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Catalytic Isomerization of Terminal Olefins in Liquid-Crystalline Polyesters at Hydrosilylation with 1-(1'-Arylethoxy)-1,1,3,3-tetramethyldisiloxanes

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Abstract—Liquid-crystalline compounds based on terephthaloyl-bis(4-oxybenzoates) with terminal double carbon-carbon bonds in aliphatic fragments were prepared. The introduction of polar and easily polarizable groups into the aliphatic fragments was shown to reduce the mesomorphic capacity. Hydrosilylation of the polyesters catalyzed by rhodium and platinum complexes was studied. The isomerization of the olefin fragment was demonstrated to be the main process.

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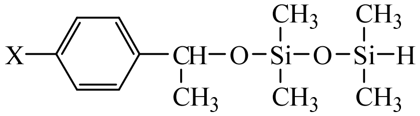
The present infotech development makes high demands on display and data storage systems which are frequently employing liquid-crystalline compounds (various displays, sensors etc.) [1]. The speed requirements of these devices motivate an extensive application therein of liquid-crystalline polymers with mesogenic groups in the side chain and a polysiloxane backbone [2]. The polymers are synthesized by a catalytic hydrosilylation with polymethylhydrosiloxanes of various mesogenic compounds containing a terminal double bond in the aliphatic spacer attached to the mesogene. The set of catalysts in use is limited to Speier's catalyst (a solution of chloroplatinous acid in 2-propanol) [3]) and Karsted catalyst {Pt(0) complex with polyvinylsiloxane [3]}, and the reaction at 70–90°C takes several days at a multifold excess of the reagent; therewith the quantitative conversion is hard to attain. As a result a problem arises of unequal unit number in the polymer [4] reducing its physical characteristics, and the presence of unreacted hydride bonds Si–H causes a time-variant instability of the polymer properties and its cross-linking into three-dimensional nets [2].

Although tens of thousands liquid-crystalline compounds are synthesized up till now [1], these compounds containing siloxane fragments are but single instances. At the same time these compounds exhibit extremely interesting ferroelectric characteristics, remarkably high piezo- and pyrofactors [5–7]. Therefore the introduction of siloxane fragments into liquid-crystalline compounds of low molecular weight and the search for efficient catalysts for hydrosilylation of these compounds and polymers remains nowadays urgent.

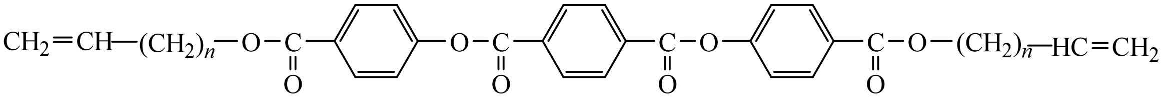
As reagents for the hydrosilylation we selected easily accessible and cheap 1,1,3,3- tetramethyldisiloxane and 1-(1'-arylethoxy)-1,1,3,3-tetramethyldisiloxanes **Ia–Id** prepared by hydrosilylation of *para*-substituted acetophenones [8]. The application of an optically active compound **Ib** allows for preparation of ferroelectric liquid-crystalline compounds.



Ia–Id

As substrates we chose aliphatic esters terephthaloyl-bis(4-oxybenzoates) with terminal double bonds **IIa** and **IIb**, compounds containing a mesogenic fragment providing a possibility to form liquid crystalls [1]. Besides the choice of the compounds was due to the simplicity of their preparation from terephthaloyl-bis(4-oxybenzoyl) chloride [9, 10] and the corresponding alcohols under the conditions of the high-temperature acceptor-free polycondensation.

The liquid-crystalline characteristics of compounds **IIa** and **IIb** are markedly distinct from their saturated ana-



IIa, IIb

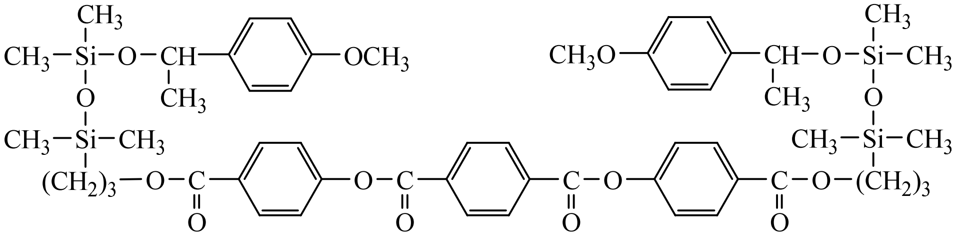
logs because of the presence at the ends of the aliphatic spacer of the polar double bond. For instance, di(*n*-propyl) terephthaloyl-bis(4-oxybenzoate) forms a stable smectic phase *A* in a temperature range 194–231°C [10] [mp 194°C, isotropization temperature 231°C (liquid crystal–isotropic liquid transition)], whereas compound **IIa** is relatively low-melting (mp 139°C) and does not possess the liquid-crystalline properties. This fact is caused by the effect of the double bond in the allyl fragment that hampers the layer stacking of the mesogenic fragments and consequently prevents the formation of a smectic liquid-crystalline phase. This proves for another time the active role of the aliphatic spacer in the formation of the liquid-crystalline order. The presence of a long aliphatic fragment in compound **IIb** results in the formation of a smectic *A* liquid-crystalline state (mp 134°C, isotropization temperature 146°C) of a cofocal texture (observed in compound **IIb** through a polarizing microscope). In this case the temperature stability of the mesophase also proved to be lower than in the corresponding completely saturated analog (for the decyl derivative the range of the meso-phase existence was 147–165°C [10]).

