==================== **MACROMOLECULAR COMPOUNDS** ====================
================================ **AND POLYMERIC MATERIALS** ================================

Development of Effective Depressor Additives to Diesel Fuel, Based on Copolymers of Stearyl Methacrylate with Monomers of Various Structures

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Abstract—Depressor additives based on stearyl methacrylate homopolymer and its copolymers with various monomers (butyl methacrylate, methacrylic acid esters of C_{10}–C_{14} fraction, maleic anhydride) were synthesized in the presence of reversible addition–fragmentation chain-transfer agents allowing control of the molecular-weight characteristics of the polymers. The low-temperature properties of the diesel fuel containing additives based on the above polymers were evaluated. The copolymers exhibit the better depressor effect compared to the stearyl methacrylate homopolymer. Modification of the stearyl methacrylate–maleic anhydride copolymer with 1-octanol was performed. The modified additive well competes in performance with the modern commercial depressor-dispersing additives and can decrease the congealing point of hydrotreated diesel fuels by 20°C.

Keywords: controlled radical polymerization, depressor additive, stearyl methacrylate copolymers, low-temperature properties, diesel fuels

Oil refineries producing modern diesel fuels (DFs) for large vehicles, locomotives, and ships pay particular attention to low-temperature characteristics of the fuels [1–3] such as cloud point (T_{cl}), cold filter-plugging point (CFPP), and pour point (T_{pp}). Their optimum values ensure the normal operation of the engine and fuel-feeding system at low temperatures. The low-temperature properties of DF are particularly important for countries with cold climate. In particular, the production of winter fuel grades is very topical for the Russian Federation with its developing northern and northeastern regions. Indeed, the majority of crude oils produced in Russia are waxy crudes; i.e., they contain large amounts of linear or branched alkanes that have relatively high crystallization points and impair the low-temperature properties of both the crude oil itself and fuels produced from it [2–4].

One of the way to improve the low-temperature properties of DF, along with dewaxing and reduction of the boiling end temperature of the diesel fraction, con-sists in introduction of special depressor and depressor-dispersing additives. This approach is believed to be the most justified from the economical viewpoint; it also improves the efficiency and flexibility of oil refining processes [1–4]. The most widely used additives of this type are various macromolecular compounds, including those based on alkyl methacrylates. Interest in these polymers is due not only to their pronounced depressor effect, but also to relatively easy modification of their structure by copolymerization with diverse monomers and polymer-analogous transformations enhancing the depressor performance [5–15]. When developing depressor additives, to predict their behavior in petroleum products and enhance their performance, particular attention is paid to molecular-weight characteristics of the polymers on which the additives are based. The most known method for controlling the molecular-weight characteristics of polymers is controlled radical polymerization (CRP), including reversible addition–fragmentation chain-transfer (RAFT) polymerization [16–20]. This method allows preparing (co)polymers with strict-

Scheme 1. RAFT agents used in the study.
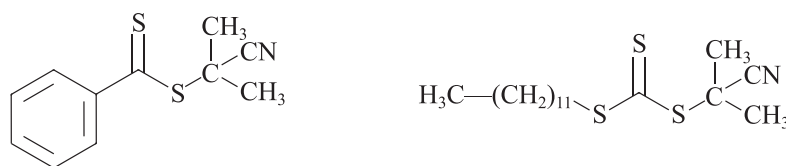
ly preset molecular weight (MW), low polydispersity, and definite structure of the polymer chain. In addition, an indubitable advantage of RAFT polymerization is its versatility, because its conditions coincide with those of classical radical polymerization.

In this study, we prepared by RAFT polymerization a series of random copolymers based on stearyl methacrylate (SMA) with butyl methacrylate (BMA), alkyl methacrylates (C_{10}–C_{14} alkyl methacrylates, AMA), and maleic anhydride (MA). We also studied the effect of the samples obtained on the low-temperature characteristics of DF. Successful control of the RAFT polymerization is determined by the choice of an appropriate chain-transfer agent, which, in turn, depends on the type of the monomer being polymerized and on the reaction conditions [18–20]. Therefore, we studied two different RAFT polymerization agents: 2-cyano-2-propyl dithiobenzoate (CPTB) and 2-cyano-2-propyl dodecyl trithiocarbonate (CPTC); their formulas are shown in Scheme 1.

The study was aimed at developing efficient methods for the synthesis of depressor additives to hydrotreated diesel fuels, based on homo- and copolymers of stearyl methacrylate with preset molecular-weight characteristics.

EXPERIMENTAL

Chemicals. CPTB was purchased from Aldrich (catalog no. 722987); CPTC was synthesized according to [21]. The monomers SMA and MA (Aldrich, catalog nos. 411442, M188) were used without preliminary purification. BMA (Aldrich, catalog no. 8.00585) was purified to remove the inhibitor by the standard procedure [22]. Commercial AMA (C_{10}–C_{14} fraction, Khimdirekt Servis, Russia) containing 16 vol % toluene was characterized by gas chromatography–mass spectrometry and was used without preliminary purification. Azobis(isobutyronitrile) (AIBN, HimReakt, catalog no. 97-98-1) used as a radical initiator was recrystallized

from ethanol. The solvents ethanol, hexane, toluene, methylene chloride, and tetrahydrofuran (THF, Komponent-Reaktiv, Russia, chemically pure grade), used in the experiments, were purified by standard procedures [23]. 1-Octanol, p-toluenesulfonic acid (both Aldrich, catalog nos. 8.20931 and 27818), NaHCO₃, and Na₂SO₄ (both REARUS, Russia, catalog nos. 141638.1210 and 214850250) were used without preliminary purification.

DF (LUKOIL-Nizhegorodnefteorgsintez) was taken from the LCh24/2000 installation before introducing the set of additives; it corresponds to GOST (State Standard) R 52368-2005 (EH590:2009): Euro Diesel Fuel. Technical Specification. Low-temperature characteristics of the DF used: $T_{cl} = -8°C$, $T_{pp} = -15°C$, CFPP = –10°C. Dodiflow, a depressor-dispersing additive based on ethylene–vinyl acetate copolymer, was provided by LUKOIL-Nizhegorodnefteorgsintez.

Synthesis of additives based on stearyl methacrylate copolymers. The calculated amounts of SMA and the second monomer, taken in the preset molar ratios, and the AIBN initiator and RAFT agent in definite amounts (see Results and Discussion) were dissolved in toluene or THF (the concentration of the monomer mixture in the solvent was 10 mol %). The solution was placed in glass ampules and deoxygenated by threefold freezing in liquid nitrogen, pumping to a residual pressure of <1.3 Pa, and thawing. The polymerization was performed at 60 and 80°C. After a definite time, the ampules with the reaction mixture were opened, the copolymers were precipitated with ethanol, and the products were dried to constant weight at reduced pressure and 40°C.

Modification of SMA–MA copolymer. The copolymers were modified with 1-octanol in accordance with [6]. A round-bottomed two-necked flask was charged in succession with the preliminarily calculated amounts of the copolymer, p-toluenesulfonic acid, and alcohol in toluene. The mixture was refluxed for 30 h, cooled to room temperature, and diluted with ethyl acetate. The organic layer was washed with distilled water and

5% NaHCO$_3$ solution and was dried over Na$_2$SO$_4$. The solvent was evaporated using a rotary evaporator. The product was dried at reduced pressure and analyzed by gel permeation chromatography (GPC) and by NMR and IR spectroscopy.

Analysis of molecular-weight characteristics of polymers. The molecular-weight characteristics of the copolymers were determined by GPC with a KNAUER liquid chromatograph (Germany) using a cascade of columns (103–106 Phenomenex, the United States). An RI Detector K-2301 differential refractometer was used as a detector. The eluent was THF (flow rate 1 mL min^{-1}, $T = 25°C$). The calibration was performed using narrow-dispersity polystyrene standards. The chromatographic data were interpreted using the ChomGate program. The number-average (M_n) and weight-average (M_w) molecular weights of the homo- and copolymers were determined using the constants K and α for poly(methyl methacrylate).

