation in crude oil. A simple and efficient method of DA synthesis in which soy oil serves as a substrate in radical homo- and copolymerization with α-olefins, was described [161]. The resulting polymers in concentration of ~2% reduced $T_{f.l.}$ of mineral oils by 3–8°C.

NANOHYBRID DEPRESSOR ADDITIVES

One of the new and intensively developing lines in chemistry is the use of nanosized solid dispersions of various materials together with the traditional polymer DA. The research in this field is progressing in the framework of the general trend to the application of nanoparticles in the technology of oil production and oil refining [162].

As was stated in 2011 by Wang et al. [163], the efficiency of nanohybrid depressors of heavy oil substantially exceeds both the depressor effect and the stability of this effect in time for traditional DA (for comparison, an EVA copolymer was taken).

It was shown that SiO_2 nanoparticles are perfect depressor additives for heavy oil containing asphaltenes and resins [164]. On one hand, SiO_2 particles act as initiators of paraffin crystallization and, on the other hand, as binders of asphaltenes and resins. As a result, a significant increase in the fluidity of heavy oil is observed. A hybrid DA based on SiO_2 nanoparticles and poly(octadecyl acrylate) was studied [165]. The results of studying composites based on nanosized SiO_2 (or montmorillonite) and EVA showed that these compounds reduce $T_{f.l.}$ of heavy oil from 34 to 5°C at the concentration of DA of 500 ppm

[166, 167]. Clearly pronounced effects of different nanohybrid DA were observed when diesel fuels were examined [168]. Finally, nanohybrid DA on the basis of organosilicon nanosized fillers polymethylsilsesquioxanes were studied recently [169−171].

The main idea of the application of nanohybrid DA is that nanosized particles form complexes with DA and simultaneously initiate the formation of paraffin microcrystals. This results in microspherical particles of crystalline paraffin in the most stable form, which are not prone to association, accompanied by a drop of $T_{f.l.}$, and owing to nanosized nucleating particles by a substantial decrease of the filterability loss temperature (this parameter is relevant for diesel fuels).

CONCLUSIONS

To date, a number of polymer and oligomer products with depressor properties have been investigated. In spite of the fact that the first attempts at finding correlations between the molecular structure and depressor characteristics of polymers were made more than a quarter century ago [172, 173], no valuable quantitative model for describing the structure−property correlations exists. Evidently the depressor polymers are unified by the capacity of cocrystallization with the paraffin molecules; thus, the molecular structure of the greater part of DA must inevitably involve extended hydrocarbon chains. However, even the fractional composition of paraffin has a disastrous effect on the efficiency of DA of different structural groups. When passing to oil, problems resulting from the chemical interaction with its components (asphaltenes, etc.) arise [174].

Heavy oil products are complex systems: the corresponding DA must combine the characteristics of modifiers of the paraffin crystallization and the capacity of coordination with asphaltenes as well as demonstrate the properties of dispersants and surfactants for lowering the viscosity. Thus, for each type of petroleum, the proper formula of DA should be chosen. The design of the new DA structures is object-oriented. For oil and petroleum products with a high content of "heavy" paraffins, the DA molecule must contain extended saturated hydrocarbon fragments. The high content of asphaltenes suggests the incorporation of aromatic and polar fragments capable of coordination with polycondensed heteroaromatic compounds into the DA macromolecule [175]. The absence of a predictive model and a number of oppositely acting factors allow one to make a conclusion that the libraries of depressor additives should be used to solve the problems of transport or efficient and trouble-free service of a specific individual product.

In recent years, the theme of depressor additives obtained a new impulse to development connected with the need for their application to improve the characteristics of "green" substitutes of petroleum products—biodiesel and biosynthetic motor oil [176−178]. The structural regularities found in development of DA for oil, diesel fuels, and hydrocarbon lubricants are inapplicable to these objects.

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