The promising compounds for preparation ferroelectric liquid-crystals are substances with the smectic *C* type of arrangement, and one of the ways to convert a compound with the smectic *A* mesophase type into that with smectic *C* is the elongation of the spacer [10]. Therewith the main means to obtain the ferroelectric state are the preparation of an optically active liquid-crystalline compound by introduction into the latter of a chiral fragment. Therefore the hydrosilylation of compounds **II** was performed using a chiral silyl ether of acetophenone **Ib** in the presence of Karsted catalyst.

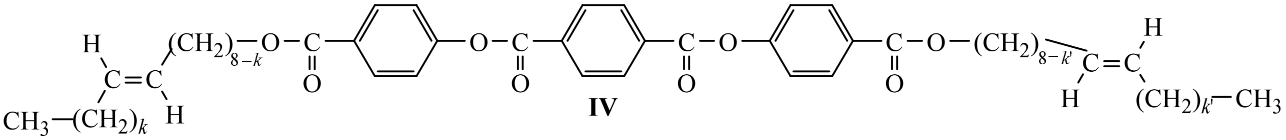
The reaction of diallyl terephthaloyl-bis(4-oxybenzoate) (**IIa**) with excess (+)-1-[1'-(*p*-methoxyphenyl)ethoxy]-1,1,3,3-tetramethyldisiloxane occurs in keeping with Farmer's rule and makes it possible to isolate addition product **III** in a 90% yield.

Compound **III** obtained is relatively high-melting (mp 185°C) and therefore does not possess liquid-crystalline properties. At the same time the specific rotation of compound **III** ($[\alpha]_D^{20}$ +27.0° in chloroform) considerably exceeds the specific rotation of initial silyl ether **Ib** ($[\alpha]_D^{18}$ +1.05° in ethanol [8]). Similar effects are frequently observed in the synthesis of polymers and liquid-crystalline compounds with a prolonged rigid fragment [11], and they are due to the influence of the supermolecular (secondary) structure. Interestingly the observed specific rotation of compound **III** does not at once become constant, and for some time (30 min) it grows in the chloroform solution from +11.8 to +27°, and thereafter remains constant. Apparently it is caused by the gradual alignment of the mesogenic fragments [12, 13] under the effect of the probing beam of the polarimeter till they attain the optimum arrangement.

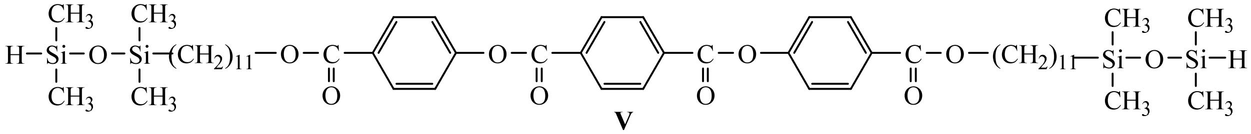
In contrast to compound **IIa** the reaction of di-(10-undecenyl) terephthaloyl-bis(4-oxybenzoatea) (**IIb**) with silyl ether **Ib** (molar ratio **II**:**I** = 1:2.5) in the presence of



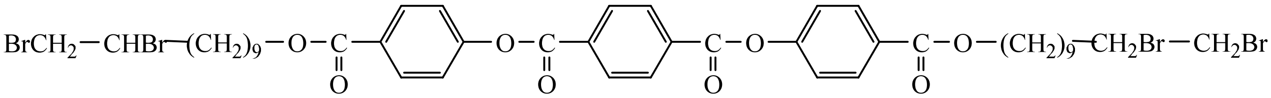
III



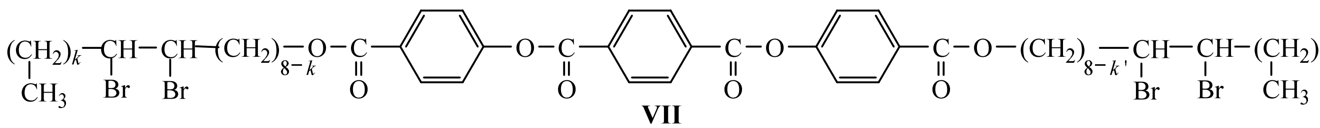
IV



V



VI



VII

Karsted catalyst did not result in the hydrosilylation but in a reduction and isomerization of the initial substrate (conversion of compound **IIb** 100%). The reaction mixture consists of diundecyl terephthaloyl-bis(4-oxybenzoate) (yield 11.2%) and a mixture of *trans*-isomers of diundecenyl terephthaloyl-bis(4-oxybenzoates) (**IV**) (overall yield 88.8%). According to NMR data the ratio of $(CH_2)_{(k+k')}$ groups in the mixture of esters **IV** is equal to 33.2:36.7:0.1 for $k,k' = 0, 1, 2$.

At the same time the control run of heating compound **IIb** in dichloromethane solution in the presence of Karsted catalyst did not cause any changes in the structure of the initial compound indicating that silyl ether **Ib** played the decisive role in the isomerization process of di(10-undecenyl)-terephthaloyl-bis(4-oxybenzoate) (**IIb**).

Employing in the reaction Wilkinson catalyst $[Rh(Ph_3P)_3Cl]$ instead of Karsted catalyst we also observed isomerization of the initial substrate (conversion of compound **IIb** 100%), but in this case compound **IIb** did not suffer the reduction. According to NMR data the ratio of $(CH_2)_k$ groups in the mixture of esters **IV** was equal to 36.5:38.4:25.1 for $k' = 0, 1, 2$. Therewith the liquid-crystalline properties of mixture **IV** were only slightly different from those of initial compound **IIb** (nonseparated mixture of esters **IV** exhibited a smectic *A* mesomorphism in the range 134–143°C].

