Changing the Structural and Mechanical Properties of Hydrocarbons after a High-Frequency Acoustic Impact

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Abstract

An effect of ultrasonic treatment exerted on the structure and mechanical properties of polyacrylamide, polyhexene, polyethylene and oil paraffin solutions was investigated. Schemes are proposed for the destruction of polyhexene and polyethylene *via* a radical mechanism. It has been found that the acoustic impact on the oil paraffin solution in decane does not affect the nature of the molecular mass distribution for *n*-alkanes, but results in increasing the temperature of phase transitions and changing the shape of crystallites.

Key words: resin, oil paraffin, ultrasonic treatment, viscosity, hydrodynamic drag reduction, microscopy, gas-liquid chromatography

INTRODUCTION

Ultrasound (US) is widely used in various fields of science and technology. The first studies of the reactions occurring in a high frequency acoustic field were conducted using aqueous solutions [1]. Most researchers believe that sonochemical reactions can take place in aqueous solutions only, because water is the most favourable environment for the generation of radicals in the cavitation fields. Just with the cavitation one associates the basic physicochemical effects those occur in the liquid phase under the action of acoustic fields [1]. The characteristic feature of ultrasonic cavitation consists in the fact that the relatively low average energy of the acoustic field is locally concentrated in a very small volume, thus providing a very high energy density. Two types of chemical effects are known caused by acoustic vibrations at frequencies higher than 15–20 kHz. The first group is presented by the reactions those are accelerated in the ultrasound field; the second group consists of the reactions those do not occur at all without US field [1].

Since the 1930s there began investigating the behaviour of polymer solutions in the acoustic field [2]. It was found that, after ultrasonic irradiation the viscosity of polymer solution is irreversibly reduced [3]. For many of these polymers after a long-term acoustic action the molecular mass approaches a certain minimum value, amounting to approximately 30 000 amu For the polymers those tend to form gels and jellies, there was thixotropic liquefaction observed under the influence of ultrasound [4].

The studies of non-aqueous systems demonstrated that the ultrasonic field also causes significantly increasing the reaction rate and the selectivity level thereof (the pyrolysis of hy-

drocarbons, the oxidation of aldehydes and alcohols, the reaction of alkyl halides, alkylation, *etc*.) [1, 5, 6]. The authors of [7] demonstrated by the example of decane that ultrasonic treatment leads to breaking the molecular bonds and the subsequent recombination of various radicals formed. The chromatographic analysis revealed the presence of H_2, CH_4, C_2H_4, C_3H_6, C_2H_2 and other products in the gas phase whose formation rate is reduced in the series listed.

The acoustic impact on dispersed systems results in the structural transformations of the components of the dispersed phase, changing the size, shape of associates are widely used for the preparation of oil for transportation and processing [8]. The ultrasonic treatment (sonication) of oil and petroleum fractions efficiently influences upon the rheological properties and fractional composition thereof [9, 10].

The purpose of this work consisted in studying an effect of ultrasonic treatment exerted on the structural and mechanical properties of the solutions of polyacrylamide (PAA), polyhexene (PHEX), polyethylene (PE) and the oil paraffin (OP).

EXPERIMENTAL

The polyacrylamide as prepared by means of acrylamide free radical polymerization in water using potassium persulphate as an initiator [11]. We used industrial grade polyethylene (technical specifications TU 2211-014-54155590−2003) and oil paraffin (State Standard GOST 23683−89). The polyhexene with the molecular mass amounting to 9 200 000 amu was synthesized a heptane solution in the presence of aluminum triisobutylate at the Boreskov Institute of Catalysis, SB RAS (Novosibirsk) by means of a method described by the authors of [12].

The PAA solutions were prepared in water, the polyethylene solutions were obtained using *o*-xylene, PHEX was dissolved in toluene, OP in decane and hexane.

The viscosity of the diluted solutions was measured using an Ubbelohde viscometer with a capillary diameter equal to 0.63 mm. The intrinsic viscosity [η] of the polymers was calculated from the plots of the viscosity depending

of the solution concentration [13]. The molecular mass (*M*) of PAA was calculated basing on the Mark−Kuhn−Houwink equation:

$$[\eta] = 6.31 \cdot 10^{-5} \cdot M^{0.80}$$

where 6.31, 0.80 are the constants characterizing the PAA−water system at 25 °C.

