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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Conditions of Synthesis and Properties of Dimethacrylate Derivatives Containing a Fragment of a Dimerized Fatty Acid

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Abstract—A series of dimethacrylate esters of a dimerized fatty acid were prepared. The dependence of their formation rate on the kind of the glycol used was examined. The correlation between the molecular-weight characteristics of the esters and their synthesis conditions is discussed.

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Recently there has been particular interest in products based on a dimerized fatty acid (DFA) [1–4]. Thanks to the high reactivity of DFA, it is possible to prepare a wide range of products finding use in diverse fields of industry [5–7]. The unique physicochemical properties and service characteristics of DFA derivatives, determined by the presence of bulky cycloaliphatic substituents in acid residues, make their studies topical.

Another important factor making DFA attractive is its production from renewable plant materials.

Previously [8–11] we reported on the synthesis of DFA oligo- and (co)polyamides, which are base raw materials for preparing hot-melt adhesives with high adhesion characteristics.

As a continuation of studies in the field of synthesis of DFA derivatives, it was interesting to introduce into a molecule containing a bulky DFA fragment methacrylate groups capable of subsequent polymerization in the presence of free-radical initiators or under UV irradiation, to obtain polymeric adhesives with internal plasticization.

Combination of properties of the DFA cycloaliphatic substituent and high capability of methacrylates for polymerization will expand the applications of DFA derivatives as adhesives and binders in production of various composite materials, anaerobic sealants, and casting compounds.

The goal of this study was to synthesize new DFA dimethacrylate derivatives and to examine how their properties depend on the starting reactants and on the conditions of synthesis and isolation.

EXPERIMENTAL

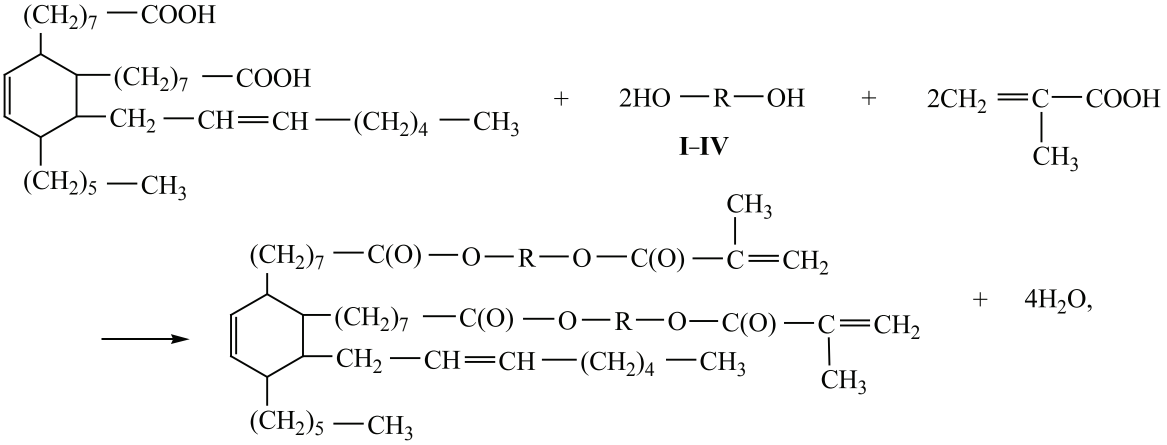
We used the following chemicals: Pripol-1013 dimerized fatty acid (linoleic acid dimer containing no less than 97% main substance, CAS no. 61788-89-4); DFA dichloride (DFA DC) synthesized according to [9]; methacrylic acid [MAA, TU (Technical Specification) 6-01-914–79]; freshly distilled glycols and their monoesters: ethylene glycol [EG, GOST (State Standard) 19710–83], diethylene glycol (DEG, GOST 10136–77), triethylene glycol (TEG, TU 6-01-5–88 with revisions 1, 2), butylene glycol (BG, TU 64-5-105–86), ethylene glycol monomethacrylate (EGM, TU 6-01-1240–80), and propylene glycol monomethacrylate [PGM, STP (Enterprise Standard) 70–2005, Research Institute of Polymers]; preliminarily distilled toluene (GOST 5789–78) and triethylamine (GOST 9966–88); hydroquinone (GOST 2549–60); *p*-methoxyphenol (TU 6-09-1248–71); *p*-toluenesulfonic acid (*p*-TSA, TU 6-09-3668–77); sodium hydroxide (GOST 4328–77 with revisions 1, 2); sodium chloride (GOST 4233–77); distilled water (GOST 6709–72); and copper(I) chloride (GOST 4164–79).