The lack of hydrosilylation of unsaturated compounds **IIb** with 1-(1'-arylethoxy)-1,1,3,3-tetramethyldisiloxanes **Ia–Id** [varying of silyl ethers (X = H, F, Cl) does not affect the result] is surprizing, for quite a number of hydrosilylation examples of α-alkenes with siloxanes is known [14–17], and the isomerization and reduction of the substrate are secondary processes [14, 17, 18]. At the same time treating compound **IIb** with a 6-fold excess of,1,3,3-tetramethyldisiloxane in the presence of Karsted catalyst led to the formation of hydrosilylation product **V** in a quantitative yield. This compound exhibited the smectic *A* mesomorphism in the temperature range 130–143°C, virtually the same as compound **IIb**.

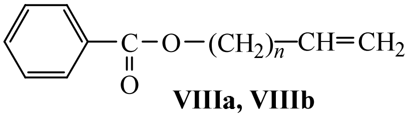
To check the validity of the signals assignment in the ^1H and ^{13}C NMR spectra of compounds **II** and **IV** we carried out their bromination into the corresponding tetrabromides **VI** and **VII**.

Compounds **VI** and **VII** proved to be relatively low-melting (mp 98 and 102–104°C respectively) and did not show any liquid-crystalline characteristics.

Thus the introduction of polar groups into the aliphatic part of the molecule results in the disappearance of its liquid-crystalline qualities, or it brings on the narrowing of the temperature range of the mesophase existence. This is caused by the changes in the anisotropic orientation-dependent interactions of dispersion character and distortions in the layer alignment of molecules which governs the appearance of the liquid-crystalline behavior in compounds of low molecular weight and in polymers [19].

The isomerization of a double bond is known to occur [20, 21] under the action of bases, acids, metal ions and complex ions containing Pd, Pt, Rh, or Ru. In the latter case at least two mechanisms can to operate. One of them requiring an external source of hydrogen is called a mechanism of metal hydride addition-elimination. The other known as a mechanism with a π-allyl complex formation does not require hydrogen introduction and involves a 1,3-shift of hydrogen. In our case no isomerization occurs in compound **IIb** on Karsted catalyst in the absence of silyl ether **I**, therefore the first mechanism seems more probable. To get more insight into the hydrosilylation with

1-(1'-arylethoxy)-1,1,3,3-tetramethyldisiloxanes **Ia–Id** we synthesized benzoic acid esters **VIIIa** and **VIIIb** making possible the analysis of reaction products not only by means of ^{1}H and ^{13}C NMR spectroscopy, but also by GLC.



$C_6H_5{-}C(=O){-}O{-}(CH_2)_n{-}CH{=}CH_2$

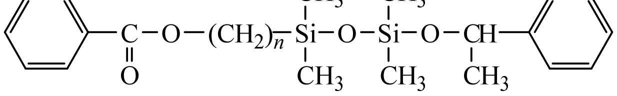
VIIIa, VIIIb

$n = 1$ (**a**), 9 (**b**).

For the comparative study of hydrosilylation we selected as catalysts platinum and rhodium complexes traditionally used in these reactions [16]. Therewith one of important factors at the choice of a homogeneous catalyst was its sufficient solubility in the reaction medium. Therefore we selected among the rhodium complexes Wilkinson catalyst and $[Rh(MeCOD)Cl]_2$ (MeCOD = 1-methylcycloocta-1,5-diene), and among the platinum coordination compounds, *cis*-$[Pt(Et_2SO)_2Cl_2]$ and $[Pt(MeCOD)Cl_2]$. The additional interest of $[Rh(MeCOD)Cl]_2$ and $[Pt(MeCOD)Cl_2]$ is due to the frequent application of cyclooctadiene as a labile ligand in the asymmetric catalysis [22]. The presence of a methyl at the double bond in MeCOD is known [23] to increase this ligand lability and favorably affects the catalytic activity of 1-methylcycloocta-1,5-diene complexes in the hydrosilylation reaction [24].

The reaction of allyl benzoate (**VIIa**) with 1-(1'-phenylethoxy)-1,1,3,3-tetramethyldisiloxane (**Ia**) (at molar ratio 1:1.2) in the presence of the mentioned catalysts permitted the isolation in a quantitative yield of the corresponding hydrosilylation product (**IXa**), 1-[3-(phenyloxycarbonyl)-propyl]-3-(1'-phenylethoxy)-1,1,3,3-tetramethyldisiloxane.

Unlike the reaction with allyl benzoate the hydrosilylation of 10-undecenyl benzoate (70°C, 24 h, conversion 100%) in the presence of Wilkinson catalyst led to the formation of compound **IXb** in only 32% yield, in the presence of $[Rh(MeCOD)Cl]_2$, in a 30% yield. Therewith the main reaction products are *trans*-undecenyl benzoates **X** where as in the case of the corresponding terephthaloyl-bis(4-oxybenzoates), *k* vary from 0 to 2. For in-stance, at the use of Wilkinson catalyst the ratio of $(CH_2)_k$ groups in esters **X** was 36.0:28.8:35.2 for $k = 0, 1, 2$.

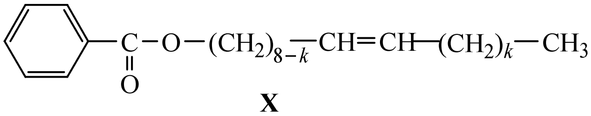


$C_6H_5{-}C(=O){-}O{-}(CH_2)_n{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}O{-}CH(CH_3){-}C_6H_5$

IXa, IXb

$n = 3$ (0), 11 (1).

The platinum complexes under these conditions give higher yields of hydrosilylation products: applying $[Pt(MeCOD)Cl_2]$ we obtained hydrosilylation product **IXb** in a 55% yield, and the overall yield of the ester mixture **X** was 45%. The best results were obtained with the complex *cis*-$[Pt(Et_2SO)_2Cl_2]$ that gave a 70% yield of compound **IXb** and only 30% of mixture **X**. Performing the reaction at room temperature (20°C, 48 h) considerably diminished the conversion of the initial substrates, and the side processes proceeded to a greater extent. In the presence of $[Rh(MeCOD)Cl]_2$ the conversion of the initial 10-undecenyl benzoate did not exceed 5%, and the reaction products were esters **X**. With *cis*-$[Pt(Et_2SO)_2Cl_2]$ the conversion of ester **VIIIb** attained 15%, and here the yield of hydrosilylation product **IXb** was 7%, and the overall yield of ester mixture **X** was 8%.