The value of *M* for PE was determined as

$$[\eta] = 1.76 \cdot 10^{-4} \cdot M^{0.83}$$

The solvent being *o*-xylene, the temperature amounting to 105 °C [11].

In order to determine the viscosity of concentrated solutions we used a Brookfield DV-III ULTRA rotary viscometer with a Rheocalc32 software package.

The PHEX solutions were tested using a Rheometer in turbulent flow (Reynolds number values amounting to 4600 and 6800) [14]. The magnitude of the hydrodynamic drag reduction (DR, %) was calculated according to the formula

$$DR = (\tau_s^2 - \tau_p^2 / \tau_s^2) \cdot 100\%$$

where τ_s^2 is the outflow time of a fixed volume of solvent through the capillary under pressure; τ_p^2 is the outflow time of the same volume of the polymer solution through the capillary at the same pressure.

The crystal structure of OP after solvent evaporation was examined by means of an AXIO LAB.A1 microscope (Carl Zeiss) in transmitted light.

The ultrasonic treatment of the samples was carried out using a 1 kW Ultrasonic TS-4M laboratory reactor (VIATECH Ltd., Moscow) at a frequency of 21.3 kHz and ultrasound intensity amounting to 10 W/cm^2 [15].

The composition and relative content of *n*-alkanes in the OP was determined by means of gas-liquid chromatography. The analysis was performed using a Perkin-Elmer SIGMA 2B gas chromatograph with a gas ionization detector; helium being used as the carrier gas. The length of the capillary column dampened with phase SE-52 was equal to 33 m.

The registration mode was a linear temperature programming with the rate of 4 °C/min within the range of 100−290 °C.

The IR spectra of PE samples were registered using a Nicolet-5700 FT-IR spectrometer within the range of 400−4000 cm^{-1}.
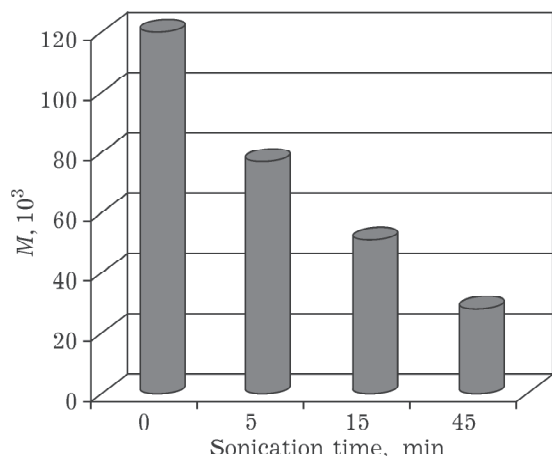
Fig. 1. Effect of the duration of ultrasound treatment (UST) on the molecular mass of the PAA solution.

RESULTS AND DISCUSSION

It is known [1] that sonochemical reactions in a most intense manner occur in aqueous solutions; therefore we treated an aqueous PAA solution, with the concentration of 0.7 g/100 cm³. The ultrasonic processing of the solutions as carried out within the duration range of 5−45 min with determining the value of [η] after immediately exposure and after 1 day. The molecular mass of the PAA, calculated basing on the Mark−Kuhn−Houwink equation diminishes from 120 000 to 77 000, 51 000 and 28 000 amu, after 5, 15 and 45 min of the treatment, respectively. Thus, after a long-term exposure the value reaches the limit equal to almost 30 000 amu (Fig. 1). These changes are irreversible: after 1 day the molecular mass of the PAA has not changed.

TABLE 1

Results of viscometric and turborheometric measurements for the solutions of polyhexene treated by ultrasound

Samples	[η], cm³/g	DR, %, at Re	
		4600	6830
Initial solution	4.3	48.9	56.4
Sonication, 30 s	2.7	35.9	49.6
The same, 2 min	1.9	−1.2	2.5
The same, 15 min	1.0	−4.7	0.7
The same, 30 min	0.6	−5.2	0.7

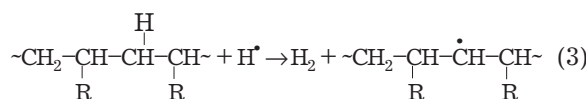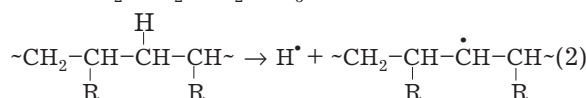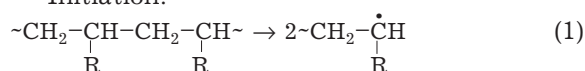*Notes.* 1. The concentration of the solutions for the turborheometric measurements is equal to 0.0115 g/cm³. 2. Re is the Reynolds number.