The structures of the synthesized DFA dimethacrylate esters were analyzed by IR and NMR spectroscopy. The IR spectra were recorded with a Specord M 82 spectrophotometer in the range 4000–400 cm^{-1} from a sample drop pressed between KBr plates. The NMR spectra were taken with a Bruker DPX-200 spectrometer operating at 200 MHz for ^{1}H and 50 MHz for ^{13}C. The samples were dissolved in $CDCl_3$. The internal reference was tetramethylsilane.

The molecular-weight distribution (MWD) of the dimethacrylate esters was determined by gel permeation chromatography (GPC) with a set of five Styragel columns with the sorbent porosity of 10^5, 3×10^4, 10^4, 10^3, and 250 Å (Waters). As detectors we used an R-403 differential refractometer (Waters) and an LCD 2563 photometer ($\lambda = 254$ nm). The eluent was tetrahydrofuran (THF). The chromatograph was calibrated using polystyrene (PS) references.

The saponification, acid, and ester numbers of the products were determined according to [12, 13].

We examined several procedures for preparing DFA dimethacrylates under different conditions. The scheme of one-step esterification starting from DFA, glycol, and MAA can be presented as follows:



I–IV

V–VIII

R = $(CH_2)_2$ (**I**, **V**); $CH_2CH_2OCH_2CH_2$ (**II**, **VI**); $CH_2CH_2OCH_2CH_2OCH_2CH_2$ (**III**, **VII**); $(CH_2)_4$ (**IV**, **VIII**).

To prepare dimethacrylate ester **V** from DFA, MAA, and ethylene glycol, a reactor equipped with a stirrer and a Dean–Stark trap with a reflux condenser was charged with the calculated amounts of the reactants (molar ratio DFA : MAA : ethylene glycol = 1 : 2.2 : 2.2), and also with hydroquinone (1 wt % of MAA), Cu_2Cl_2 (1 wt % of MAA), and *p*-TSA (2.5 wt % of the sum of the reactants). The mixture was heated with vigorous stirring to 108–120°C until the water evolution ceased. The reaction progress was monitored by the amount of the released water (Fig. 1) and by the acid numbers characterizing the change in the content of the starting acids in the reaction mixture (Fig. 2).

As shown in Fig. 1 (curve *1*), the reaction proceeds, on the average, within 10 h. More than a half of the stoichiometric amount of water is released in the first hour, after which the reaction decelerates and practically ceases. Performing the reaction for the time exceeding 10 h leads to only a slight increase in the reactant conversion, but it is accompanied by pronounced tarring, so that light diester **V** cannot be prepared in high yield in this case because of large loss in the isolation step.

The observed deceleration of the reaction between

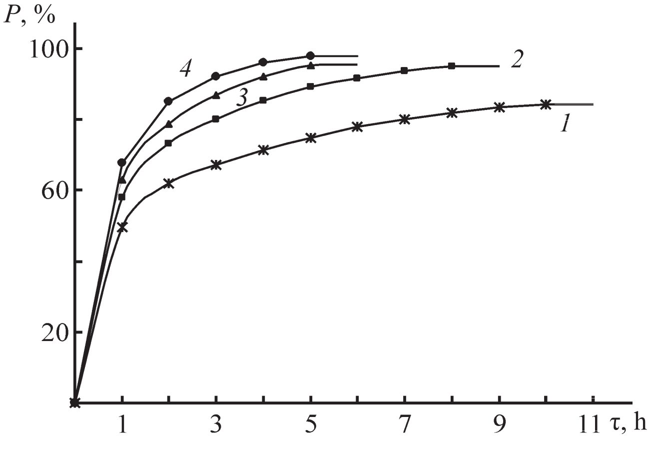


Fig. 1. Reactant conversion *P* in synthesis of dimethacrylates as a function of time τ. Dimethacrylate: (*1*) **V**, (*2*) **VI**, (*3*) **VII**, and (*4*) **VIII**; the same for Fig. 2.

DFA, MAA, and ethylene glycol on reaching 85% conversion with respect to the released water is confirmed by measurements of the acid number of the reaction mixture (Fig. 2, curve *1*), which decreases only to 3.8 (mg KOH) g^{-1} and then does not decrease further.