Determination of the qualitative and quantitative composition of polymers by NMR and IR spectroscopy. The composition of random copolymers based on stearyl methacrylate, synthesized in the presence of RAFT agents, was determined with an Agilent DD2 400 NMR spectrometer operating at 400 MHz. The ^{1}H NMR spectra were recorded in CDCl$_3$ at room temperature using the residual proton signal of the deuterated solvent as a reference. The spectra were interpreted and simulated using the ACD NMR processing program.

The IR spectra were recorded with an FTIR 8400S Fourier spectrometer in the wavenumber range 4000–400 cm–1. The copolymer samples were pelletized with KBr.

Introduction of additives into diesel fuel. Copolymers based on SMA with BMA or alkyl methacrylates are sufficiently soluble in DF and were introduced in the solid state. Portions of the copolymers were accurately weighed on an analytical balance and dissolved in the calculated amount of the fuel to obtain the concentration on the level of 1600 ppm. For complete dissolution of the additive, the vessel with the fuel and additive was heated with vigorous stirring to no more than 40°C to avoid thermal and thermal oxidative degradation. The additives based on SMA with MA were introduced into DF as a 1% solution of the copolymer in toluene, because direct dissolution of the solid copolymer in the diesel fuel is difficult.

Determination of low-temperature characteristics of diesel fuel. The low-temperature properties of diesel fuel (T_{pp}, T_{cl}, and CFPP) were determined in accordance with GOST (State Standard) 20287–91: Petroleum Products. Methods for Determining the Pour and Congealing Points, and GOST 22254–92: Diesel Fuel. Method for Determining the Limiting Filterability Temperature on a Cold Filter. The arithmetic mean of three replicate measurements was taken as the cloud/congealing point of the petroleum product being tested.

RESULTS AND DISCUSSION

Specific features of homo- and copolymerization of higher alkyl methacrylates in the presence of RAFT agents. To choose the optimum conditions for RAFT polymerization, we took RAFT agents differing in the structure and reactivity (Scheme 1). The screening of the performance of these RAFT agents was performed with SMA homopolymerization as an example.

The effect of the examined RAFT agents on the SMA homopolymerization is somewhat different. In the case of using 0.005 M CPTB, the polymerization rate slightly decreases compared to that on AIBN (Fig. 1a).

An increase in the CPTB concentration to 0.01 M leads to a more significant decrease in the rate in the initial time moment in contrast to the polymerization on AIBN without introducing the RAFT agent. However, irrespective of the dithiobenzoate concentration chosen, the overall SMA homopolymerization rate is comparable to that on the traditional initiator.

Analysis of the SMA homopolymerization in the presence of 0.02 M CPTC shows that, in the initial steps of the monomer conversion, the SMA polymerization rate is comparable to that on the traditional initiator, but at high conversions the decrease in the SMA homopolymerization rate is more significant (Fig. 1b).

The dependences of the molecular-weight characteristics of the polymers obtained using RAFT agents on the conversion are shown in Fig. 2. In the presence of both RAFT agents, the molecular weight (MW) of poly(stearyl methacrylate) (PSMA) linearly increases, in contrast to PSMA obtained on the traditional AIBN initiator with which MM does not vary with the monomer conversion and is higher (50 000–90 000 depending on the initiator concentration used). The polydispersity (M_w/M_n) of the PSMA samples synthesized in the presence of RAFT agents remains
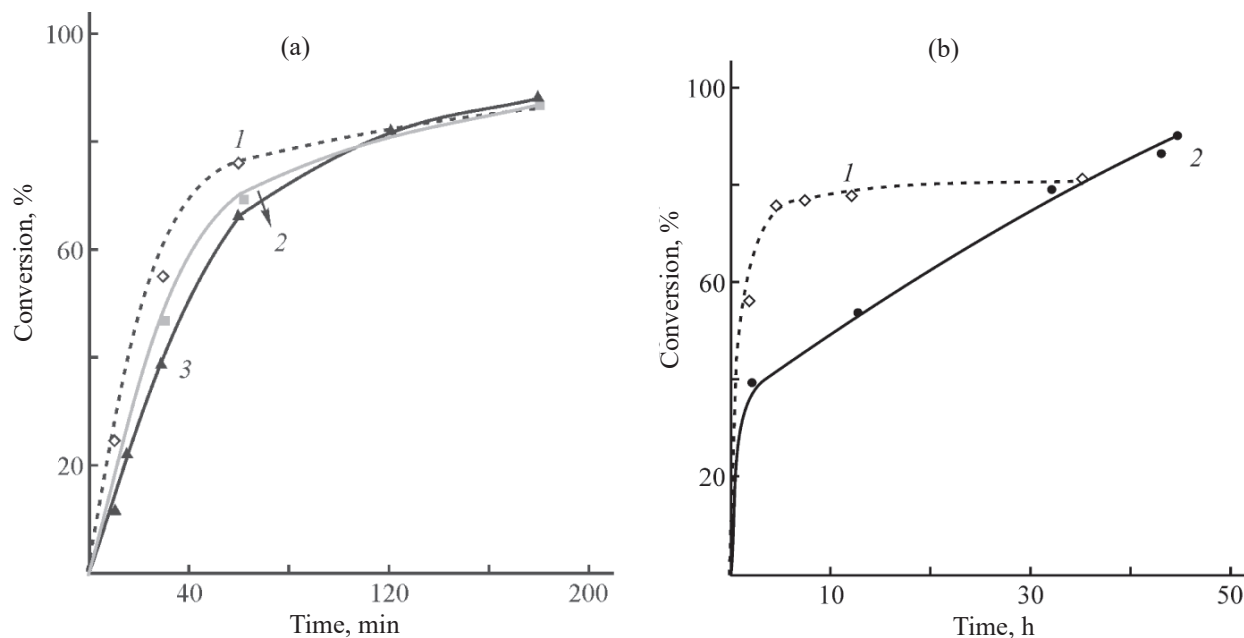
Fig. 1. Degree of stearyl methacrylate polymerization as a function of time. Polymerization in toluene solution, stearyl methacrylate concentration 10 mol %. Synthesis conditions: (a) in the presence of 0.01 M azobis(isobutyronitrile) and 2-cyano-2-propyl dithiobenzoate, $T = 80°C$; 2-cyano-2-propyl dithiobenzoate concentration, M: (*1*) 0, (*2*) 0.005, and (*3*) 0.01; (b) in the presence of 0.001 M azobis(isobutyronitrile) and 2-cyano-2-propyl dodecyl trithiocarbonate, $T = 60°C$; 2-cyano-2-propyl dodecyl trithiocarbonate concentration, M: (*1*) 0 and (*2*) 0.002.

