Synthesis and thermal and rheological properties of carboxyl-containing polydimethylsiloxanes

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A number of polydimethylsiloxanes modified with fragments of undecenoic acid and its esters were synthesized. The structures of polymers were confirmed by ^{1}H and ^{29}Si NMR spectroscopy. The rheological properties of obtained polymers were studied, as well as their thermal properties were studied by DSC.

Key words: carboxyl-containing polymers, polydimethylsiloxanes, undecenoic acid, *tert*-butyl undecenoate, hydrosilylation.

Introduction of functional groups into the polymer structure, which provide additional intermolecular interactions of polymer chains both between each other and with other moieties of a system due to hydrogen bonding and formation of donor-acceptor complexes or ion pairs, allows one to obtain thermoplastic elastomers and materials with improved adhesive properties.[1,2]

Modification of polydimethylsiloxanes (PDMSs) by introduction of substituents other than methyl groups into the macromolecule allows one to control their properties in a tailor-made fashion in a wide range, as well as to expand the field of their practical applications. The introduction of carboxyl groups into the structure of PDMSs is used to obtain heat stabilizers of siloxane liquids[3] and siloxane ionomers.[2] In contrast to covalently bound materials, these materials containing labile ionic "cross-links" can be processed easily into goods.

It has been noted earlier[4—8] that polydimethylsiloxanes containing from 1% to 5% of carboxyl groups in the substituent at the silicon atom can undergo reversible transition from the liquid to elastomeric state on heating above 70 °C. In these polymers, the formation of reversible physical networks is provided by the interaction of carboxyl groups not only between each other, but also with the oxygen atoms of the carbosiloxane backbone.

A similar effect, gel formation at higher temperatures, was observed also in polydimethylsiloxanes containing 3-carboxypropyl,[9] 2-carboxyethyl,[10—12] and 10-carboxydecyl[2] substituents regularly arranged over the polymer backbone. It was found during the rheological studies of these polymers that, on heating to 70 °C, their viscosity decreases as for typical unmodified polydimethylsiloxanes; however, with further increase in the temperature the viscosity increases.

It was noted that the emergence of hydrogen bonds in mixtures of carboxyl-containing and unmodified PDMSs also results in the formation of rubber-like materials.[13,14]

The aim of the present work was to study the effect of carboxyl-containing substituents (taking into account their content in the polymer and position in the siloxane chain) on the thermal behavior and rheological properties of modified PDMSs.

Experimental

The reagents and auxiliary materials used in the work were as follows: octamethylcyclotetrasiloxane (D_4) (ABCR), 1,1,3,3-tetramethyldisiloxane (Sigma-Aldrich), CT-175 sulfonic acid resin (Purolite), undecenoic acid (97%, Sigma-Aldrich), hexamethyldisilazane (Ekos-1), thionyl chloride (Chimmed), potassium *tert*-butoxide (Sigma-Aldrich), a 2% solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (Karstedt catalyst) (ABCR), chlorodimethylsilane (ABCR), and BS-94 polymethylhydrosiloxane (Wacker Chemie AG). The above-listed substances were used as received.

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The molecular-weight characteristics of polymers were determined by GPC relative to polystyrene standards using a chromatographic system including the following components: a STAYER s.2 high-pressure pump (Akvilon, Russia), a Smartline RI 2300 refractometer (KNAUER, Germany), and JETSTREAM 2 PLUS thermostat (KNAUER, Germany). The studies were performed on Phenogel columns (5 μm, 300×7.8 mm, pore size from 10^3 to 10^5 Å) (Phenomenex, United States) at 40±0.1 °C using toluene—THF (2%) as the eluent, the flow rate was 1.0 mL $\min^{-1}$.

^{1}H NMR spectra were recorded on a BrukerWP-250 SY spectrometer in $CDCl_3$ and processed using the ACD LABS software.

DSC studies were performed on a DSC-822e differential scanning calorimeter (Mettler-Toledo, Switzerland) at a heating rate of 10 deg $\min^{-1}$.

GLC analysis was performed on a Chromatec Analytic 5000 chromatograph (Russia) equipped with a thermal conductivity detector, the carrier gas was helium, 2 m×3 mm columns packed with a Chromaton-H-AW-supported SE-30 (5%); the chromatographic data were processed using the Chromatec Analytic software (Russia).