In order to study the behaviour of hydrocarbon systems in organic media after the sonication we took polymeric samples (high molecular mass PHEX, PE) and OP.
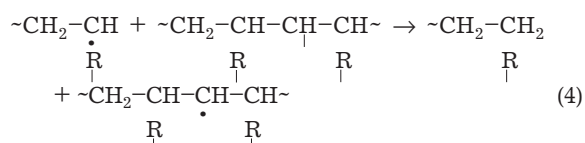
The acoustic action on high molecular mass PHEX solutions results in a 1.6-fold decrease of the intrinsic viscosity already after the treatment during 30 s, whereas after the treatment for 30 min there is a 7.2-fold decrease thereof (Table 1). Such a destructive aftermath of the sonication has reflected in the magnitude of reducing the hydrodynamic drag of the PHEX solutions in a turbulent flow (Toms effect): there is a 6−13 % decrease of DR value observed as compared to the initial sample, even after a short-time treatment (30 s) of the solution under investigation (see Table 1) [14, 16]. After a longer sonication the time of the turbulent outflow for the fixed volume of the polymer solution becomes equal to (at Re = 6830) or greater than (at Re = 4600) the outflow time inherent in the pure solvent; the value of DR in this case tends to zero or becomes negative. The observed decrease of [η] and DR for the solutions under investigation is irreversibly over time, which indicates the degradation of PHEX macromolecules in the ultrasonic field.

Basing on these studies [1, 3, 7], we could present the following scheme of PHEX destruction *via* a radical mechanism.
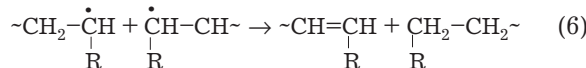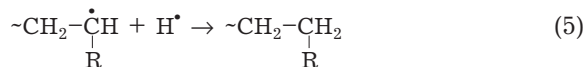
Initiation:

$$\sim CH_2-\underset{R}{CH}-CH_2-\underset{R}{CH}\sim \rightarrow 2\sim CH_2-\underset{R}{\overset{\bullet}{C}H} \qquad (1)$$

$$R = -CH_2-CH_2-CH_2-CH_3$$

$$\sim CH_2-\underset{R}{CH}-\overset{H}{\underset{}{C}H}-\underset{R}{CH}\sim \rightarrow H^\bullet + \sim CH_2-\underset{R}{CH}-\overset{\bullet}{C}H-\underset{R}{CH}\sim (2)$$

$$\sim CH_2-\underset{R}{CH}-\overset{H}{\underset{}{C}H}-\underset{R}{CH}\sim + H^\bullet \rightarrow H_2 + \sim CH_2-\underset{R}{CH}-\overset{\bullet}{C}H-\underset{R}{CH}\sim \quad (3)$$

Chain transfer:

$$\sim CH_2-\underset{\overset{\bullet}{R}}{CH} + \sim CH_2-\underset{R}{CH}-\underset{R}{\overset{\bullet}{C}H}-\underset{R}{CH}\sim \rightarrow \sim CH_2-CH_2$$

$$+ \sim CH_2-\underset{R}{CH}-\underset{R}{\overset{\bullet}{C}H}-CH\sim \qquad (4)$$