After the synthesis completion, the reaction mixture was purified to remove excess MAA and ethylene glycol and residual amounts of the catalyst, after which it was transferred into a separation funnel and washed with water. The washing was accompanied by strong emulsification, which considerably complicated the separation of the organic and aqueous phases. With the aim to improve the phase separation, the reaction mixture was diluted by a factor of 2 with toluene, with the subsequent washing performed with 10% aqueous NaCl. The emulsion formed underwent separation in 20–30 h. After washing, we determined the acid number of the mixture and neutralized the residual acidity with the calculated amount of NaOH. Excess alkali may lead to saponification of DFA dimethacrylate, which, in turn, may cause strong emulsification of the system due to formation of DFA sodium salts. The neutralized reaction mixture was also washed with a 10% aqueous NaCl solution and then with distilled water to neutral reaction.

The toluene solution of DFA dimethacrylate ester, separated from the aqueous layer, was filtered through a fabric filter, after which 0.05 wt % hydroquinone was added, and the toluene was distilled off at 50–60°C/8.0–1.33 kPa. The dimethacrylate was additionally kept in a vacuum (1.33–0.67 kPa) for 1–2 h at 50–60°C. The properties of the synthesized dimethacrylate ester **V** are given in Table 1.

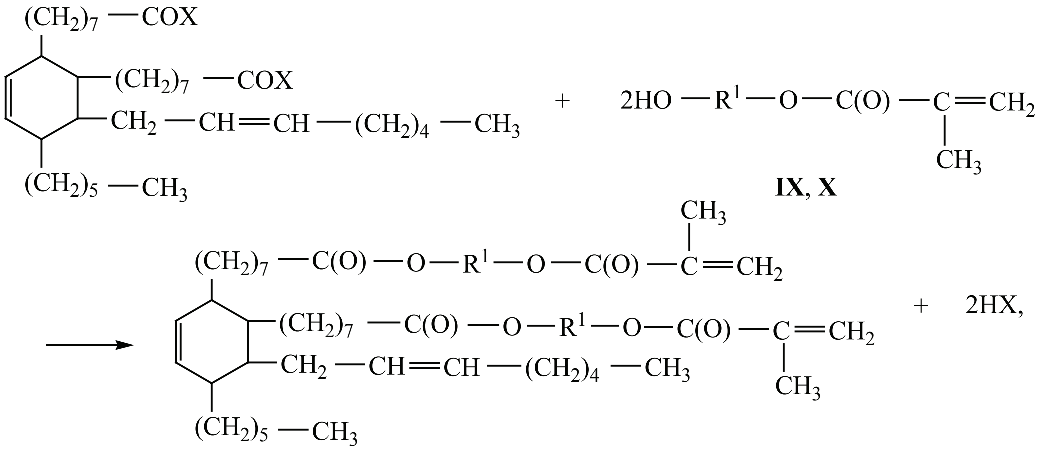
It was interesting to study how the structure of the glycol component affects the characteristics of the dimethacrylates obtained and simultaneously to determine the optimal conditions for DFA esterification. For this purpose, with synthesized DFA dimethacrylates with DEG, TEG, and BG fragments.

Dimethacrylate esters **VI–VIII** were prepared similarly to **V** from DFA, MAA, and the above glycols.

When monitoring the reaction water evolution and the variation of the acid numbers (Fig. 2), we found that the esterification rate sharply increases with an increase in the distance between the hydroxy groups in the glycols: BG > TEG > DEG > EG. This may be due to the fact that, with an increase in the number of methylene or ethylene oxide fragments in the glycol structure, the position of its OH groups becomes more and more favorable kinetically [14].

It should also be noted that, in the synthesis of the dimethacrylates with DEG, TEG, or BG, the phase separation of the washed reaction mixture and aqueous layer occurred faster than in the synthesis of the diester with ethylene glycol.

In our further experiments, we synthesized the dimethacrylates by the reaction of DFA or DFA DC with ethylene glycol monomethacrylate or propylene glycol monomethacrylate:



XI–XIV

where X = OH, R^1 – CH_2CH_2 (**IX**, **XI**); $-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2$ (**X**, **XII**); X = Cl, R^1 – CH_2CH_2 (**IX**, **XIII**); $-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2$ (**X**, **XIV**).