$C_6H_5{-}C(=O){-}O{-}(CH_2)_{8-k}{-}CH{=}CH{-}(CH_2)_k{-}CH_3$

X

$k = 0$–2.

The application of 1,1,3,3-tetramethyldisiloxane as a hydrosilylating agent in the presence of all mentioned catalysts permitted, in contrast to the reactions with silyl ethers **I**, the preparation (70°C, 24 h) in a quantitative yield of the corresponding hydrosilylation products of compounds **VIIIa** and **VIIIb**.

Thus the hydrosilylation with 1,1,3,3-tetramethyldisiloxane of the terminal double bond in benzoates occurs in keeping with the general rules of the α-alkenes hydrosilylation [15, 25, 26]. At the use of 1-(1'-arylethoxy)-1,1,3,3-tetramethyldisiloxanes in the presence of rhodium complexes the isomerization prevails, and in the presence of the coordination complexes of platinum(II) dominates the hydrosilylation, but the low selectivity prevents the application of the catalysts in question to the preparative hydrosilylation of benzoates.

The hydrosilylation of alkenes is often accompanied by isomerization, and it is often brought about by the rhodium compounds [27]. This process occupied an important place in the establishing of the hydrosilylation mechanism assumed by Chalk and Harrod [28]. To compare the isomerization processes in the α-alkenes and silyl ether **IIb** we investigated the behavior of 1-heptene (70°C, 24 h) in the presence of a rhodium and a platinum catalysts $[Rh(Ph_3P)_3Cl]$ and *cis*-$[Pt(Et_2SO)_2Cl_2]$. According to NMR spectroscopy, for the platinum catalyst the isomerization was below 1%, whereas at the use of Wilkinson catalyst it reached 81% [the ratio of 2-heptene (CH_3, 0.94 ppm):3-heptene (CH_3, 0.89 ppm) was 52.1:47.9]. The reaction of 1-heptene with 1-(1'-phenylethoxy)-1,1,3,3-tetramethyldisiloxane (**Ia**) (at molar ratio 1-heptene : **I a** = 1 : 1.2) under the same conditions resulted in the 100% conversion of the substrate; therewith the platinum catalyst gave rise to 17.3% of the isomerization products (2-heptene:3-heptene ≈1:1) and to 82.7% of the hydrosilylation product, 1-(1'-phenylethoxy)-3-heptyl-1,1,3,3-tetramethyldisiloxane. With the rhodium catalyst the isomerization products were obtained in a 71.4% yield (2-heptene:3-heptene 49.9:50.1), the hydrosilylation product in a 28.6% yield. Thus the pattern was reproduced of the reaction of silyl ethers **I** with the corresponding benzoate **VIIIb**. However by the hydrosilylation of 1-heptene with 1,1,3,3-tetpamethyldisiloxane in the presence of Wilkinson catalyst (70°C, 24 h) the target product was obtained in a 77% yield, and the overall yield of the mixture of isomeric *trans*-heptenes was 23%.

Therefore the hydrosilylation of terephthaloyl-bis(4-oxybenzoates) **IIb** proceeds analogously to this process with α-alkenes and various silanes, but reaction with **IIb** leads to the formation of larger amounts of the isomerization products.

The cause of this low reactivity of 1-(1'-arylethoxy)-1,1,3,3-tetramethyldisiloxanes **Ia–Id** in the hydrosilylation process and consequently the high probability of the isomerization in the α-olefin fragment of oxybenzoate **IIb** is due to the higher strength of the Si–H bond in the silyl ethers **Ia–Id** compared to that in the tetramethyldisiloxane. The quantum-chemical calculation (ab initio in the orbital basis STO-3G) for compounds **Ia–Id** and tetramethyldisiloxane shows a significant increase in the positive charge on the silicon atom of the Si–H bond at the introduction into the molecule of the tetramethyldisiloxane of arylethoxy groups (for instance, the charge in compound **Ia** is +0.990 against +0.622 in the tetramethyldisiloxane). This hampers the coordination of silyl ethers **Ia–Id** on the platinum atom. As a result the coordination of α-olefin prevails resulting in the isomerization with a shift of the double bond. At the same time due to the low activity of the internal double bonds with respect to the hydrosilylation [15, 16] the competing isomerization process occurs predominantly as the α-alkene is consumed.

EXPERIMENTAL

IR spectra were recorded on a spectrometer Bruker IFS-88 from films on a KBr lens (for liquids) or in KBr pellets (for powders). NMR spectra were registered using pulse sequence DEPT on spectrometers Bruker DPX-300 or Bruker AC-200 from solutions in $CDCl_3$ measuring chemical shifts from the solvent signals. The refraction indices were measured on a refractometer of Abbe type IFS-22, the specific rotation was determined using polarimeter Perkin Elmer 241A from solutions in chloroform. The phase transition temperatures were measured on a Boëtius heating block equipped with a polarizing microscope. The quantum-chemical calculations were performed *ab initio* using orbital basis STO-3G applying Hyper-Chem version 6.03 software.

Hydrosilylation and isomerization was carried out at 70°C in sealed ampules at concentration of complexes in the reaction mixture $(1–20) \times 10^{-4}$ mol $^{l-1}$.