The rheological properties of modified PDMSs were studied on a MCR 302 rotary rheometer (Anton Paar, Austria) in a plane—plane measuring cell. In the mode of steady shear strain, the measurements were performed at constant shear rate in a range of 0.1—100 s^{-1}. Dynamic mechanical tests were performed in the region of linear viscoelastic behavior (the strain amplitude was 1%) in a frequency range from 0.1 to 100 Hz.

Synthesis of α,ω-dihydrooligodimethylsiloxanes (hydride telechelics). Octamethylcyclotetrasiloxane (100 g, 0.3371 mol), 1,1,3,3-tetramethyldisiloxane (10.14 g, 0.0674 mol), and a Purolite CT-175 sulfonic acid resin (3.30 g) were loaded in a 250-mL one-necked flask equipped with a reflux condenser. The reaction mixture was stirred for 8—10 h at 70 °C, dissolved in hexane, and filtered to remove the sulfonic acid resin. The solution was evaporated on a rotary evaporator and cyclic products were distilled off *in vacuo* for 8 h at 120 °C (1 Torr) to yield 93.95 g (84%) of α,ω-dihydrooligodimethylsiloxane with $M_n = 2500$, $M_w/M_n = 1.6$. ^{1}H NMR ($CDCl_3$), δ: 0.08 (s, 3 H, Me (PMDS)); 4.71 (m, 1 H, H—Si).

Synthesis of PDMS samples containing statistically chain distributed methylhydrosiloxane units. A 250-mL one-necked flask equipped with a reflux condenser was charged with octamethylcyclotetrasiloxane (100 g, 0.3371 mol), BS-94 polymethylhydrosiloxane (9.4144 g, 0.0025 mol), 1,1,1,3,3,3-hexamethyldisiloxane (4.46 g, 0.02752 mol), and a Purolite CT-175 sulfonic acid resin (3.42 g). The reaction mixture was stirred for 8—10 h at 70 °C, dissolved in hexane, and filtered to remove the sulfonic acid resin. The solution was evaporated on a rotary evaporator and cyclic products were distilled off for 20 h at 120 °C (1 Torr) to yield 82.52 g (75%) of the product with $M_n = 4300$, $M_w/M_n = 2$. ^{1}H NMR ($CDCl_3$), δ: 0.08 (s, 3 H, Me (PMDS)); 4.71 (m, 1 H, H—Si).

Trimethylsilyl undecenoate was synthesized according to the earlier described procedure.**[15]**

Synthesis of *tert*-butyl undecenoate. A 100-mL three-necked flask equipped with a thermometer, a reflux condenser, a dropping funnel, and a magnetic stirring bar was charged with thionyl chloride (21.3 g, 0.18 mol). Undecenoic acid (30 g, 0.163 mol) was added dropwise with stirring and the reaction mixture was stirred for additional ~2 h until gas evolution was terminated. The excess of thionyl chloride was distilled off and undecenoic acid chloride was isolated by vacuum distillation at T_b = 75 °C (1 Torr). The yield was 95%. A 500-mL three-necked round-bottom flask equipped with a reflux condenser, a dropping funnel, and a thermometer was charged with a 10% solution of potassium *tert*-butoxide in dry THF (170 g, 0.15 mol of $KOCMe_3$) and undecenoic acid chloride (30 g, 0.137 mol) was added dropwise with stirring at ~0 °C. The reaction mixture was stirred for additional 2 h. The mixture was evaporated on a rotary evaporator. The resulting mass was dissolved in toluene and washed with water three times to remove potassium chloride. The organic layer was kept for 12 h over sodium sulfate, concentrated on a rotary evaporator, and distilled *in vacuo* at T_b = 80 °C (1 Torr). The yield was 70%. ^{1}H NMR ($CDCl_3$), δ: 5.80 (m, 1 H, $CH_2{=}C\underline{H}{-}CH_2{-}$); 4.95 (t, 2 H, $C\underline{H}_2{=}CH{-}CH_2{-}$); 2.20 (t, 2 H, $-CH_2{-}C\underline{H}_2{-}COOCMe_3$); 2.02 (q, 2 H, $CH_2{=}CH{-}C\underline{H}_2{-}$); 1.57 (t, 2 H, $-C\underline{H}_2{-}CH_2{-}COOCMe_3$); 1.44 (s, 9 H, $-CH_2{-}COOCMe_3$); 1.29 (m, 10 H, $CH_2{=}CH{-}CH_2{-}(C\underline{H}_2)_5{-}CH_2{-}CH_2{-}COOCMe_3$).