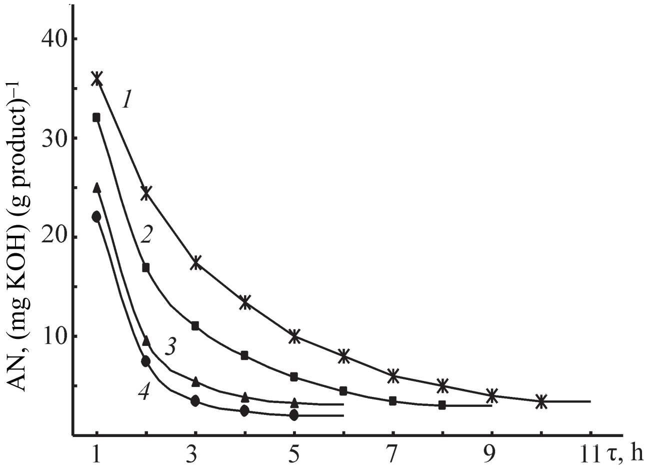


Fig. 2. Total acid number AN of the reaction mixture in synthesis of dimethacrylates as a function of time τ.

The data we obtained show that it is appropriate to prepare DFA dimethacrylates using compounds **IX** and **X**, because introduction of a ready glycol monomethacrylate into the reaction system considerably simplifies the condensation process.

Dimethacrylates **XI** and **XII** were prepared at the molar ratio DFA : glycol monomethacrylate = 1 : 2.4 in toluene in the presence of a catalyst, *p*-TSA.

The reaction of DFA with EGM completes in 4.5–5 h on reaching 95–96% conversion. Thus, in esterification of the dimerized acid with glycol monomethacrylate the reaction time is considerably shorter (by a factor of 2) than in the system with EG and methacrylic acid, the yield of dimethacrylate **XI** is approximately 10% higher than that of **V**, and the product is washed with faster phase separation.

At the same time, dimethacrylate **XII** in the reaction with PGM is formed slowly. The reaction completes in 10–11 h on reaching 95.6% conversion. In this case, the decreased reaction rate is due to specific features of the structure and reactivity of PGM containing a secondary hydroxy group.

The formation of DFA dimethacrylates occurs at elevated temperatures (108–120°C) and therefore is accompanied by formation of certain amounts of by-products and tars. Therefore, it was of interest to examine the possibility of preparing FDA dimethacrylates under milder conditions, e.g., by nonequilibrium condensation with DFA dichloride [10].

Synthesis of dimethacrylates **XIII** and **XIV** from DFA DC and glycol monomethacrylates was performed as follows. To a calculated amount of EGM or PGM, dissolved in excess toluene in the presence of triethylamine (TEA) as acid acceptor, we added dropwise with stirring a toluene solution of DFA DC at the molar ratio glycol monomethacrylate : DFA DC : TEA = 2.2 : 1 : 2.8. The mixture was vigorously stirred for 1 h at 20°C, after which it was heated at 40°C for an additional 2 h. After cooling, the mixture was filtered to remove TEA hydrochloride, and the filtrate was transferred into a separation funnel in which it was washed 5–6 times with water to neutral reaction. To the washed solution, we added 0.01–0.04 wt % *p*-methoxyphenol, after which the toluene was distilled off.

High reactivity of DFA dichloride allowed the condensation to be performed at a lower temperature and in a shorter time, compared to azeotropic esterification, and the DFA dimethacrylates to be obtained in high yield.

All the synthesized dimethacrylates are viscous transparent liquids with the color from yellow to dark brown and with a weak methacrylate odor. The physicochemical and chemical properties of **V–VIII** and **XI–XIV** and the IR and NMR data for them are given in Table 1.

It seems also important to study the molecular-weight characteristics of the DFA dimethacrylates prepared and their dependence on the synthesis conditions.

It is known [15–17] that the structure of the oligoester acrylates formed does not always meet the expectations, despite agreement between the calculated and experimentally determined characetristics. Probably, deeper condensation of the bifunctional components (glycol, DFA) leads to the formation of a wide range of mono- and oligomeric products, and the dimethacrylates formed are actually polydisperse multicomponent mixtures.

In this connection, we examined the molecular-weight characteristics of the DFA methacrylates prepared from different starting compounds. Depending on the synthesis conditions, the products can be subdivided into three groups: **V–VIII**; **XI** and **XII**; and **XIII** and **XIV**.