We used in the experiments 1,1,3,3-tetramethyldi-siloxane (Fluka), dichloromethane (Merk), 1-heptene of the “chemically pure” grade, 1-(1'-arylethoxy)-1,1,3,3-tetramethyldisiloxanes **Ia–Id** were obtained as described in [8], terephthaloyl-bis(4-oxybenzoyl) chloride, as in [9], $[Rh(Ph_3P)_3Cl]$, $[Pt(MeCOD)Cl_2]$, and *cis*-$[Pt(Et_2SO)_2Cl_2]$ were prepared by standard procedures [29], and the complex $[Rh(MeCOD)Cl]_2$ was provided by the courtesy of V.M. Uvarov.

Diallyl terephthaloyl-bis(4-oxybenzoate) (IIa). A mixture of 1 g (2.25 mmol) of terephthaloyl-bis-4-oxybenzoyl chloride and 3 ml (44 mmol) of allyl alcohol in 5 ml of tetradecane was heated for 30 min at the bath temperature 150°C. Then the reaction mixture was poured into petroleum ether, the precipitate was filtered off and recrystallized from tetradecene. We obtained 1.05 g of compound **IIa**. Yield quantitative, mp 139°C. IR spectrum, cm^{-1}: 1020, 1090, 1120, 1165, 1215, 1280, 1310, 1415, 1468, 1505, 1605, 1720, 1730, 2850, 2920. ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.85 d (4H, *J* 4.9), 5.28, 5.34, 5.38, 5.47 (4H, CH_2=), 5.94–6.15 m (2H, CH=), 7.34 d ($4H_{arom}$, *J* 8.54), 8.18 d ($4H_{arom}$, *J* 8.54), 8.35 s ($4H_{arom}$). Found, %: C 68.72; H 4.42. $C_{28}H_{22}O_8$. Calculated, %: C 69.13; H 4.56.

Di(10-undecenyl) terephthaloyl-bis(4-oxybenzoate) (IIb) was prepared similarly in a quantitative yield, mp 134°C. IR spectrum, cm^{-1}: 1020, 1075, 1085,1120, 1160, 1215, 1285, 1310, 1410, 1465, 1505, 1605, 1710, 1730, 2850, 2920, 2950. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.31 (shoulder 1.38) br.s (24H), 1.71–1.82 m (4H), 1.99–2.09 m (4H), 4.34 t (4H, *J* 7.5), 4.91–5.03 m (4H, CH_2=), 5.71–5.91 m (2H,CH=), 7.34 d ($4H_{arom}$, *J* 8.54), 8.16 d ($4H_{arom}$, *J* 8.54), 8.35 s ($4H_{arom}$). ^{13}C, δ, ppm: 25.89 ($C^{\gamma}H_2$), 28.59 ($C^{\delta}H_2$), 28.79 ($C^{\theta}H_2$), 28.97 ($C^{\varepsilon}H_2$), 29.12

$(C^{\eta}H_2)$, 29.27 $(C^{\zeta}H_2)$, 29.33 $(C^{\beta}H_2)$, 33.66 $(C^{\iota}H_2)$, 65.22 $(OC^{\alpha}H_2)$, 114.0 $(CH_2{=})$, 121.45 (C^{m}), 128.40 (C^{i}), 130.28 (C^{o}), 131.14 (C^{o}), 133.57 (C^{i}), 139.06 (CH=), 154.06 (C^{p}), 163.56 (CO, terephthaloyl), 165.67 (CO, benzoyl). Found, %: C 74.72; H 7.54. $C_{44}H_{54}O_8$. Calculated, %: C 74.34; H 7.66.

(+)-Di[4-(3-{1-[1-(*p*-methoxyphenyl)ethoxy]-1,1,3,3-tetramethyldisiloxanyl}propyl] (oxybenzoato)terephtalate (III). A mixture of 160 mg (0.3 mmol) of ester **IIa,** 400 mg (0.8 mmol) of compound **Ib**, and a solution of Karsted catalyst in CH_2Cl_2 (C_{cat} 1.5 × 10^{-3} mol l^{-1} in the reaction mixture) was heated in a sealed ampule at 70 °C for 21 h. Then the reaction mixture was filtered through a thin layer of silica gel on a glass frit, the silica gel was washed with a small volume of CH_2Cl_2, and the combined filtrate was poured into petroleum ether. The separated precipitate was filtered off, dried, and reprecipitated from a mixture CH_2Cl_2–petroleum ether. Yield 280 mg (90%), mp 185 °C, $[\alpha]_D^{20}$ +27.0° (*C* 0.2, $CHCl_3$). IR spectrum, cm^{-1}: 703, 805, 960, 1020, 1060, 1103, 1275, 1410, 1450, 1600, 1715, 1730, 2850, 2950, 3025, 3060. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.08, 0.12, 0.13 (24H, Si–CH_3), 0.50–0.57 m (4H, Si–CH_2),1.74–1.88 m (4H, CH_2), 3.79 s (6H, OCH_3), 4.31 t (4H, CH_2O, *J* 6.9), 6.86 d (4H_{arom}, *J* 8.54), 7.34 d (4H_{arom}, *J* 8.54), 7.38 d (4H_{arom}, *J* 8.54), 8.16 d (4H_{arom}, *J* 8.54), 8.35 s (4H_{arom}).