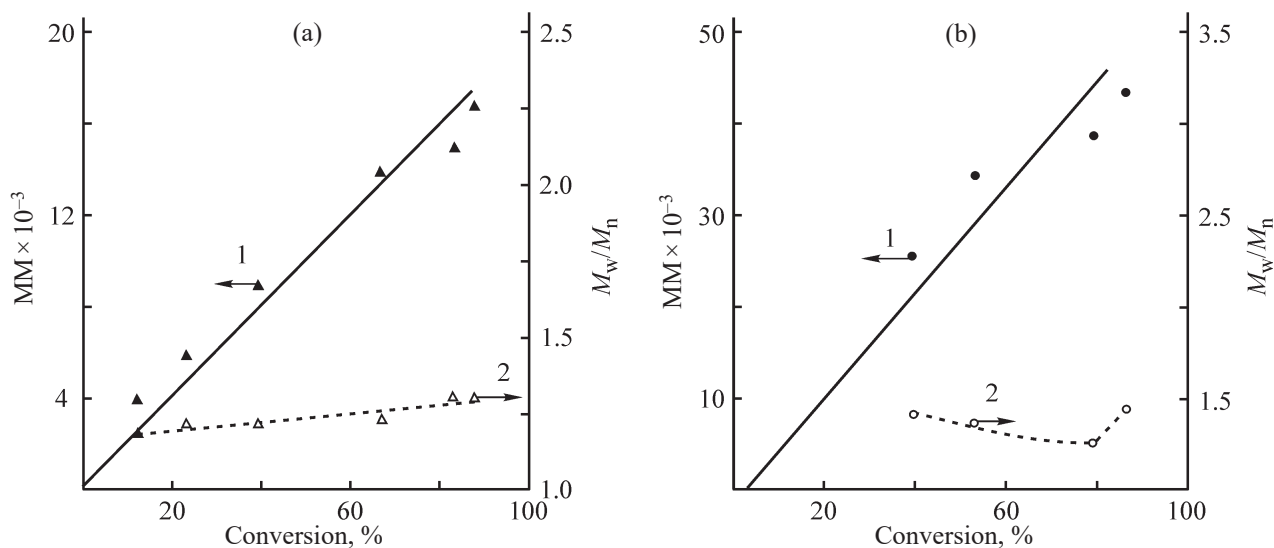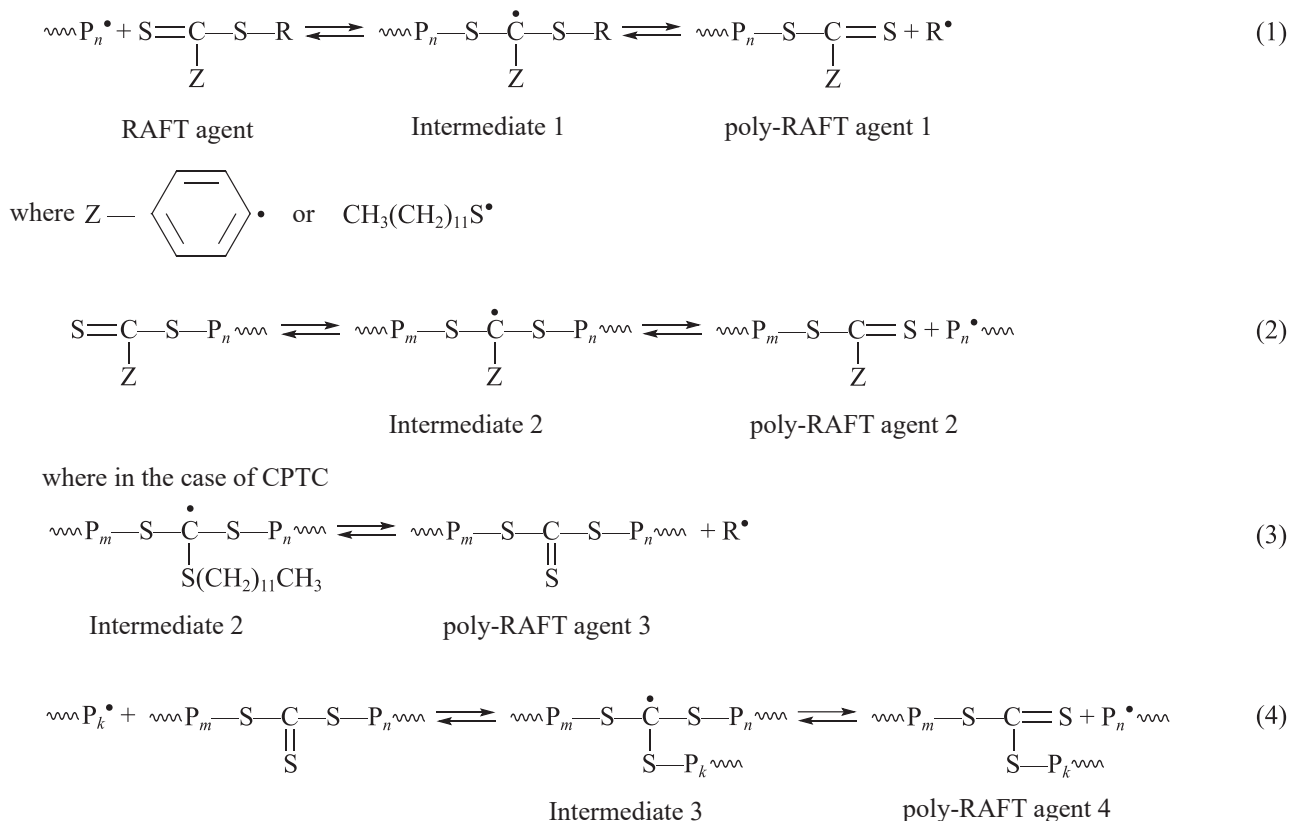**Fig. 2.** (*1*) Number-average molecular weight and (*2*) polydispersity as functions of stearyl methacrylate conversion. Polymerization in toluene solution, stearyl methacrylate concentration 10 mol %. Conditions of polymer synthesis: (a) in the presence of 0.01 M azobis(isobutyronitrile) and 0.01 M, $T = 80°C$; (b) in the presence of 0.001 M azobis(isobutyronitrile) and 0.002 M 2-cyano-2-propyl dodecyl trithiocarbonate, $T = 60°C$.

low throughout the polymerization process and at high conversions is 1.30 for CPTB and 1.44 for CPTC, in contrast to PSMA homopolymers obtained on AIBN without RAFT agent ($M_w/M_n = 2.5–3.0$).

On the whole, a study of the SMA polymerization in the presence dithiobenzoate and trithiocarbonate shows that both these RAFT agents strongly influence the course of the PSMA synthesis and allow preparation of

Scheme 2. Mechanism of RAFT polymerization.

$$\sim\!\!\sim P_n^\bullet + S\!\!=\!\!\underset{Z}{C}\!\!-\!\!S\!\!-\!\!R \rightleftarrows \sim\!\!\sim P_n\!\!-\!\!S\!\!-\!\!\underset{Z}{\overset{\bullet}{C}}\!\!-\!\!S\!\!-\!\!R \rightleftarrows \sim\!\!\sim P_n\!\!-\!\!S\!\!-\!\!\underset{Z}{C}\!\!=\!\!S + R^\bullet \tag{1}$$

RAFT agent   Intermediate 1   poly-RAFT agent 1

where Z — ⟨phenyl⟩• or CH₃(CH₂)₁₁S•

$$S\!\!=\!\!\underset{Z}{C}\!\!-\!\!S\!\!-\!\!P_n\!\!\sim\!\!\sim \rightleftarrows \sim\!\!\sim P_m\!\!-\!\!S\!\!-\!\!\underset{Z}{\overset{\bullet}{C}}\!\!-\!\!S\!\!-\!\!P_n\!\!\sim\!\!\sim \rightleftarrows \sim\!\!\sim P_m\!\!-\!\!S\!\!-\!\!\underset{Z}{C}\!\!=\!\!S + P_n^\bullet\!\!\sim\!\!\sim \tag{2}$$

Intermediate 2   poly-RAFT agent 2

where in the case of CPTC

$$\sim\!\!\sim P_m\!\!-\!\!S\!\!-\!\!\underset{S(CH_2)_{11}CH_3}{\overset{\bullet}{C}}\!\!-\!\!S\!\!-\!\!P_n\!\!\sim\!\!\sim \rightleftarrows \sim\!\!\sim P_m\!\!-\!\!S\!\!-\!\!\underset{S}{\overset{\|}{C}}\!\!-\!\!S\!\!-\!\!P_n\!\!\sim\!\!\sim + R^\bullet \tag{3}$$

Intermediate 2   poly-RAFT agent 3

$$\sim\!\!\sim P_k^\bullet + \sim\!\!\sim P_m\!\!-\!\!S\!\!-\!\!\underset{S}{\overset{\|}{C}}\!\!-\!\!S\!\!-\!\!P_n\!\!\sim\!\!\sim \rightleftarrows \sim\!\!\sim P_m\!\!-\!\!S\!\!-\!\!\underset{S\!-\!P_k\sim}{\overset{\bullet}{C}}\!\!-\!\!S\!\!-\!\!P_n\!\!\sim\!\!\sim \rightleftarrows \sim\!\!\sim P_m\!\!-\!\!S\!\!-\!\!\underset{S\!-\!P_k\sim}{C}\!\!=\!\!S + P_n^\bullet\!\!\sim\!\!\sim \tag{4}$$

Intermediate 3   poly-RAFT agent 4

polymers with the preset molecular-weight characteristics (relatively low polydispersity and molecular weight controlled in a wide range, from 4000 to 50 000), but, to obtain PSMA samples with the narrowest molecular-weight distribution, it is preferable to use CPTB.