The molecular-weight characteristics of the compounds prepared were studied by gel permeation chromatography. The GPC data show that FDA dimethacrylates **V–VIII** are not monodisperse. The gel chromatogram of dimethacrylate **VIII**, shown in Fig. 3a, reflects its complex oligomer composition: Along with the expected main compound, it contains compounds of lower and higher molecular weights, which

Table 1. Properties, spectral characteristics, and yields of DFA dimethacrylate esters

Compd.	n_D^{20}	d_4^{20}	Saponification number, (mg KOH) (g product)$^{-1}$		Acid number	Ester number	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm	Yield, %
			calcd.	found	mg KOH (g product)$^{-1}$				
V	1.4779	0.9976	286.22	279.20	1.85	277.35	1150–1080 (C–O–C stretching bands); 1730–1715 (C=O groups conjugated with C–C bond)	0.88 m (CH_3); 1.28 s [–$(CH_2)_n$]; 1.62 m (CH_2); 1.96 s [$OC(O)C\underline{H}_3C{=}CH_2$]; 2.30 t [$CH_2C(O)O$]; 2.53 m ($C\underline{H}_2CH$); 4.10–4.18 m [$CH_2OC(O)$]; 5.57 and 6.15 оба s (–$C{=}CH_2$); 6.70–7.02 m (CH=CH)	87.5
VI	1.4799	1.0023	257.34	267.10	0.70	266.40	1350–1100 (C–O–C groups); 1640 (C=C bonds); 1720 (C=O groups conjugated with C–C-bond) and 1740 (nonconjugated); 725 [$(CH_2)_n$ bending bands]	0.88 m (CH_3); 1.26 s [–$(CH_2)_n$]; 1.64 m (CH_2); 1.95 s [$OC(O)C\underline{H}_3C{=}CH_2$]; 2.33 t [$CH_2C(O)O$]; 3.61–3.79 m ($OCH_2CH_2O$); 4.23 and 4.31 both t [$CH_2OC(O)$]; 5.58 and 6.14 both s (–$C{=}CH_2$)	88.4
VII	1.4821	1.0106	233.75	245.60	2.30	243.30	1350–1100 (C–O–C groups); ~1730 (C=O groups)	3.66 s (OCH_2CH_2O) and 3.60–3.77 m; 4.22 and 4.30 t [$CH_2OC(O)$]	92.1
VIII	1.4825	0.9794	267.14	256.75	1.36	255.39	1340–1100 (C–O–C groups); 1730–1715 (C=O groups)	1.70–1.81 m [$C(O)OCH_2C\underline{H}_2C\underline{H}_2CH_2O(O)C$]; 1.94 s [$OC(O)CH_3C{=}CH_2$]; 2.29 t [$CH_2C(O)O$]; 4.09–4.21 m [$CH_2OC(O)$]; 5.55 and 6.10 both s ($C{=}CH_2$); 4.95–5.46 and 6.68–7.10 both m (CH=CH)	95.3
XI	1.4824	0.9981	286.22	284.40	3.78	280.62	1150–1080 (C–O–C groups); 1730–1715 (C=O groups)	1.95 s [$OC(O)C\underline{H}_3C{=}CH_2$]; 2.33 t [$CH_2C(O)O$]; 2.53 m ($C\underline{H}_2CH$); 4.34 s ($OCH_2CH_2O$); 5.59 and 6.13 both s (–$C{=}CH_2$); 6.73–7.01 m (CH=CH)	88.7
XII	1.4799	0.9938	276.35	278.30	1.98	276.32	1300–1150 (C–O–C groups); 1750–1735 (C=O groups)	1.94 and 1.96 both s [$OC(O)C\underline{H}_3C{=}CH_2$]; 2.33 t [$CH_2C(O)O$]; 2.53 m ($C\underline{H}_2CH{=}C$); 4.00–4.25 m ($OC\underline{H}_2CCH_3O$); 5.0–5.40 m ($OCH_2C\underline{H}CH_3O$); 5.59–5.60 m ($C{=}CH_2$); 6.10 and 6.15 both s (–$C{=}CH_2$); 6.70–7.25 m (CH=CH)	94.2
XIII	1.4851	1.0082	286.22	283.50	2.40	281.10	1150–1070 (C–O–C groups); 1745–1715 (C=O groups)	2.34 t [$CH_2C(O)O$]; 2.55 m ($C\underline{H}_2CH{=}C$); 4.33 s [$O(CH_2)_2O$]; 5.57 and 6.12 both s (–$C{=}CH_2$); 6.69–7.0 m (CH=CH)	87.6
XIV	1.4782	0.9922	276.35	275.85	2.63	273.22	1350–1150 (C–O–C groups); 1740–1715 (C=O groups)	1.95 and 1.97 both s [$OC(O)C\underline{H}_3C{=}CH_2$]; 2.33 t [$CH_2C(O)O$]; 2.54 m ($C\underline{H}_2CH{=}C$); 4.00–4.28 m ($OC\underline{H}_2CCH_3O$); 4.99–5.50 m ($OC\underline{H}_2CCH_3O$); 5.58–5.59 m (–$C{=}CH_2$); 6.10 and 6.15 both s (–$C{=}CH_2$); 6.71–7.25 m (CH=CH)	85.4