Hydrosilylation. A two-necked flask, which was preannealed and cooled in the argon stream, equipped with a reflux condenser was charged with a 10% solution of PMDS with hydrosiloxane groups in dry toluene (0.00594 mol of PDMS) and undecenoic ester in an amount providing the equimolar ratio between the hydrosiloxane and vinyl groups. The Karstedt catalyst was added and the reaction mixture was stirred for 8—15 h in the argon stream at 100 °C. The process was controlled by the disappearance of the signals for the vinyl and hydrosiloxane groups in the ^{1}H NMR spectrum. On completion of the reaction, the mixture was evaporated on a rotary evaporator and treated under vacuum (1 Torr).

Removal of the trimethylsilyl protection group. The sample of PDMS containing the trimethylsilyl undecenoate fragment was dissolved in toluene—methanol mixture (60 : 40) and refluxed for 5 h, the mixture was evaporated on a rotary evaporator, and low-molecular-weight products were distilled off at 1 Torr. The correspondence of resulting modified polyorganosiloxanes to the specified composition was confirmed by ^{1}H NMR spectroscopy (in $CDCl_3$). The NMR spectra of 10-carboxydecyl telechelic polydimethylsiloxanes displayed five main signals. ^{1}H NMR, δ: 2.35 (t, 2 H, $-CH_2{-}C\underline{H}_2{-}COOH$); 1.64 (t, 2 H, $-C\underline{H}_2{-}CH_2{-}COOH$); 1.28 (m, 14 H, $-Si{-}CH_2{-}(C\underline{H}_2)_7{-}CH_2{-}CH_2{-}COOH$); 0.53 (t, 2 H, $-Si{-}C\underline{H}_2{-}(CH_2)_7{-}CH_2{-}CH_2{-}COOH$); 0.08 (s, $-[Si(C\underline{H}_3)_2{-}O]_n{-}$).

The spectra for the samples of PDMS with statistically distributed modifying units displayed five main signals. ^{1}H NMR, δ: 2.35 (t, 2 H, $-CH_2{-}C\underline{H}_2{-}COOH$); 1.64 (t, 2 H, $-C\underline{H}_2{-}CH_2{-}COOH$); 1.27 (m, 14 H, $-Si{-}CH_2{-}(C\underline{H}_2)_7{-}CH_2{-}CH_2{-}COOH$); 0.51 (t, 2 H, $-Si{-}C\underline{H}_2{-}(C\underline{H}_2)_7{-}CH_2{-}CH_2{-}COOH$); 0.08 (s, $-[Si(C\underline{H}_3)_2{-}O]_n{-}$).

Results and Discussion

Synthesis of modified PDMSs

Polydimethylsiloxanes containing the fragments of undecenoic acid and its esters were synthesized in three steps. PDMS with hydrosiloxane units and undeceoic acid esters were prepared first, the hydrosilylation of PDMS with trimethylsilyl or *tert*-butyl undecenoate was performed second, and, at the final step, the protective groups were removed.

1. Preparation of polydimethylsiloxanes with hydrosiloxane groups. At the first step, a series of copolymers containing the SiH groups at the chain ends (see Scheme 1, Eq. 1) or in the polysiloxane backbone (Eq. 2) were synthesized by the cationic polymerization of octamethylcyclotetrasiloxane with 1,1,3,3-tetramethyldisiloxane or polymethylhydrosiloxane and hexamethyldisiloxane. The process was performed at different reagent ratios in the presence of the sulfonic acid resin for 8—10 h at 70 °C.

Scheme 1

$$[Me_2SiO]_4 + HMe_2Si—O—Me_2SiH \xrightarrow{i} \qquad (1)$$

$$\longrightarrow H—[Me_2SiO]_n—SiMe_2H$$

$$[Me_2SiO]_4 + Me_3SiO[MeSi(H)O]_{60}SiMe_3 + \qquad (2)$$

$$+ Me_3SiOSiMe_3 \xrightarrow{i} Me_3SiO[MeSi(H)O]_m[Me_2SiO]_kSiMe_3$$

Reagents and conditions: *i*. sulfonic acid resin.

Low-molecular-weight reaction products were removed by vacuum distillation. The yield of linear products was from 75 to 88%. The composition and molecular-weight characteristics of the synthesized copolymers are given in Tables 1 and 2.

It is seen from the data obtained that the composition of the synthesized products is close to that specified by the starting reagent ratio. A slight decrease in the number of hydride groups in the reaction product relative to the calculated one is likely due to side dehydrocondensation and disproportionation of silicon hydride groups to form higher-molecular-weight compounds.