The revealed features of the SMA polymerization in the presence of dithiobenzoate and trithiocarbonate suggest the realization of the RAFT mechanism (Scheme 2). Reactions (1) and (2) will be characteristic of dithiobenzoate, whereas in the case of trithiocarbonate additional stages (3) and (4) are possible.

Thus, when using different RAFT agents, polymers of different structure (poly-RAFT agents) can be formed in the course of the polymerization. When using PCTB, poly-RAFT agents 1 and 2 will be formed, and with PCTC the formation of poly-RAFT agents 3 and 4 (Scheme 2) is possible. To prove the formation of polymers of such structure, we performed modification of SMA homopolymers obtained in the presence of both dithiobenzoate and trithiocarbonate by replacing the sulfur-containing groups by the cyanoisopropyl radical at a 100-fold excess of AIBN and 80°C for 24 h. The modified polymers were examined by GPC. In the case of using CPTB, the molecular-weight characteristics of the polymer did not change noticeably ($M_{n,init}$ = 9100, $M_w/M_{n,init}$ = 1.22; $M_{n,mod}$ = 9200, $M_w/M_{n,mod}$ = 1.23). The molecular-weight distribution (MMD) curves remained identical to that of the initial sample. This fact suggests the presence in the polymer of terminal sulfur-containing chains (poly-RAFT agents 1 and 2, Scheme 2) whose replacement by the cyanoisopropyl radical does not alter the molecular-weight characteristics of the polymer. In contrast to SMA prepared in the presence of dithiobenzoate, in decomposition of PSMA synthesized using trithiocarbonate (CPTC) a low-molecular-weight mode (with $M_{n,mod} \approx 1000$, $M_w/M_{n,mod}$ = 1.08) appears in the MMD curve (Fig. 3). This fact suggests that the PSMA synthesized in the presence of trithiocarbonate contains structures of the type of poly-RAFT agents 3 and 4, whose heating with excess radical initiator results in successive elimination of the polymeric substituents with a decrease in

Table 1. Copolymerization of stearyl methacrylate with various monomers (concentration of the monomer mixture in toluene 10%)

Compound no.	Second co-monomer	SMA : comonomer molar ratio, %	T, °C	[AIBN], M	[RAFT agent], M	Time, h	Conver-sion, %	$M_n \times 10^{-3}$	M_w/M_n
1	MA	50 : 50	60	0.001	–	17	74	53.5	4.69
2	MA	50 : 50	60	0.001	CPTC, 0.001	5	25	18.5	2.10
3	MA	50 : 50	60	0.001		6	30	18.2	1.94
4	MA	50 : 50	60	0.001		16	48	18.9	1.88
5	MA	50 : 50	60	0.001		30	60	18.8	1.94
6	MA	50 : 50	60	0.001		82	76	18.8	2.00
7	BMA	80 : 20	80	0.01	–	3	88	26.7	2.32
8	BMA	80 : 20	80	0.01	CPTB, 0.01	0.08	23	10.5	1.26
9	BMA	80 : 20	80	0.01		0.25	41	29.0	1.15
10	BMA	80 : 20	80	0.01		0.5	63	46.1	1.13
11	BMA	80 : 20	80	0.01		1	84	58.0	1.18
12	BMA	80 : 20	80	0.01		3	93	64.1	1.23
13	AMA	80 : 20	80	0.01	–	3	83	27.4	2.23
14	AMA	80 : 20	80	0.01	CPTB, 0.01	0.08	18	9.3	1.28
15	AMA	80 : 20	80	0.01		0.25	39	25.7	1.16
16	AMA	80 : 20	80	0.01		0.5	67	43.4	1.14
17	AMA	80 : 20	80	0.01		1	81	52.2	1.20
18	AMA	80 : 20	80	0.01		3	89	57.7	1.25

MM and with their replacement by the initiator fragments. However, not all the polymer fractions but only a part of them are modified (Fig. 3) because the high-molecular-weight mode whose molecular-weight characteristics virtually coincide with those of the initial sample ($M_{n,init}$ = 11 500, $M_w/M_{n,init}$ = 1.60; $M_{n,mod}$ = 14 600, $M_{n,mod}$ = 1.57) remains.

Certain "apparent" increase in MM of the remaining high-molecular-weight fraction of the product after the modification is due to degradation of a part of fractions corresponding to poly-RAFT agents 3 and 4 and to the presence of poly-RAFT agents 1 and 2 in the PSMA structure (Scheme 2).

Experiments on the copolymerization of SMA with monomers of various structures (BMA, AMA, and MA) have shown that, as in the case of the SMA homopolymerization, CPTC influences the copolymerization kinetics more strongly than CPTB does (Table 1). Such effect of CPTC on the kinetics of both homopolymerization and copolymerization of SMA with MA may be due to the stability of the intermediates formed (Scheme 2).

Indeed, in a number of systems the lifetime of the intermediates can be sufficiently long, leading to the "freeze" of the polymerization or to possible occurrence of side reactions, e.g., capture of propagating radicals or initiation of new chains. The more stable is the radical intermediate formed, the more pronounced is the polymerization inhibition [19].

The RAFT agents also affect the molecular-weight characteristics of the polymers synthesized (Table 1). Certain features of the copolymerization of various co-monomer systems should be noted. In the case of SMA copolymerization with various alkyl acrylates (BMA, AMA), which are similar in nature to SMA, in the presence of CPTB, MM shows a pronounced tendency to increase with the conversion, and the polydispersity is low (M_w/M_n = 1.13–1.28). As demonstrated by the example of SMA–BMA copolymers, the MMD curves are gradually shifted toward high MM with increasing conversion (Fig. 4). These facts demonstrate clear control of the molecular-weight characteristics and the RAFT polymerization mechanism (Scheme 2).
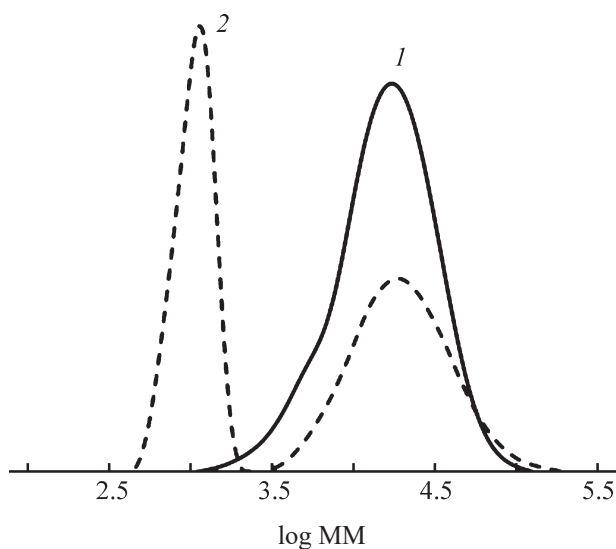
Fig. 3. Molecular-weight distribution of the (*1*) initial poly(stearyl methacrylate) and (*2*) modified product obtained in the presence of azobis(isobutyronitrile) (AIBN) at 80°C.