A mixture of **diundecenyl terephthaloyl-bis(4-oxybenzoates) (IV)** was prepared in a similar way. Yield 95%, mp 134 °C. IR spectrum, cm^{-1}: 1020, 1075, 1085, 1120, 1160, 1215, 1285, 1310, 1410, 1465, 1505, 1605, 1710, 1730, 2850, 2920, 2950. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.30–1.45 m (24H), 1.60–1.67 m (2H), 1.75–1.84 m (4H), 1.96–2.08 m (6H), 4.34 t (4H, *J* 7.5), 5.35–5.50 m (4H, CH=), 7.34 d (4H, H_{arom}, *J* 8.54), 8.16 d (4H, *J* 8.54), 8.35 s (4H); *k* 0, 0.98 t (CH_3); *k* 1, 0.91 t (CH_3); *k* 2, 0.90 t (CH_3). ^{13}C NMR spectrum, δ, ppm: 65.19 $(OC^{\alpha}H_2)$, 121.45 (C^{m}), 128.40 (C^{i}), 130.28 (C^{o}), 131.14 (C^{o}), 133.57 (C^{i}), 154.06 (C^{p}), 163.56 (CO, terephthaloyl), 165.67 (CO, benzoyl); *k* 0, 17.77 (CH_3), 28.8–29.4 $(C^{\beta-\eta}H_2)$, 34.54 $(C^{\theta}H_2)$, 124.45 $(=CHCH_3)$, 131.44 (=CH); *k* 1, 13.86 (CH_3), 129.08 (=CH), 131.85 $[=CHCH_2CH_3]$; *k* 2, 13.96 (CH_3), 32.36 $(\underline{C}H_2CH_3)$, 32.43 $(=CH\underline{C}H_2)$, 129.66 (=CH), 133.64 $[=CH(CH_2)_2CH_3]$.

Di{4-[11-(1,1,3,3-tetramethyldisiloxanyl)-undecyl]} (oxybenzoato) terephtalate (V). A mixture of 210 mg (0.3 mmol) of ester **IIb**, 0.4 ml (2.4 mmol) of 1,1,3,3-tetramethyldisiloxane, and a solution of Karsted catalyst in CH_2Cl_2 (C_{cat} 1.42×10^{-3} mol l^{-1} in the reaction mixture) was heated in a sealed ampule at 70°C for 21 h. Then the reaction mixture was filtered through a thin layer of silica gel on a glass frit, the silica gel was washed with a small volume of CH_2Cl_2, and the combined filtrate was poured into petroleum ether. The separated precipitate was filtered off, dried, and reprecipitated from a mixture CH_2Cl_2–petroleum ether. Yield 260 mg (90%), mp 130°C. IR spectrum, cm^{-1}: 703, 805, 960, 1020, 1060, 1103, 1275, 1410, 1450, 1600, 1715, 1730, 2850, 2950, 3025, 3060. ^1H, δ, ppm (*J*, Hz): 0.08, 0.12, 0.13 (24H, Si–CH_3), 0.50–0.57 m (4H, Si–CH_2), 1.33 br.s (24H), 1.63 br.s (4H), 1.79–1.84 m (4H), 4.31 t (4H, *J* 6.9), 7.34 d (4H_{arom}, *J* 8.54), 8.16 d (4H_{arom}, *J* 8.54), 8.35 s (4H_{arom}). Found, %: C 64.32; H 6.83; Si 11.32. $C_{52}H_{68}O_{10}Si_4$. Calculated, %: C 64.69; H 7.10; Si 11.64.

Di(10,11-dibromoundecyl) terephthaloyl-bis(4-oxybenzoate) (VI). In 3 ml of chloroform was dissolved 0.5 g (0.75 mmol) of ester **IIb**, and 1 ml of bromine was added. After 30 min the product was poured into methanol, the precipitate was filtered off and once more reprecipitated from chloroform into methanol. Yield 0.6 g, quantitative, mp 98 °C. IR spectrum, cm^{-1}: 715, 880, 1020, 1072, 1095, 1112, 1162, 1275, 1310, 1455, 1465, 1502, 1605, 1720, 1730, 2850, 2920. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.33 br.s (24H), 1.63 br.s (4H), 1.79–1.84 m (4H), 3.62 t (*J* 9.77, *trans*), 3.82, 3.87 d.d (4H, *cis*, CH_2Br, *J* 9.77, 4.26), 4.10–4.20 m (2H, CHBr), 4.34 t (4H, *J* 7.5), 7.34 d (4H_{arom}, *J* 8.54), 8.16 d (4H_{arom}, *J* 8.54), 8.35 s (4H_{arom}). Found, %: C 60.72; H 6.53; Br 18.20. $C_{44}H_{54}O_8Br_2$. Calculated, %: C 60.69; H 6.25; Br 18.35.

A mixture of **di(dibromoundecyl) terephthaloyl-bis-(4-oxybenzoates) (VII)** was likewise obtained, mp 102–104 °C. IR spectrum, cm^{-1}: 715, 880, 1020, 1072, 1095, 1112, 1162, 1275, 1310, 1455, 1465, 1502, 1605, 1720, 1730, 2850, 2920. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.95 (6H), 1.33 br.s (24H), 1.63 br.s (4H), 1.79–1.84 m (4H), 4.10–4.20 m (4H, CHBr), 4.34 t (4H, *J* 7.5), 7.34 d (4H_{arom}, *J* 8.54), 8.16 d (4H_{arom}, *J* 8.54), 8.35 s (4H_{arom}).

Allyl and 10-undecenyl benzoates VIII were synthesized by a high-temperature acceptor-free condensation of the corresponding alcohol and benzoyl chloride. **Compound VIIIa,** bp 96 °C (5 mm Hg), n_D^{20} 1.5180 {publ.: bp 106 °C (12 mm Hg), n_D^{20} 1.5180 [30]}. **Compound VIIIb,** bp 162 °C (2 mm Hg), n_D^{20} 1.4967. IR spectrum, cm^{-1}: 1020, 1075, 1085, 1120, 1160, 1215, 1285, 1310, 1410, 1465, 1505, 1605, 1730, 2850, 2920, 2950. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.31 br.s (12H), 1.78 m (2H), 2.06 q (2H, *J* 6.75), 4.34 t (2H, *J* 6.75), 4.93–5.04 m (2H, $CH_2{=}$), 5.76–5.90 m (1H, CH=), 7.44 t

(2H, H^m, J 6.75), 7.56 t (1H, H^p, J 7.5), 8.07 d (1H, H^o, J 6.75). ^{13}C NMR spectrum, δ, ppm: 25.85 ($\mathrm{C^{\gamma}H_2}$), 28.54 ($\mathrm{C^{\theta}H_2}$), 28.72 ($\mathrm{C^{\delta}H_2}$), 28.91 ($\mathrm{C^{\varepsilon}H_2}$), 29.07 ($\mathrm{C^{\eta}H_2}$), 29.21 ($\mathrm{C^{\zeta}H_2}$), 29.27 ($\mathrm{C^{\beta}H_2}$), 33.61 ($\mathrm{C^{\iota}H_2}$), 64.88 ($\mathrm{OC^{\alpha}H_2}$), 113.94 ($\mathrm{CH_2}$=), 128.09 (C^m), 129.32 (C^o), 130.36 (C^i), 132.54 (C^p), 138.91 (CH=), 166.41 (CO).