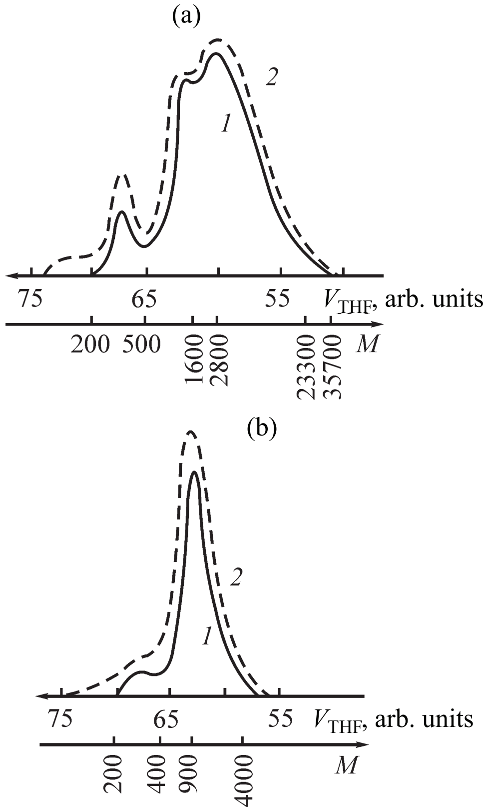


Fig. 3. Gel chromatograms of dimethacrylate esters (a) **VIII** and (b) **XI**. (V_{THF}) THF volume and (M) PS molecular weight. Detector: (*1*) refractometric and (*2*) spectrophotometric.

is confirmed by high polydispersity index (Table 2). Diesters **V–VII** are characterized by the same molecular-weight distribution. In turn, the gel chromatogram of dimethacrylate **XI** (Fig. 3b) suggests formation of the practically monodisperse product. The other esters **XII–XIV** prepared by reactions of glycol monomethacrylates with DFA or DFA DC have also fairly homogeneous composition (Table 2).

The dependence we obtained is primarily determined by the nature and functionality of the starting reactants and by mild esterification conditions. A decrease in the number of functional groups, in combination with the low reaction temperature, leads to a decrease in the probability of side reactions, whereas high activity of the starting chloride and better accessibility of the reaction sites favor predominant formation of the expected dimethacrylates.

The synthesized DFA dimethacrylate derivatives **V–VIII** and **XI–XIV** are of considerable interest as components of various adhesive formulations, sealing and binding materials, and insulation casting or impregnation compounds.

Table 2. Molecular parameters of DFA dimethacrylate esters

Compd.	Number-average molecular weight M_n	Weight-average molecular weight M_w	Polydispersity index M_w/M_n
V	1900	3300	1.74
VI	1800	3000	1.67
VII	2000	3100	1.56
VIII	2200	4300	1.95
XI	900	1200	1.33
XII	850	1100	1.29
XIII	950	1200	1.26
XIV	900	1100	1.22

Our tests showed that the use of FDA dimethacrylate derivatives **V–VIII** and **XI–XIV** as components of anaerobic adhesive formulations for thread joints of elements not only enhances by a factor of 1.4–2.0 the gluing strength on oiled surfaces, but also ensures high level of preservation of the unscrewing moment, compared to the known commercially available sealant.

CONCLUSIONS

(1) Dimethacrylate esters of dimerized fatty acid, containing bulky cycloaliphatic groups imparting high adhesion properties to these compounds, were synthesized by high- and low-temperature oligoesterification.

(2) The esterification rate and the molecular-weight characteristics of the dimerized fatty acid dimethacrylate derivatives largely depend on the structure of the reactants (glycols, glycol monometharylates).

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