The distribution of miscellaneous siloxane units in polydimethylmethylhydrosiloxanes was evaluated by ^{29}Si NMR spectroscopy (Fig. 1). The ^{29}Si NMR spectra of the resulting polymers were found to contain no signals at δ_{Si} −(35.0—35.5) corresponding to the triads of $D^H\underline{D}^HD^H$ (where D is the dimethylsiloxane unit and D^H is the methylhydrosiloxane unit) and $D\underline{D}^HD^H$ units (δ_{Si} −(36.0—36.7)). The spectrum contains only signals corresponding to the triads $D\underline{D}^HD$ (δ_{Si} −(37.0—37.7)), DDD (δ_{Si} −(21.0—22.3)) and $D^H\underline{D}D$ (δ_{Si} −(20.0—20.7)). Thus, one can conclude that there are no block sequences $D^HD^HD^H$ in the copolymer.

Table 1. Properties of the synthesized α,ω-dihydrooligodimethylsiloxanes

Sample	[H(Me)$_2$Si] (mol.%)		M$_n$**	M$_w$/M$_n$**	Yield (%)
	Theory	Experiment*			
1	10	5.5	2500	1.6	84
2	5	3.5	4200	1.9	87
3	1.7	1.1	8300	1.7	85
4	0.8	0.6	9300	2.1	79

* Determined by ^{1}H NMR.

** Determined by GPC.

Table 2. Properties of the synthesized α,ω-bis(trimethylsiloxy)-polydimethylmethylhydrosiloxanes

Sample	[Me(H)SiO] (mol.%)		M$_n$**	M$_w$/M$_n$**	Yield (%)
	Theory	Experiment*			
5	50	46.2	3200	2.6	83
6	20	20.7	3000	2.6	84
7	10	8.6	4300	2.0	75
8	4	3.3	4400	2.0	88
9	1	0.9	4600	1.9	82
10	0.3	0.5	10500	1.8	80
11	0.2	0.2	18500	2.3	81
12	1	0.7	24000	2.3	85
13	4	3.6	14100	1.9	80

* Determined by ^{1}H NMR.

** Determined by GPC.

2. Preparation of undecenoic esters. At the second step, undecenoic esters which are reagents for modification of hydride-containing PDMSs were synthesized.

Tert-butyl undecenoate was synthesized according to Scheme 2 (Eq. 1).

Trimethylsilyl undecenoate (TMSU) was prepared according to the earlier described procedure[12] by the reaction between hexamethyldisilazane with a solution of undecenoic acid in toluene according to Scheme 2 (Eq. 2).

3. Preparation of modified PDMS copolymers. Siloxane copolymers containing the fragments of undecenoic acid and its esters were synthesized by addition of trimethylsilyl or *tert*-butyl undecenoate to the silicon hydride groups of polydimethylmethylhidrosiloxanes *via* hydrosilylation (Scheme 3 and 4).

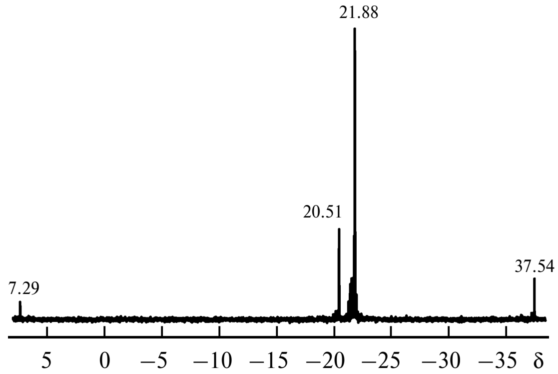
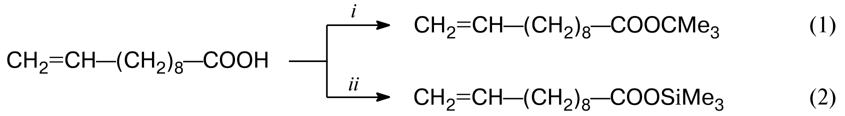


Fig. 1. ^{29}Si NMR spectrum of the PDMS sample (8.6 mol.% of Si—H).