Fig. 4. Molecular-weight distribution of stearyl methacrylate–butyl methacrylate copolymers synthesized in the presence of 0.01 M azobis(isobutyronitrile) and 0.01 M 2-cyano-2-propyl dithiobenzoate at 80°C. Conversion, %: (*1*) 23, (*2*) 41, and (*3*) 84.

As seen from Table 1, in copolymerization of SMA with MA, in contrast to the SMA homopolymerization (Fig. 2a), M_n of the copolymers synthesized in the presence of CPTC remains constant throughout the process. Its value is considerably lower than M_n of the copolymer synthesized on a common radical initiator without RAFT agent. The polydispersity coefficients for SMA–MA copolymers synthesized in the presence of CPTC, as well as their MM, do not noticeably change in the course of the process and remain on the level of 2.0, but this value is considerably lower than M_w/M_n for the sample synthesized on AIBN. Thus, the dependence of the conversion on time and the molecular-weight characteristics of SMA–MA copolymers obtained in the presence of CPTC demonstrate its role as an irreversible chain-transfer agent capable of inhibiting the copolymerization. Indeed, RAFT agents and irreversible chain-transfer agents such as, e.g., mercaptans can inhibit the polymerization [19, 24].

Because the monomers incorporated in SMA–BMA and SMA–AMA copolymers are close in the nature and structure, it was impossible to determine the composition of these copolymers. The relative activities of the above comonomers in the copolymerization can be logically assumed to be comparable because of their similar structure and close reactivity. In contrast to the above-described monomer pairs, SMA and MA differ essentially in the structure and activity in the copolymerization. As
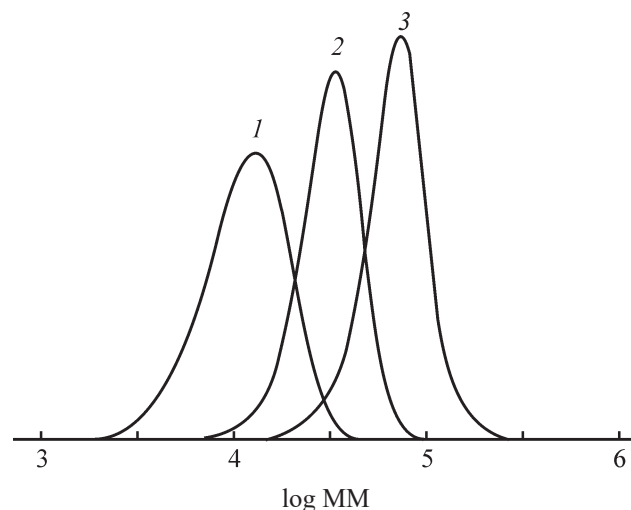
demonstrated by the example of the copolymerization of methyl methacrylate with MA, the relative activities of the monomers in copolymerization of methacrylic acid esters with MA differ considerably (by virtually two orders of magnitude) [25]. MA itself is incapable of homopolymerization. This fact can significantly affect the incorporation of MA into the SMA–MA copolymer in the case of both traditional copolymerization processes and "living" polymerization processes occurring by the RAFT mechanism. In this connection, it was necessary to estimate the compositions of SMA–MA copolymers by various spectroscopic methods. Incorporation of MA units into SMA was unambiguously proved by the presence of characteristic anhydride absorption bands in the region of 1857 cm^{-1} along with the characteristic absorption bands of the ester fragment of SMA in the region of 1784 cm^{-1} (Fig. 5).

The quantitative composition of the SMA–MA copolymer was studied in more detail by ^{1}H NMR spectroscopy. As seen from Figs. 6A and 6B, the spectra of PSMA and SMA–MA copolymer are different. In the spectrum of the copolymer, there are signals characteristic of MA units at 2.6–3.0 ppm. The copolymer compositions were calculated from the integral intensities of the signals corresponding to methylene protons at the oxygen atom of the SMA ester group at 3.8–4.1 ppm (signal d, Fig. 6B) and to methine protons of maleic anhydride at 2.6–3.0 ppm (signal e, Fig. 6B) [6]. The data
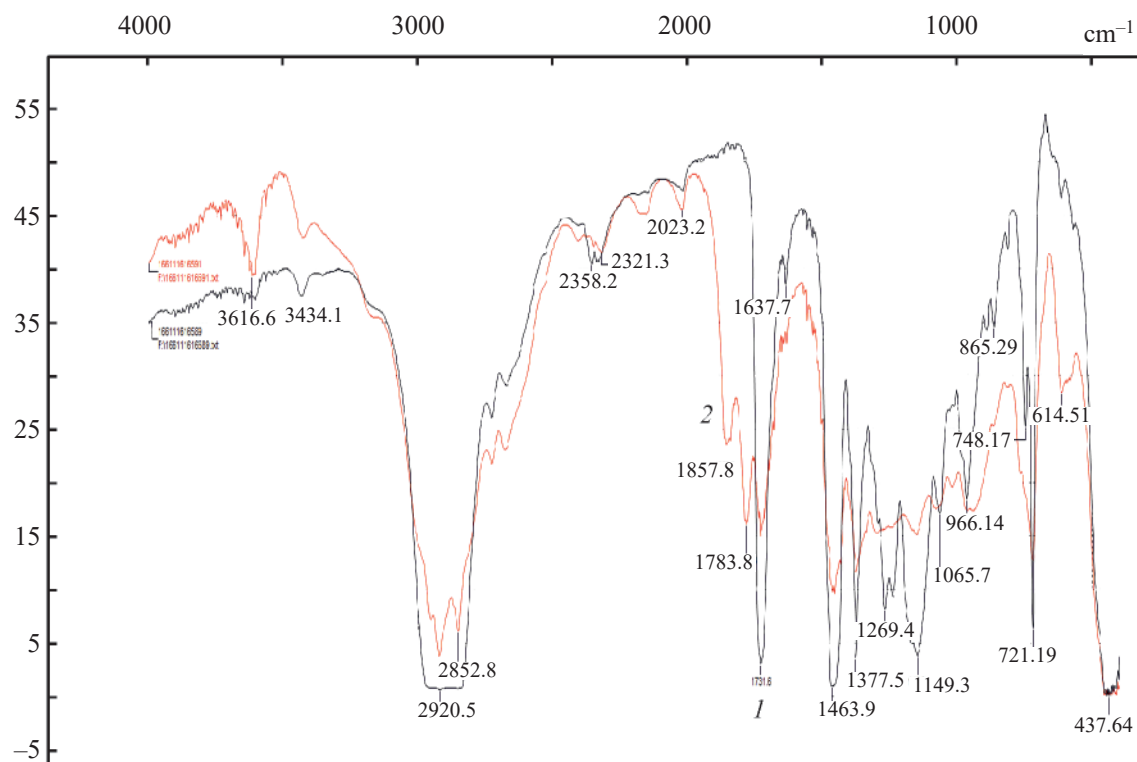
Fig. 5. IR spectra of (*1*) poly(stearyl methacrylate) and (*2*) stearyl methacrylate–maleic anhydride copolymer.
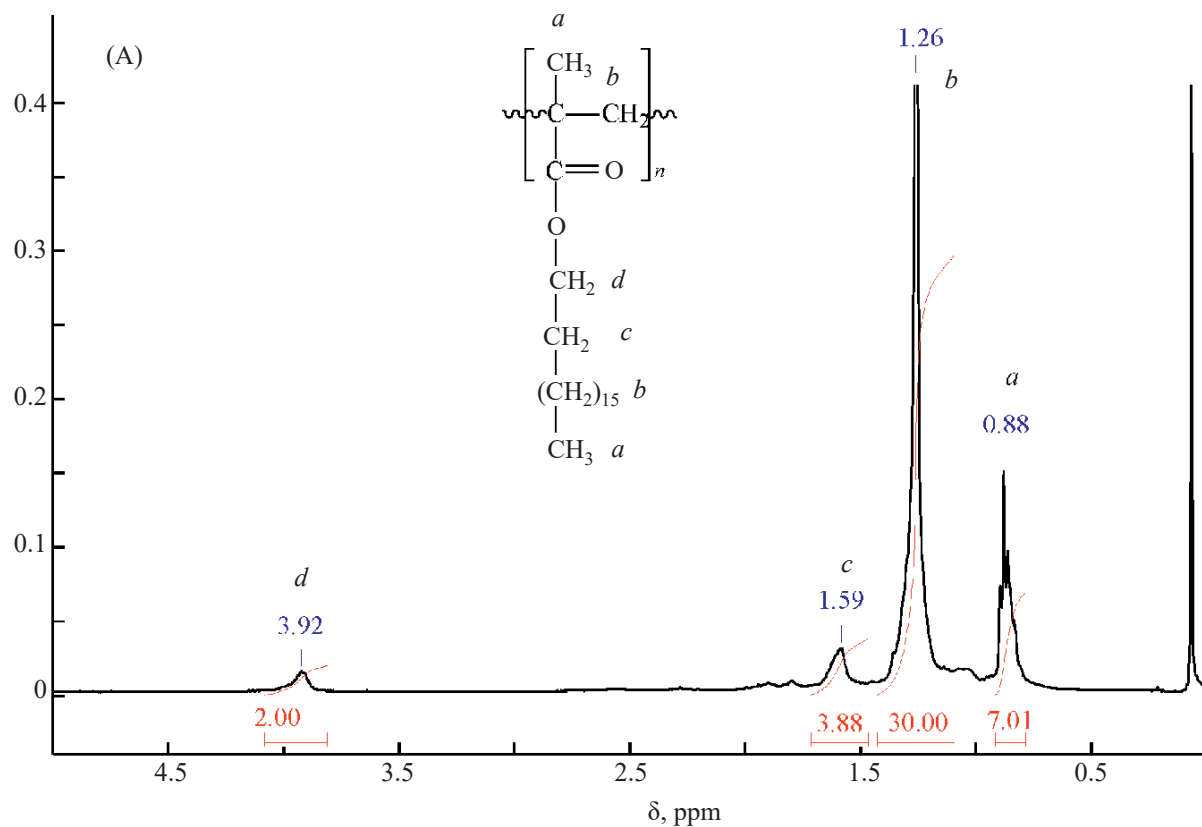