Chain termination:

$$\sim CH_2-\underset{R}{\overset{\bullet}{C}H} + H^\bullet \rightarrow \sim CH_2-\underset{R}{CH_2} \qquad (5)$$

$$\sim CH_2-\underset{R}{\overset{\bullet}{C}H} + \underset{R}{\overset{\bullet}{C}H}-CH\sim \rightarrow \sim CH=\underset{R}{CH} + \underset{R}{CH_2}-CH_2\sim \quad (6)$$
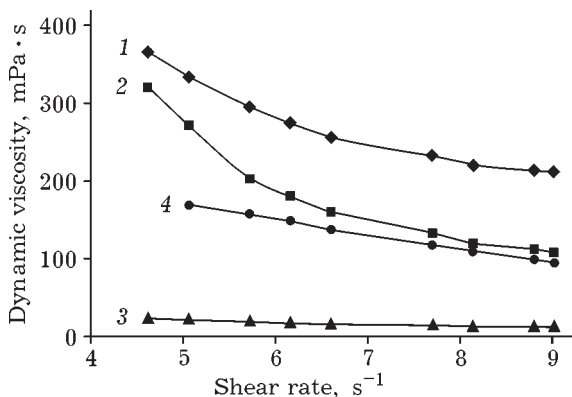
Fig. 2. Dynamic viscosity of polyethylene solution depending on shear rate after 15 min sonication at 25 °C. Treatment time, min: 0 (*1*) 15 (*2*), 120 (*3*) 1200 (*4*).

In addition to the initiation reactions (1)−(3) there is possible an abstraction of rather long side substituents and formation of a macroradical. As far as the chain termination is concerned, a more likely reaction could be presented by reaction (5).
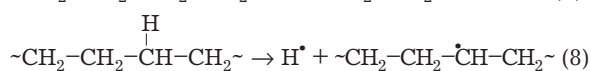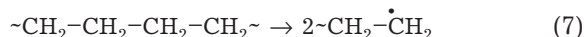
Polyethylene whose molecular mass amounts to only 49 000 amu, is degraded in the ultrasound field, to a not so great extent as PHEX. The molecular mass of the sample determined using a capillary viscometer, after 15 and 30 min of sonication exhibits a decrease to 42 000 and 29 000 amu, respectively.

Other rheological behaviour after the sonication is demonstrated by more concentrated PE − *o*-xylene systems. The initial system (1.8 mass % of PE in *o*-xylene) represents a typical thixotropic gel-like liquid whose viscosity decreases with increasing the shear rate (Fig. 2). The vis-

cosity measured immediately after 15 min of sonication demonstrates a 1.2−1.5-fold decrease in comparison with the initial value, whereas in 2 h after the removal of the load it exhibits a more than 10-fold decrease, whereas the viscosity of the system is almost independent of the shear rate (see Fig. 2, curve *3*). The liquefaction of the system observed after the sonication is caused by the gel-sol transition inherent in some thixotropic gels [4]. After 20 h, the viscosity increases, but its value does not reach the initial values. The results obtained may indicate the fact that in addition to overcoming the energy of van der Waals interactions those relax over time, the effect of ultrasonic waves leads to the breaking of chemical bonds in the macromolecules of PE.

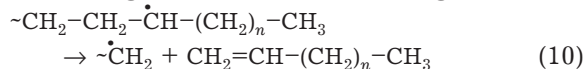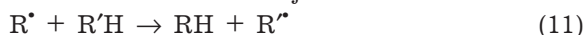The reaction scheme could be presented as it follows [18, 19]:

Initiation:

$$\sim CH_2-CH_2-CH_2-CH_2\sim \rightarrow 2\sim CH_2-\overset{\bullet}{C}H_2 \qquad (7)$$

$$\sim CH_2-CH_2-\overset{\overset{\displaystyle H}{|}}{C}H-CH_2\sim \rightarrow H^\bullet + \sim CH_2-CH_2-\overset{\bullet}{C}H-CH_2\sim \quad (8)$$

The development of the chain could involve isomerising the radicals:

$$\sim CH_2-CH_2-CH_2-(CH_2)_n-\overset{\bullet}{C}H_2$$
$$\rightarrow \sim CH_2-CH_2-\overset{\bullet}{C}H-(CH_2)_n-CH_3 \qquad (9)$$
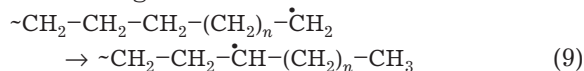
cleavage of the molecules of higher olefins:

$$\sim CH_2-CH_2-\overset{\bullet}{C}H-(CH_2)_n-CH_3$$
$$\rightarrow \sim \overset{\bullet}{C}H_2 + CH_2=CH-(CH_2)_n-CH_3 \qquad (10)$$

chain transfer to adjacent macromolecules:

$$R^\bullet + R'H \rightarrow RH + R'^\bullet \qquad (11)$$

and the breaking of macromolecules:

$$\sim CH_2-CH_2-\overset{\bullet}{C}H-CH_2\sim \rightarrow \sim \overset{\bullet}{C}H_2 + CH_2=CH-CH_2\sim \quad (12)$$