Scheme 2

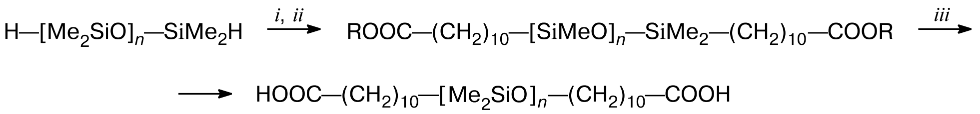


$$CH_2{=}CH{-}(CH_2)_8{-}COOH \xrightarrow{i} CH_2{=}CH{-}(CH_2)_8{-}COOCMe_3 \quad (1)$$

$$CH_2{=}CH{-}(CH_2)_8{-}COOH \xrightarrow{ii} CH_2{=}CH{-}(CH_2)_8{-}COOSiMe_3 \quad (2)$$

Reagents: *i.* $SOCl_2$, Me_3COK, THF; *ii.* $Me_3SiN(H)SiMe_3$, toluene.

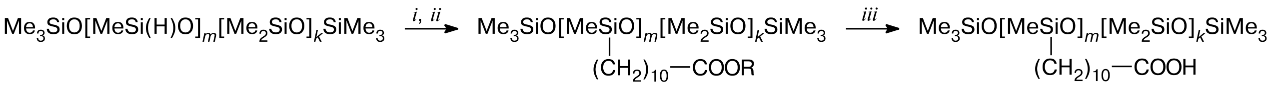
Scheme 3



$$H{-}[Me_2SiO]_n{-}SiMe_2H \xrightarrow{i,\,ii} ROOC{-}(CH_2)_{10}{-}[SiMeO]_n{-}SiMe_2{-}(CH_2)_{10}{-}COOR \xrightarrow{iii} HOOC{-}(CH_2)_{10}{-}[Me_2SiO]_n{-}(CH_2)_{10}{-}COOH$$

Reagents: *i.* $CH_2{=}CH{-}(CH_2)_8{-}COOCMe_3$, toluene, Pt^0; *ii.* $CH_2{=}CH{-}(CH_2)_8{-}COOSiMe_3$, toluene, Pt^0.

Scheme 4



$$Me_3SiO[MeSi(H)O]_m[Me_2SiO]_kSiMe_3 \xrightarrow{i,\,ii} Me_3SiO[\underset{(CH_2)_{10}-COOR}{MeSiO}]_m[Me_2SiO]_kSiMe_3 \xrightarrow{iii} Me_3SiO[\underset{(CH_2)_{10}-COOH}{MeSiO}]_m[Me_2SiO]_kSiMe_3$$

Reagents: *i.* $CH_2{=}CH{-}(CH_2)_8{-}COOCMe_3$, toluene, Pt^0; *ii.* $CH_2{=}CH{-}(CH_2)_8{-}COOSiMe_3$, toluene, Pt^0; *iii.* MeOH, toluene.

The trimethylsilyl protective groups were removed by treatment of the copolymers with methanol. The resulting copolymers were characterized by ^{1}H NMR spectroscopy, GPC, and DSC (Tables 3—6).

The increase in M_n and polydispersity of the polymers and the decrease in the content of modifying units relative to the starting precursors are likely due to side dehydrocondensation and disproportionation reactions of

Table 3. Properties of the *tert*-butyl decanoate telechelic PDMSs

Polymer	M_n**	M_w/M_n**	[*X*]*** (mol.%)	T_g	T_{cc}	T_{m_1}/T_{m_2}	ΔH_{cc}	ΔH_m
					°C		J g^{-1}	
PDMS-E-3	2900	2.1	5.0	−120	—	—	—	—
PDMS-E-5	5200	2.3	2.4	−123	−71	−8	7.0	7.0
PDMS-E-17	17300	2.5	1.0	−125	−113	−49/−37	9.0	32.0
PDMS-E-19	19100	3.7	0.6	−127	−97	−45/−39	1.7	33.0

* Hereinafter, the polymer name is PDMS — type of modifying group (E is *tert*-butyl undecenoate and A is undecenoic acid) — molecular weight 10^{-3}.

** Determined by GPC.

*** [*X*] is the content of modifying units determined by ^{1}H NMR.

Table 4. Properties of the 10-carboxydecyl telechelic PDMSs

Polymer	M_n*	M_w/M_n*	[*X*]** (mol.%)	T_g	T_{cc}	T_{m_1}/T_{m_2}	ΔH_{cc}	ΔH_m
					°C		J g^{-1}	
PDMS-A-2	2100	3.5	4.4	−124	—	−67	—	11.0
PDMS-A-5	5200	3.5	2.4	−125	—	−72	—	8.0
PDMS-A-13	13000	3.5	1.1	−126	−95	−48/−39	78.0	32.0
PDMS-A-16	16400	3.5	0.6	−126	−91	−39/−46	4.0	32.0

* Determined by GPC.