Fig. 6. ¹H NMR spectra of (A) poly(stearyl methacrylate), (B) stearyl methacrylate–maleic anhydride copolymer (inset: range 2.0–5.0 ppm), and (C) stearyl methacrylate–maleic anhydride copolymer modified with 1-octanol.
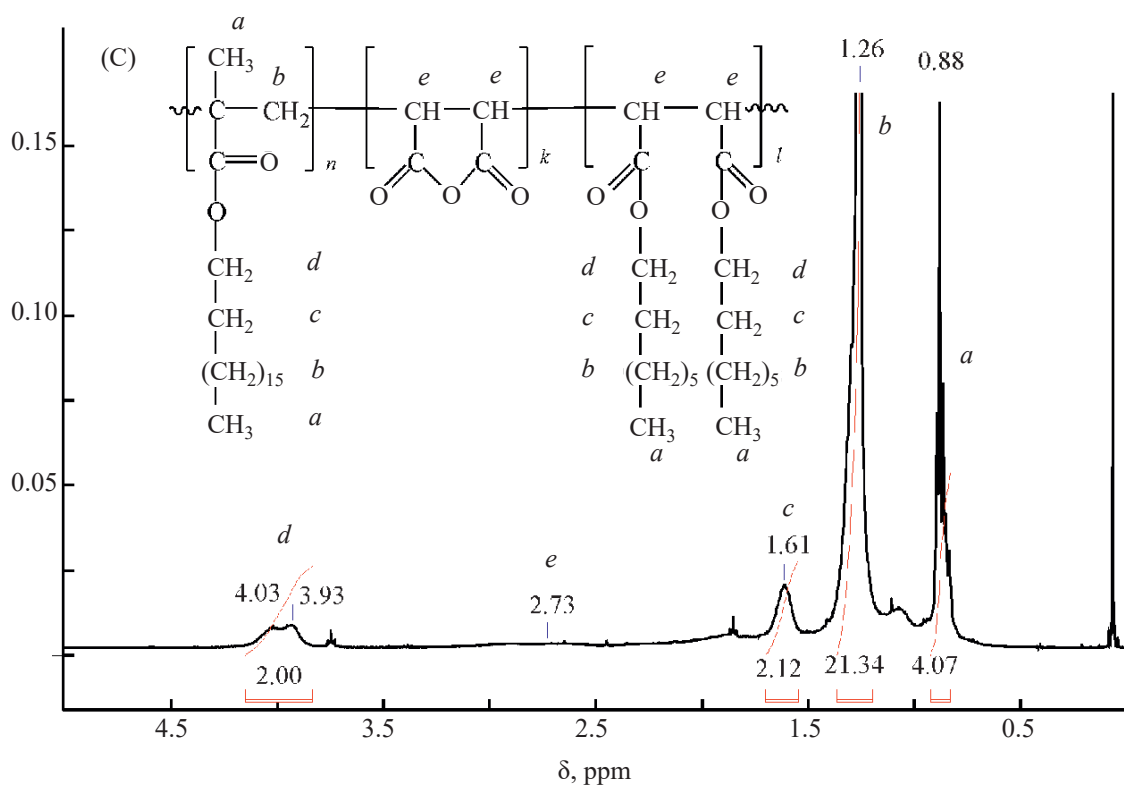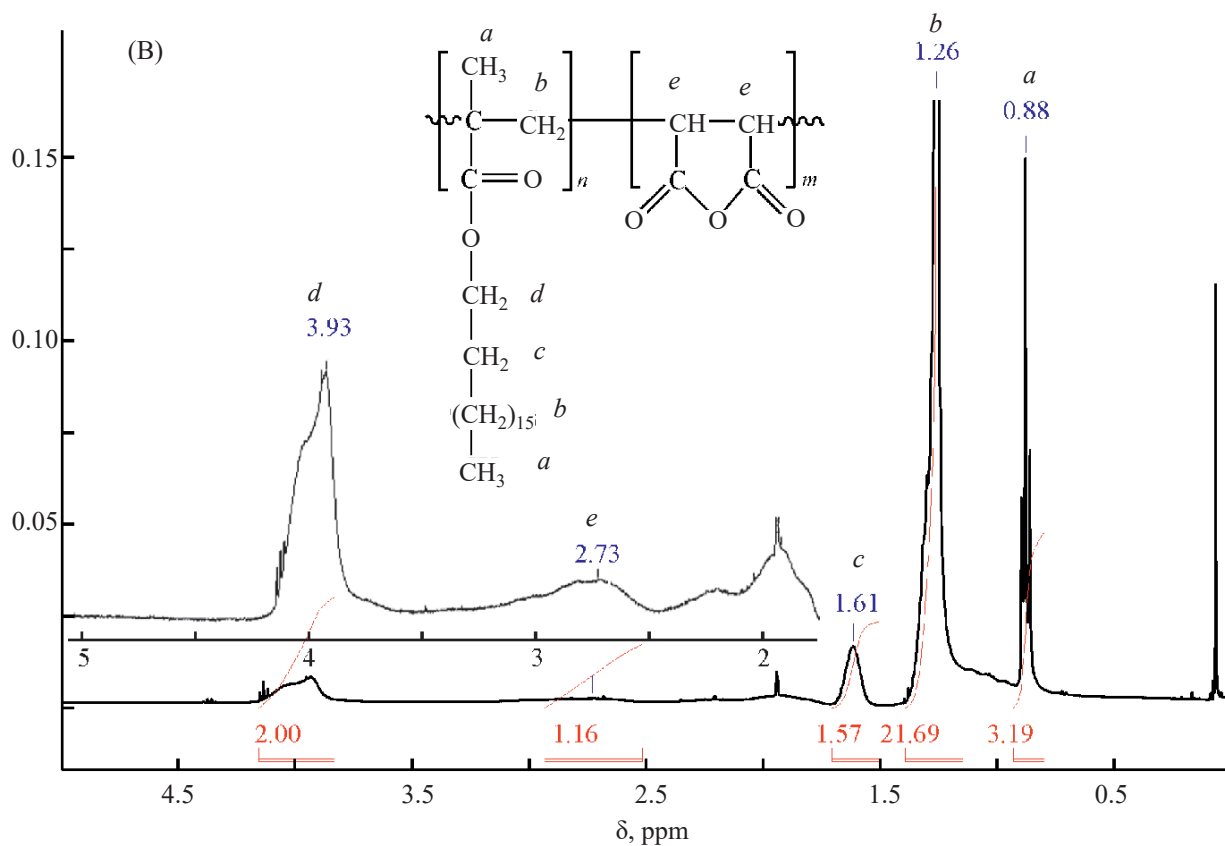
Fig. 6. (Contd.)