Chain termination:

$$\sim CH_2-\overset{\bullet}{C}H_2 + H^\bullet \rightarrow \sim CH_2-CH_3 \qquad (13)$$
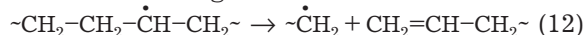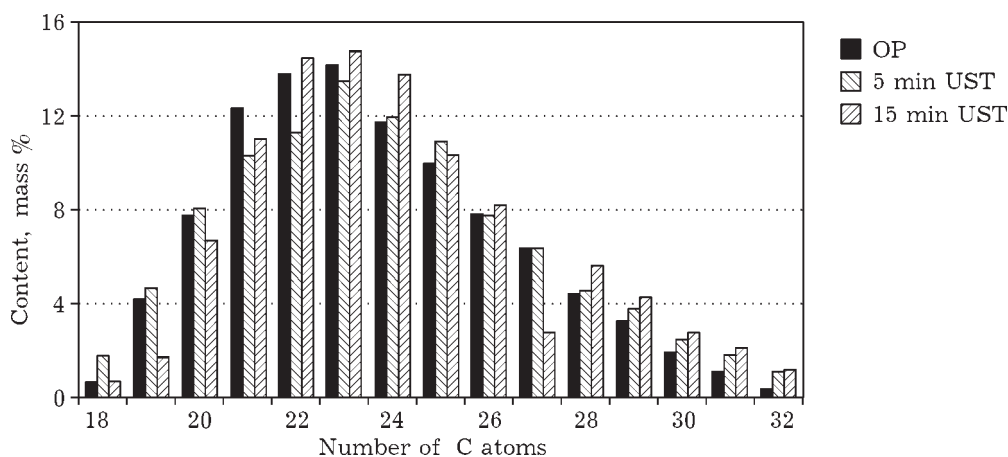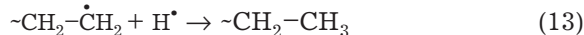

Fig. 3. Molecular mass distribution of *n*-alkanes for the original and ultrasonically treated (UST) oil paraffin (OP).
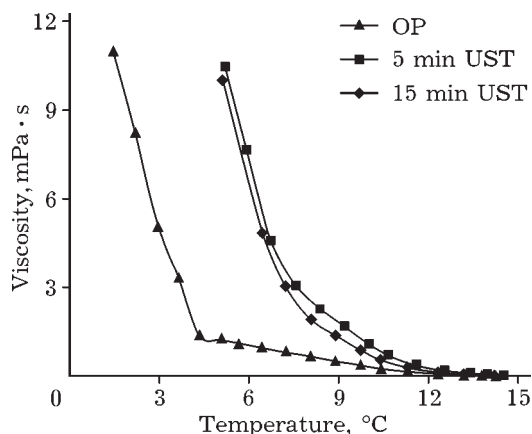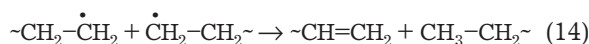
Fig. 4. Thermographic profiles of changing the viscosity for a 6 mass % OP solution of in decane in the course of sonication at the shear rate equal to 1 s^{-1}.

$$\sim CH_2 - \overset{\bullet}{C}H_2 + \overset{\bullet}{C}H_2 - CH_2 \sim \; \rightarrow \; \sim CH = CH_2 + CH_3 - CH_2 \sim \quad (14)$$

The IR spectra of the treated PE samples exhibit the band at 1640 cm^{-1} to be absent, which band corresponds to the absorption of R−CH=CH$_2$ bonds. The ratio between the intensities of the absorption bands CH$_2$/CH$_3$ (720/1380 cm^{-1}) for the treated PE is somewhat lower, which may indicate a partial degradation of macromolecules with the longest chain. Therefore it is more likely that there occurs breaking the chains by means the recombination of H$^{\bullet}$ radicals and $\sim$CH$_2$−C$^{\bullet}$H$_2$ macroradicals (reaction (13)).