** According to the ^{1}H NMR spectral data.

Table 5. Properties of PDMSs with *tert*-butyl undecenoate residues statistically distributed along the chain

Polymer	M_n*	M_w/M_n*	[*X*]** (mol.%)	T_g	T_{cc}	T_{m_1}/T_{m_2}	ΔH_{cc}	ΔH_m
				°C			J g^{-1}	
PDMS-E-4-7.7	4800	2.4	7.7	−115	—	—	—	—
PDMS-E-5-1.6	5400	1.5	1.6	−125	—	—	—	—
PDMS-E-6-1.7	6100	1.7	1.7	−124	—	—	—	—
PDMS-E-10-0.5	10600	2.1	0.5	—	—	−48/−35	—	38
				(−126)***	—	−47/−36***	−77/30***	(33)***
PDMS-E-11-0.2	11600	2.9	0.2	—	—	−43/−36	—	35
				(−125)***	—	−44/−36***	−92/22***	(33)***

* Determined by GPC.

** [*X*] is the content of modifying units determined by ^{1}H NMR.

***After quenching in liquid nitrogen.

Table 6. Properties of PDMSs with 10-carboxydecyl substituents statistically distributed over the chain

Polymer	M_n*	M_w/M_n*	[*X*]** (mol.%)	T_g	T_{cc}	T_{m_1}/T_{m_2}	ΔH_{cc}	ΔH_m
				°C			J g^{-1}	
PDMS-A-3-40	—	—	40.0	—	—	−6	—	31
PDMS-A-3-16.6	—	—	16.6	−96	—	−52	—	9
PDMS-A-2-6.5	2400	2.8	6.5	−117	—	—	—	—
PDMS-A-5-2.5	5700	2.1	2.5	−125	—	—	—	—
PDMS-A-6-0.9	6400	1.6	0.9	−126	—	—	—	—
PDMS-A-10-0.5	10100	2.7	0.5	−126	−86	−49/−37	24	34
PDMS-A-14-0.2	14400	3.3	0.2	—(−126)***	—	−44/−37 (−49/37)***	−90/23***	36 (34)***
PDMS-A-30-0.6	30000	3.1	0.6	−125	−88	−43	14	29
PDMS-A-14-2.6	14000	2.2	2.6	−123	—	—	—	—

* Determined by GPC.

** [*X*] is the content of modifying units determined by ^{1}H NMR.

***After quenching in liquid nitrogen.

the hydrosiloxane groups in the presence of the platinum catalyst.

The DSC study of *tert*-butyl decanoate PDMS telechelics allowed us to establish that the increase in the molecular weight of these polymers from 2900 to 19000 has an effect on their crystallizability. For example, the PDMS-E-3* sample with M_n = 2900 is amorphous; its DSC curve displays only a heat capacity change at the glass transition temperature (T_g = −120 °C) (Fig. 2). The DSC curve for the PDMS-E-5 polymer with M_n = 5200 displays, besides the heat capacity change (T_g = −123 °C), also an exothermic effect (T_{cc} = −71 °C) caused by cold crystallilzation and the *endo*-effect of melting of the PDMS crystalline phase (T_m = −8 °C). It should be noted that the heat effects of cold crystallization and melting in this case are identical (ΔH_{cc} = ΔH_m = 7.0 J g^{-1}) (see Table 3). The increase in M_n of PDMS to 17300 and 19000 (PDMS-E-17 and PDMS-E-19 samples, respectively) results in a considerable increase in the ΔH_m value

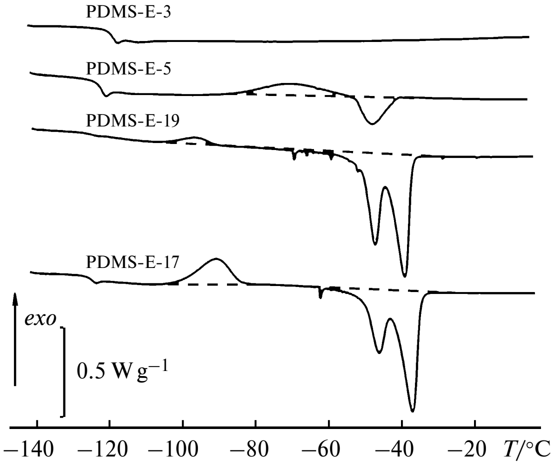


Fig. 2. DSC curves for *tert*-butyl decanoate PDMS telechelics.