1-[3-(Phenyloxycarbonyl)propyl]-3-(1'-phenylethoxy)-1,1,3,3-tetramethyldisiloxane (IXa). A mixture of 375 mg (2.3 mmol) of allyl benzoate, 540 mg (2.7 mmol) of 1-(1'-phenylethoxy)-1,1,3,3-tetra-methyldisiloxane (molar ratio 1:1.2), and a solution of Karsted catalyst in $\mathrm{CH_2Cl_2}$ (C_{cat} 1.42×10^{-3} mol l^{-1} in the reaction mixture) was heated in a sealed ampule at 70°C for 20 h. Then the reaction mixture was distilled in a vacuum. Yield 560 mg (85%), clear colorless liquid, bp 134°C (2 mm Hg), n_D^{20} 1.4790. IR spectrum, cm^{-1}: 703, 805, 960, 1020, 1060, 1103, 1275, 1410, 1450, 1600, 1730, 2850, 2950, 3025, 3060. ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.03, 0.12, 0.13 (12H, Si–$\mathrm{CH_3}$), 0.4 s (2H, Si–$\mathrm{CH_2}$), 1.56 d (3H, $\mathrm{CH_3}$, J 6.9), 1.78–1.86 m (2H), 4.28 t (2H, J 6.9), 5.09 q (1H, CH, J 6.9), 7.25–7.31 m (1H, H^p), 7.33–7.46 m (4H, H^o, H^p), 7.44 t (2H, J 6.75), 7.55 t (1H, J 6.75), 8.07 d (2H, J 6.75). Found, %: C 63.72; H 7.89; Si 13.68. $\mathrm{C_{22}H_{32}O_4Si_2}$. Calculated, %: C 63.42; H 7.74; Si 13.48.

1-[11-(Phenyloxycarbonyl)undecyl]-3-(1'-phenylethoxy)-1,1,3,3-tetramethyldisiloxane (IXb) was prepared in the same way. Yield 15%, clear colorless liquid, bp 164 °C (2 mm Hg), n_D^{20} 1.4771. IR spectrum, cm^{-1}: 703, 805, 960, 1020, 1060, 1103, 1275, 1410, 1450, 1600, 1730, 2850, 2950, 3025, 3060. ^{1}H NMR spectrum, δ, ppm (J, Hz): 0.03, 0.12, 0.13 (12H, Si–$\mathrm{CH_3}$), 0.57 s (2H, Si–$\mathrm{CH_2}$), 1.34 C (16H), 1.49 d (3H, $\mathrm{CH_3}$, J 6.9), 1.79–1.86 m (2H), 4.34 t (2H, J 6.9), 5.08 q (CH, 1H, J 6.9), 7.22–7.31 m (1H, H^p), 7.30–7.36 m (4H, H^o, H^p), 7.46 t (2H, J 6.75), 7.57 t (1H, J 6.75), 8.08 d (2H, J 7.5). ^{13}C NMR spectrum, δ, ppm: 0.02, 0.88, 0.99 ($\mathrm{SiCH_3}$), 18.08 ($\mathrm{C^{\lambda}H_2}$), 23.06 ($\mathrm{C^{\kappa}H_2}$), 25.86 ($\mathrm{C^{\gamma}H_2}$), 26.58 ($\mathrm{CH_3}$), 28.56 ($\mathrm{C^{\delta}H_2}$), 29.12 ($\mathrm{C^{\eta}H_2}$), 29.27 ($\mathrm{C^{\zeta}H_2}$), 29.36 ($\mathrm{C^{\varepsilon}H_2}$), 29.44 ($\mathrm{C^{\beta}H_2}$), 29.51 ($\mathrm{C^{\theta}H_2}$), 33.28 ($\mathrm{C^{\iota}H_2}$), 64.87 ($\mathrm{OC^{\alpha}H_2}$), 69.91 (CH), 125.12 (C^o, benzyl), 126.57 (C^p, benzyl), 127.89 (C^m, benzyl), 128.08 (C^m), 129.32 (C^o), 130.38 (C^i), 132.52 (C^p), 146.08 (C^i, benzyl), 166.35 (CO). Found, %: C 69.32; H 8.80; Si 10.54. $\mathrm{C_{32}H_{48}O_4Si_2}$. Calculated, %: C 69.51; H 8.75; Si 10.16.