The processing of OP solutions, whose average molecular mass is low as compared to the PHEX and PE (270 amu), did not led to any change in the OP structural parameters. The kinematic viscosity of the diluted solution at 25 °C remained constant, whereas the maximum of n-alkane distribution for both the original and the treated samples falls at C$_{23}$ (Fig. 3).

However, the constancy of the molecular characteristics of the OP treated does not mean that in the system there are no changes at the supramolecular level, especially as far as the crystallization process is concerned. To study the kinetics of the OP crystallization from the 6 mass % solutions in decane we used a rheological method [19]. The viscosity was measured at a shear rate equal to 1 s^{-1} at which the destruction of the disperse system structure is minimal. The temperature of the viscosimeter cell was lowered at a rate of 0.3 °C/min. The viscosity of the initial solution begins to rise at 15 °C, which could be associated with the nucleation of OP crystals, whereas at the temperature values below 5 °C there occurs a spontaneous increase in viscosity, which is caused by the growth of crystalline structures (Fig. 4). At the temperature of about 1.5 °C there is formed a continuous 3D network of paraffin that captures the liquid phase (decane) with stabilizing by means of van der Waals forces [19]. At this temperature, the sol-gel phase transition is observed and the system loses the fluidity. The ultrasonic treatment of the OP solution significantly alters the course of the viscosity depending on the temperature (see Fig. 4). So, the viscosity of the treated solutions is higher within the entire temperature range under investigation, whereas the temperature of spontaneous crystallization is not distinctly expressed.

The sol-gel transition in the treated solutions is observed at the temperature values amounting to about 5 °C.
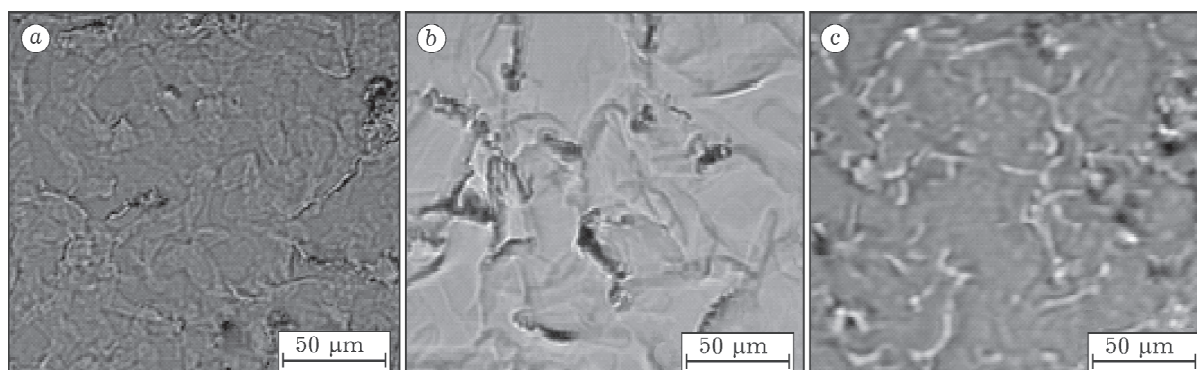

Fig. 5. Micrographs of OP crystallization from the solution in hexane: a − original solution; b, c − the solution after 5 and 15 min of sonication, respectively.

An effect of the treatment of the OP solution in hexane exerted on the appearance of crystalline entities formed after the evaporation of the solvent was studied. It is known that hydrocarbon molecules in solutions can exist in the form of linear chains, single-crystalline lamellas, fibrils and annular or spherical spherolites [21, 22]. The shape and the size of crystalline structures depend on many factors, particularly on the pre-history of their formation. The original sample of OP is crystallised in the form of plate-like structures (Fig. 5, *a*). After the sonication of the solution under investigation during 5 min the OP molecules crystallise into a continuous lamellar structure with the inclusion of bulky crystallites (see Fig. 5, *b*). A longer sonication (for 15 min) leads to the formation of extended crystalline structures (see Fig. 5, *c*), which could cause, to all appearance, a decrease in the viscosity of the system (see Fig. 4).