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* Hereinafter, the polymer name is PDMS — type of modifying group (E is *tert*-butyl undecenoate and A is undecenoic acid) — molecular weight 10^{-3}.

for PDMS with regard to ΔH_{cc} (see Table 3). Introduction of the bulky *tert*-butyl decanoate terminal groups into the PDMS structure has an effect predominantly on T_c whose value decreases in the order PDMS-E-3—PDMS-E-19 in a symbate manner with an increase in their M_n. Note that the PDMS oligomers show an opposite dependence of T_g on M_n. It is entirely possible that the bulky terminal groups are responsible for a high T_{cc} value in the case of the PDMS-E-5 sample (−71 °C).

The samples of PDMSs with 10-carboxydecyl substituents at low M_n values has several features compared to the *tert*-butyl decanoate derivatives. For example, the DSC curves for the PDMS-A-2 and PDMS-A-5 polymers (M_n = 2100 and 5200, respectively) with molecular weights close to the M_n values for the earlier considered PDMS-E-3 and PDMS-E-5 polymers display a heat capacity change (glass transition) and an endothermic melting peak (Fig. 3). With an increase in M_n, the T_g, T_m, and ΔH_m values decrease (see Table 4). In the PDMS-A-2 and PDMS-A-5 samples, T_m of the crystalline phase are −67 and −72 °C, respectively, which are significantly lower than the melting point of PDMS. It is obvious that the observed result is due to the fact that the fragments containing 10-carboxydecyl terminal groups segregate into a separate crystalline phase, i.e., a microphase separation occurs in the polymer and the observed endothermic melting peaks correspond exactly to melting of this phase. The probable reason for such behavior is the increase in the level of intermolecular interactions when the structure contains terminal carboxyl groups. The increase in M_n to 13000 and 16400 (PDMS-A-13 and PDMS-A-16 samples, respectively) leads to a shift in the endothermic peaks to the region of –(40—50) °C typical of melting of the PDMS crystalline phase. The T_g value for the samples with 10-carboxydecyl substituents decreases with an increase in M_n analogously to that for the *tert*-butyl decanoate derivatives. Thus, upon an increase in M_n the effect of bulky terminal substituents becomes less noticeable.

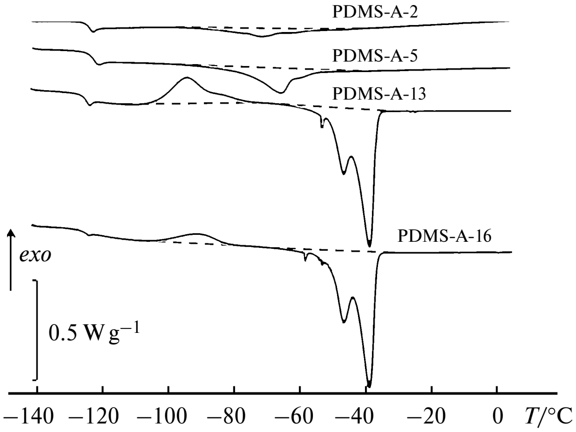

Fig. 3. DSC curves for the PDMS samples containing terminal 10-carboxydecyl fragments.

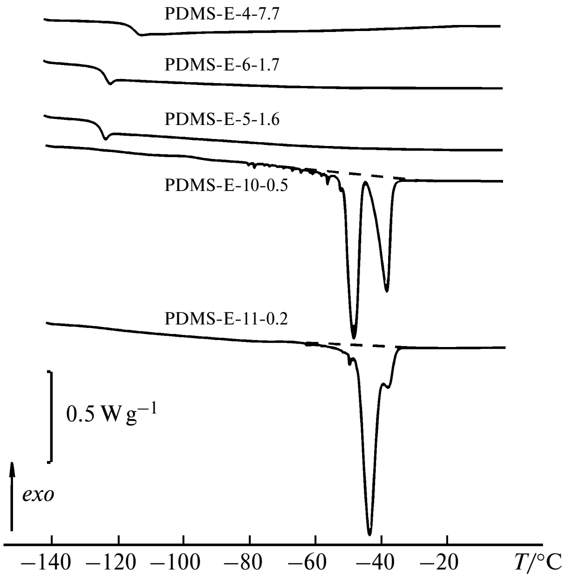

Fig. 4. DSC curves for the copolymers containing the *tert*-butyl undecenoate residues statistically distributed along the siloxane chain.