for the copolymers isolated at approximately 60–70% conversion are given in Table 2 and demonstrate relatively high fraction of MA in the copolymer at high conversions. In this case, the molar content of MA in the copolymer only weakly depends on the initial composition of the monomer mixture.

Thus, the dithikobenzoate and trithiocarbonate that we used allow efficient control of the molecular-weight characteristics not only of PSMA and SMA copolymers with higher alkyl acrylates, but also of SMA–MA copolymers. Despite significant difference in the relative activities of methacrylates and MA, synthesis of SMA–MA copolymers occurs to high conversions of both comonomers to give copolymers containing up to 40 mol % MA.

Effect of polymers based on stearyl methacrylate on the low-temperature properties of the diesel fuel. The polymers prepared were tested as depressor additives to base DF containing no additives. The structure, composition, and molecular-weight characteristics of the additives exert the major influence on the low-temper-

ature properties of DF [1–4]. The RAFT agents used, depending on the chosen concentration, allow preparation of the polymers with MM clearly preset in the range 20 000–700 000 and low polydispersity, irrespective of their kind. Therefore, in this section we will consider the effect of the (co)polymers on the low-temperature properties of the diesel fuels irrespective of the RAFT agent used.

The polymers were introduced into DF in the concentration of 1600 ppm, which corresponds to the practically used optimum range for additives based on alkyl (meth)acrylates [7–13]. Introduction of low-molecular-weight homopolymers prepared in the presence of RAFT agents into DF does not lead to noticeable changes in its low-temperature characteristics (T_{cl} and CFPP). For example, on adding into DF the additive based on PSMA with M_n 20 900, T_{cg} decreases by only 2°C (Table 2). An increase in MM of PSMA to 40 000–70 000 enhances the depressor effect. The congealing point depression (ΔT_{cg}) on introducing these additives is 5°C (Fig. 7). As demonstrated by the example of PSMA homopolymers synthesized in the presence of RAFT agents, the de-

Table 2. Low-temperature properties of diesel fuel in the presence of depressor additives of various types. Stearyl methacrylate homopolymers and copolymers with maleic anhydride were synthesized at 60°C in the presence of 0.001 M azobis(isobutyronitrile) and 0.001 M 2-cyano-2-propyl dodecyl trithiocarbonate in toluene, conversion ~65–70%

Compound no.	Additive	Composition, mol %		M_n	M_w/M_n	Low-temperature characteristics of DF		
		of SMA : MA monomer mixture	of poly(SMA–MA) copolymer			T_{cl}, °C	T_{pp}, °C	CFPP, °C
1[a]	None	–	–	–	–	–8	–15	–10
2	Dodiflow[b]	–	–	–	–	–8	–24	–10
3	Dodiflow[b]	–	–	–	–	–8	–25	–17
4	PSMA[c]	–	–	49000	3.0	–8	–20	–10
5	PSMA	–	–	20900	1.9	–9	–17	–10
6	poly(SMA–MA)	80 : 20	64 : 36	28200	2.3	–13	–21	–14
7	poly(SMA–MA)	60 : 40	61 : 39	21000	2.0	–13	–20	–13
8	poly(SMA–MA)	50 : 50	64 : 36	18800	2.0	–13	–21	–14
9	poly(SMA–MA)	40 : 60	60 : 40	21000	2.0	–13	–20	–13
10	poly(SMA–MA)	50 : 50	Modified	20800	2.0	–15	–35	–20

[a] Initial DF.
[b] Commercial additive based on ethylene–vinyl acetate copolymer, introduced in the concentration of 400 (compound no. 2) and 1600 ppm (compound no. 3).
[c] Homopolymer prepared without RAFT agent.

Scheme 3. Modification of SMA–MA copolymer with 1-octanol.
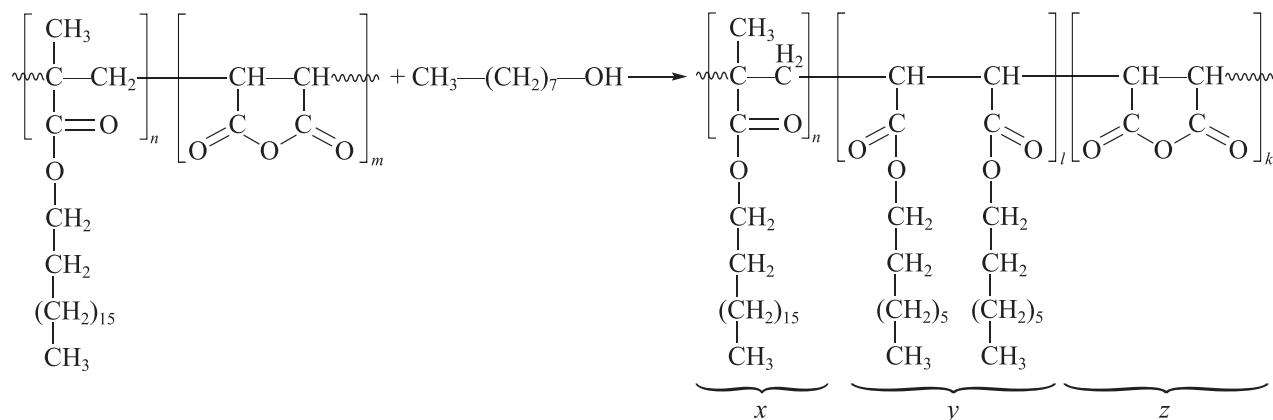
pressor effect is enhanced with an increase in MM of the additives. Similar effect of additives on the low-temperature characteristics of DF was demonstrated by the example of PSMA prepared in the presence of the traditional initiator, AIBN, having M_n = 49 000 (Table 2). The polymers synthesized in the presence of RAFT agents and containing terminal functional groups, in contrast to PSMA prepared on AIBN, can be used in the future for modifying the composition, structure, and architecture of polymers, in particular, for developing depressor additives with improved low-temperature characteristics.