CONCLUSION

An effect of ultrasonic treatment exerted on the structure and mechanical properties of polyacrylamide solutions, polyhexene, polyethylene and oil paraffin was studied. Treating the solutions of high molecular mass compounds (polyacrylamide and polyhexene) leads to an irreversible reduction in molecular mass. The fact that the treated solutions of polyhexene are low-efficient as the agents reducing the hydrodynamic drag in the case of turbulent flow is caused by the degradation of its macromolecules. The rheological characteristics of concentrated polyethylene solutions after the sonication exhibit changing over time: the initial significant decrease of the viscosity is caused by the system liquefaction whereas the subsequent increase is due to the relaxation of destroyed intermolecular bonds. The ultrasonic treatment of oil paraffin solutions exerts no effect on the molecular mass distribution of *n*-alkanes, but it causes increasing the spontaneous crystallization temperature and enhancing the phase transition of the sol-gel type under cooling the solutions. The results obtained could be useful to explain the behaviour of hydrocarbon dispersed systems,

in particular oil systems, after high-frequency acoustic impact.

The use of low-energy technologies allows to a considerable extent disrupting the oil associates formed by asphaltene-resinous components and crystalline paraffinic hydrocarbons in order to carry out mass transfer processes during the relaxation of the viscosity−temperature characteristics of the dispersed system.

Acknowledgements

REFERENCES

1 Margulis M. A., Zvukokhimicheskiye Reaktsiii Sonolyuminestsentsii, Khimiya, Moscow, 1986.
2 Szalai A. Z., *Phys. Chem.*, A164 (1933) 234.
3 Baramboym N. K., Mekhanokhimiya Vysokomoleku-lyarnykh Soyedineniy, Khimiya, Moscow, 1971.
4 Freindlich H., Sollner K., *Trans. Faradey Soc.*, 32 (1936) 966.
5 Kukharskaya E. V., Skorik Yu. I., *DAN SSSR*, 159 (1964) 369.
6 Weissler A., Pecht I., Anbar M., *Science*, 150 (1965) 1288.
7 Suslick K. S., Gawlenowski J. J., Schubert P. F., Wang H. H., *J. Phys. Chem.*, 87 (1983) 2299.
8 Promtov M. A., Avseev A. S., *Neftepererab. Neftekhim.*, 6 (2007) 22.
9 Klolova T. P., Volodin Yu. A., Glagoleva O. F., *Khim. Tekhnol. Topliv Masel*, 1 (2006) 32.
10 Volkova G. I., Prozorova I. V., Anufriev R. V., Yudina N. V., Mullakaev M. S., Abramov V. O, *Neftepererab. Neftekhim.*, 2 (2012) 3.
11 Kurenkov V. F., Budarina L. A., Zaikin A. E., Praktikum po Khimii i Fizike Vysokomolekulyarnykh Soyedineniy, KolosS, Moscow, 2008.
12 RU Pat. No. 2230074, 2004.
13 Rafikov S. R., Budtov V. P., Monakov Yu, B., Vvedeniye v Fiziko-Khimiyu Rastvorov Polimerov, Nauka, Moscow, 1978.
14 Manzhay V. N., Echevskaya L. G., Ilyushnikov A. V., *Zh. Prikl. Khim.*, 77, 3 (2004) 456.
15 Mullakaev M. S., Abramov V. O, Volkova G. I., Prozorova I. V., Yudina N. V., *Oborudov. Tekhnol. Neftegaz. Kompleksa*, 5 (2010) 31.
16 Manzhay V. N., *Izv. Vuzov. Khim. Khim. Tekhnol.*, 1 (2009) 84.
17 Manzhay V. N., Echevskaya L. G., Ilyushnikov A. V., Ocheredko A. V., Zakharov V. A., Mikenas T. B., Sergeev S. A., *Zh. Prikl. Khim.*, 77, 3 (2004) 456.
18 Emanuel' N. M., *Usp. Khim.*, 48, 12 (1979) 2113.
19 Destruktsiya Polimerov,
   URL: http://www.xumuk.ru/encyklopedia/1229.html
20 Lopes-da-Silva J. A., Coutinho Joro A. P., *Energy &Fuels*, 21 (2007) 3612.
21 Tronov V. P., Mekhanizm Obrazovaniya Smolopara-finovykh Otlozheniy i Bor'ba s Nimi, Nedra, Moscow, 1969.
22 Kazakova L. P., Tverdye Uglevodorody Nefti, Khimiya, Moscow, 1986.