A mixture of **undecenyl benzoates X,** bp 148–154°C (2 mm Hg). IR spectrum, cm^{-1}: 1020, 1075, 1085, 1120, 1160, 1215, 1285, 1310, 1410, 1465, 1505, 1605, 1730, 2850, 2920, 2950. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.30–1.45 m (24H), 1.60–1.67 m (2H), 1.75–1.84 m (4H), 1.96–2.08 m (6H), 4.34 t (4H, J 7.5), 5.35–5.50 m (4H, CH=), 7.34 d (4H$_{\mathrm{arom}}$, J 8.54), 8.16 d (4H$_{\mathrm{arom}}$, J 8.54), 8.35 s (4H$_{\mathrm{arom}}$); k 0, 0.98 t ($\mathrm{CH_3}$); k 1, 0.91 t ($\mathrm{CH_3}$); k 2, 0.90 t ($\mathrm{CH_3}$). ^{13}C NMR spectrum, δ, ppm: 64.87 ($\mathrm{OC^{\alpha}H_2}$), 128.08 (C^m), 129.32 (C^o), 130.38 (C^i), 132.52 (C^p), 166.35 (CO); k 0, 17.77 ($\mathrm{CH_3}$), 28.8–29.4 ($\mathrm{C^{\beta-\eta}H_2}$), 34.54 ($\mathrm{C^{\theta}H_2}$), 124.45 (=$\mathrm{CHCH_3}$), 131.44 (=CH); k 1, 13.86 ($\mathrm{CH_3}$), 129.08 (=CH), 131.85 (=$\mathrm{CHCH_2CH_3}$); k 2, 13.96 ($\mathrm{CH_3}$), 32.43 (=$\mathrm{CH\underline{C}H_2}$), 32.36 ($\mathrm{\underline{C}H_2CH_3}$), 129.66 (=CH), 133.64 [=$\mathrm{CH(CH_2)_2CH_3}$].

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REFERENCES

1. *Handbook of Liquid Crystals*, Demus, D., Goodby, J., Gray, G.W., Spiess, H.W., and Vill, V., Eds, Weinheim: Wiley-VCH, 1998, p. 1.
2. Wang, X.-J. and Zhou, Q.-F., *Liquid Crystalline Polymers*, Imperial College Press, 2004, 388 p.
3. Pukhnarevich, V.B., Lukevits, E., Kopylov, L.I., and Voronkov, M.G., *Perspektivy gidrosililirovaniya* (Prospects of Hydrosilylation). Riga: Izd. Inst. Org. Sinteza, Latv. Akad. Nauk, 1992, 383 p.
4. Korshak, V.V., *Raznozvennost'polimerov* (Variation in Units Naber in Polymers), Moscow: Nauka, 1977, 301 p.
5. Naciri, J., Ruth, J., Crawford, G., Shashidhar, R., and Ratna, B.R., *Chem. Mater.*, 1995, vol. 7, p. 1397.
6. Naciri, J., Shenoy, D.K., Keller, P., Gray, S., Crandall, K., and Shashidhar, R., *Chem. Mater.*, 2002, vol. 14, p. 5134.
7. Keith, C., Reddy, R.A., Baumeister, U., and Tschirske, C., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 312.
8. Zuev, V.V., de Vekki, D.A., Kuchaev, A.V., Vorob'ev, M.V., and Skvortsov, N.K., *Zh. Obshch. Khim.*, 2004, vol. 74, p. 1804.
9. Zuev, V.V. and Skorokhodov, S.S., *Vysokomol. Soedin. B,* 1987, vol. 29, p. 440.
10. Bilibin, A.Yu., Piraner, O.N., and Skorokhodov, S.S., *Khimiya i fizika vysokomolekulyarnykh soedinenii* (Chemistry and Physics of Macromolecule Compounds), Leningrad: IVS Russian Akad. Nauk, 1983, p. 39.
11. Elser, W. and Ennulat, R.D., *Adv. Liq. Cryst.*, 1976, vol. 2, p. 76.
12. Grosberg, A.Yu., *Vysokomol. Soedin. A,* 1980, vol. 22, p. 90.
13. Zuev, V.V., Denisov, I.G., and Skorokhodov, S.S., *Vysokomol. Soedin. A,* 1989, vol. 31, p. 1056.
14. Lukevits, E.Ya., *Usp. Khim.,* 1977, vol. 46, p. 507.
15. Andrianov, K.A., Souchek, I., and Khananashvili, L.M., *Usp. Khim.,* 1979, vol. 48, p. 1233.

16. *Comprehensive Handbook on Hydrosilylation*, Marcinec, B., Ed., Oxford: Pergamon Press, 1992, 776 p.
17. Marciniec, B., *Appl. Organometal. Chem.,* 2000, vol. 14, p. 527.
18. Marciniec, B. and Gulinski, J., *J. Organometal. Chem.,* 1993, vol. 446, p. 15.
19. Flory, P.J., in *Recent Advances in Liquid Crystalline Polymers*, Chapoy, L.L., Ed., Elsevier Appl. Sci. Publ, 1985, p. 99.
20. Hubert, A.J. and Reimlinger, H., *Synthesis*, 1969, p. 97.
21. March, J., *Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*, New York: Wiley-Interscience, 1985.
22. Brunner, H., *J. Organometal. Chem*., 1986, p. 39.
23. De Vekki, D.A., Uvarov, V.M., and Skvortsov, N.K., *Zh. Obshch. Khim.,* 2005, vol. 75, p. 353.
24. De Vekki, D.A., Ol'sheev, V.A., Spevak, V.N., and Skvortsov, N.K., *Zh. Obshch. Khim.,* 2001, vol. 71, p. 2017.
25. Wu, X., Malpert, J.H., Zang, H., Neckers, D.C., *Tetrahedron, Lett.,* 1999, vol. 40, p. 8309.
26. Skvortsov, N.K., *Zh. Obshch. Khim.,* 1993, vol. 63, p. 961.
27. Hegedus, L.S., *Comprehensive Organometallic Chemistry,* Wilkinson, G., Stone, G.A., and Abel, E.W., Eds., Oxford: Pergamon Press, 1995, vol. 12, p. 515.
28. Chalk, A.J. and Harrod, J.F., *J. Am. Chem. Soc.,* 1965, vol. 87, p. 16.
29. *Handsbuch der Praparativen Anorganischen Chemie*, Brauer, G., Ed., Stuttgart: Ferdinand Enke Verlag, 1978.
30. *Beilsteins Handbuch der organischen Chemie*, vol. 9, p. 402.