Similar influence of MM of the additives on the low-temperature properties of DF was observed for the SMA–BMA and SMA–AMA copolymers. The copolymers with MM of up to 10 000 exert a minimal effect on the low-temperature characteristics of the fuel. No significant effect on T_{cl}, T_{cg}, and CFPP was revealed on introducing such additives in a concentration of 1600 ppm. The depression of these parameters was as small as 1°C. An increase in MM of the additives to 60 000 leads to improvement of their depressor effect. The depression of T_{cg} for SMA–BMA copolymers is 8°C, and for SMA–AMA copolymers it is 11°C (Fig. 7). However, no significant effect on T_{cl} and CFPP was revealed in this case either. In particular, T_{cl} and CFPP decrease by only 3°C.

The SMA–MA copolymers showed more promise as depressor additives (Table 2). In particular, introduction of additives based on SMA–MA in a concentration of 1600 ppm into hydrotreated DF leads to a decrease in the low-temperature characteristics of DF to a greater

extent compared to the PSMA homopolymer and copolymers with BMA and AMA of similar MM (Fig. 7). It should be emphasized once again that the SMA–BMA and SMA–AMA copolymers with MM ~10 000–20 000 do not decrease T_{cg} of DF. Because the composition of SMA–MA copolymers obtained at high conversions is virtually independent of the monomer ratio in the starting mixture, the monomer mixture composition in the examined interval does not noticeably influence the low-temperature properties of DF (Table 2). Somewhat stronger effect of SMA–MA copolymers on the depression of T_{cl} and CFPP (Table 2) compared to SMA copolymers with alkyl methacrylates should also be noted.

It is known that modified copolymers based on MA have more pronounced depressor properties [6]. Therefore, we modified with 1-octanol the SMA–MA copolymer synthesized in the presence of RAFT agents at the molar ratio of the starting monomers of 50 : 50 (Scheme 3).

The product obtained was characterized by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectra contain no signals of carboxyl protons at 10–12 ppm. No characteristic OH stretching vibration bands of acid groups in the range 3100–2800 cm^{-1} were observed in the IR spectra either. These facts show that there are no free carboxyl groups in the copolymers and that two octyl fragments are incorporated into one MA units (Scheme 3). The product composition was estimated from the integral intensities of the ^{1}H NMR signals corresponding to the total content of methylene protons at the oxygen atom in SMA ester groups and in the units modified with 1-octanol (3.8–4.1 ppm, signal *d*,
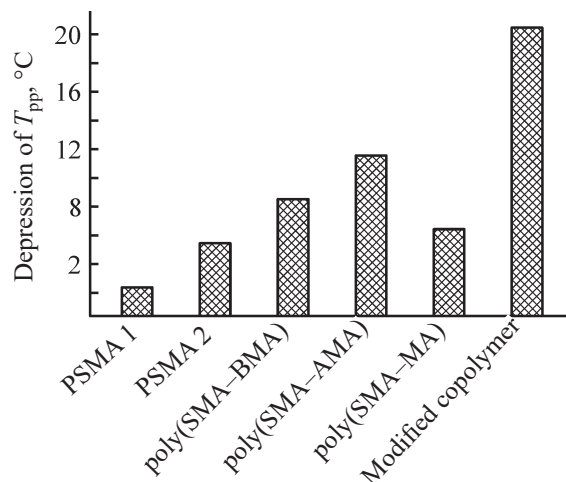
Fig. 7. Depressor effect of additives based on stearyl methacrylate, synthesized in the presence of reversible addition–fragmentation chain-transfer agents. Concentration of additives in diesel fuel 1600 ppm. Mn: poly(stearyl methacrylate) PSMA 1 20900, PSMA 2 70000; stearyl methacrylate–butyl methacrylate copolymer [poly(SMA–BMA)] 58000; stearyl methacrylate–alkyl methacrylates copolymer [poly(SMA–AMA)] 58000; stearyl methacrylate–maleic anhydride copolymer [poly(SMA–MA)] 18800; modified stearyl methacrylate–maleic anhydride copolymer 20800.

Fig. 6C) and from the intensity of the signal in the region of 1.27 ppm (signal b, Fig. 6C), corresponding to the sum of the remaining methylene groups of SMA and 1-octanol in ester moieties and of SMA methylene units in the copolymer backbone. The solution of the system of Eqs. (1) allowed determination of the content of 1-octanol incorporated in the modified product:

$$\begin{cases} 2x + 4y = 2, \\ 32x + 20y = 21, \\ x + y + z = 1, \end{cases} \tag{1}$$

where x is the molar content of SMA; y, molar content of 1-octanol incorporated into the copolymer upon modification; and z, molar content of the remaining MA units. The product modified with 1-octanol has the following composition (mol %): [DMS : modified units : MA] = 50 : 25 : 25. The degree of modification of the SMA–MA copolymer was 25%, or 50% based on MA units.

We have studied the effect of the modified product on the low-temperature characteristics of DF (Fig. 7) and found the SMA–MA copolymer modified with 1-octanol considerably improves the low-temperature proper-

ties of the fuel. The depressor effect for the congealing point is 20°C. In our opinion, this effect is associated with changes in the copolymer structure. In particular, long octyl fragments in the modified poly(SMA–MA) copolymer sterically hinder the paraffin agglutination, thus reducing the congealing point of the DF [4]. In addition, this modified copolymer with M_n = 20 800 influences T_{cl} and CFPP (Table 2) more strongly than SMA copolymers with BMA and AMA do: In the presence of the latter copolymers of similar MM, no noticeable effect on the low-temperature properties was revealed. The suggested additives based on modified SMA–MA copolymers well compete in the depressor effect with the widely used imported commercial additive, Dodiflow (Table 2), and with the known additives based on alkyl methacrylates, with which the depressor effect on T_{cg} is 7–18°C [8, 10].

CONCLUSIONS

The use of reversible addition–fragmentation chain-transfer agents (2-cyano-2-propyl dithiobenzoate and 2-cyano-2-propyl dodecyl trithiocarbonate) in homo- and copolymerization of stearyl methacrylate with various alkyl methacrylates and maleic anhydride is very promising for preparing functional polymers in the controlled mode. This approach allowed synthesis of (co) polymers with clearly preset molecular weight and low polydispersity indices. The effect of these (co)polymers on the low-temperature properties of diesel fuel was studied. The copolymers based on stearyl methacrylate and alkyl methacrylates are more effective depressors than stearyl methacrylate homopolymers. Modification of the stearyl methacrylate–maleic anhydride copolymer with 1-octanol allowed reaching the strongest depressor effect for the summer diesel fuel among all the additives tested. The modified additive allowed the congealing point of the hydrotreated diesel fuel to be decreased from –15 to –35°C. Therefore, the additive that we developed can be of indubitable interest as a depressor additive and as an effective alternative to the presently used imported depressor-dispersing additives to hydrotreated diesel fuel.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

AUTHOR CONTRIBUTION

E.V. Kolyakina: collection, analysis, and interpretation of the results of experiments on polymerization of monomers in the presence of 2-cyano-2-propyl dithiobenzoate (CPTB), study of the low-temperature characteristics of diesel fuel, manuscript preparation, major contribution to writing the Results and Discussion section, and approval of the final version of the paper; M.V. Pavlovskaya: collection, analysis, and interpretation of the results of experiments on polymerization of monomers in the presence of 2-cyano-2-propyl dodecyl trithiocarbonate (CPTC), study of the low-temperature characteristics of diesel fuel, collection of literature data and preparation of the literature review, and approval of the final version of the paper; Yu.S. Pronina: development and description of the experimental procedures for modifying stearyl methacrylate–maleic anhydride copolymers, analysis of the copolymers by IR and NMR spectroscopy, description of the results, and approval of the final version of the paper; S.D. Zaitsev: synthesis of 2-cyano-2-propyl dodecyl trithiocarbonate, participation in the data processing by critical revision of the results and manuscript, and approval of the final version of the paper; D.F. Grishin: significant contribution to the concept of the study, evaluation and analysis of the results obtained, participation in the data processing by critical revision of the results and manuscript, and approval of the final version of the paper.

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