The regularities of the thermal behavior of the copolymers with *tert*-butyl decanoate groups distributed along the siloxane chain (Fig. 4) are close to those for the *tert*-butyl decanoate PDMS telechelics. The T_g value for such copolymers decreases with an increase in their M_n, i.e., the effect of bulky pendent groups becomes less pronounced. One should note a higher tendency of the polydimethylsiloxane moiety to crystallization in such polymers compared to the copolymers containing *tert*-butyl decanoate groups at the chain ends. For the PDMS-E-10-0.5 and PDMS-E-11-0.2 polymers, we succeeded in determining the T_g value only after their quenching in liquid nitrogen (see Table 5).

The replacement of the *tert*-butyl butanoate ester group for the carboxyl one has a significant effect on the thermal behavior of modified PDMSs. The DSC curve for the sample of PDMS-A-3-40 with 10-carboxydecyl groups distributed over the backbone, which contains 40 mol.% of modifying units, is characterized by a broad *endo* peak at −6 °C (Fig. 5), which apparently corresponds to melting of 10-carboxydecyl fragments segregating into a separate phase. The decrease in their content to 16.6 mol.% in the PDMS-A-3-16.6 sample results in a dramatic decrease in the T_m and ΔH_m values (see Table 6). In addition, a slight temperature change appears at −96 °C. Further decrease in the content of 10-carboxydecyl groups results in a shift in T_g of polymers to the temperature region typical of PDMS (PDMS-A-2-6.5—PDMS-A-6-0.9, see Table 6) and the formation of the PDMS crystalline phase in the PDMS-A-10-0.5 and PDMS-A-14-0.2 samples. For the latter, the T_g value was determined only after quenching in liquid nitrogen

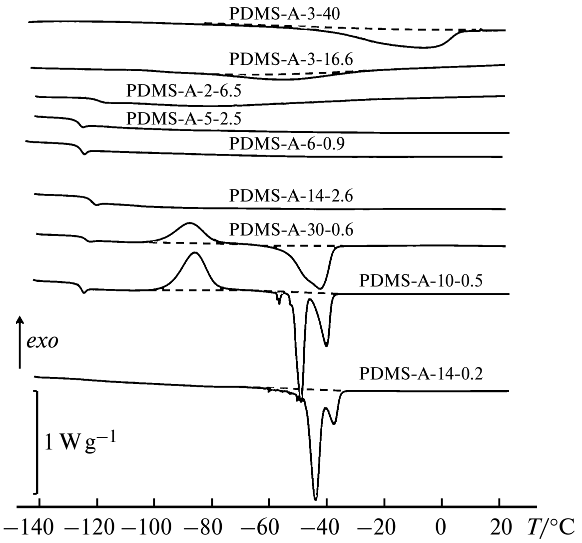

Fig. 5. DSC curve for the copolymers 10-carbodecyl groups distributed along the siloxane chain.

(see Table 6). Note that the increase in M_n of polymers results in an increase in T_c with the main regularities of thermal behavior remaining unchanged (compare PDMS-A-5-2.5 and PDMS-A-30-0.6, PDMS-A-10-0.5 and PDMS-A-14-2.6, see Table 6, Fig. 5), which agrees good with the known dependence of T_g of PDMS on M_n.[16]

Thus, upon introduction of a slight amount of substituents (up to 0.5 mol.%) the T_g values of the polymers decreases; however, upon further increase in their content they increase. At a high content of modifying units, the modifier undergoes crystallization as a separate phase. It should be noted also that the thermal behavior of the modified PDMSs is influenced to the highest degree by introduction of the 10-carboxydecyl fragments into their structure both into the polymer backbone and as terminal substituents compared to the *tert*-butyl decanoate fragments. This is obviously due to the higher polarity of the former and, as a consequence, the increase in the intermolecular interaction.

Features of the rheological behavior of modified PDMSs

PDMSs with modifying units statistically distributed along the copolymer backbone. Figures 6 and 7 show the flow curves for PDMSs modified with *tert*-butyl decanoate (PDMS-E) and 10-carboxyldecyl (PDMS-A) substituents with close molecular weights in the "shear rate (γ) — dynamic viscosity (η)" coordinates.

As Figs 6 and 7 show, for almost all polymer under study the viscosity does not depend on the shear rate (i.e., the flow of these polymer is Newtonian) and the viscosity of polymers with identical contents of modifying units is always higher for PDMS-A compared to PDMS-E.

With an increase in the content of modifying units, the viscosity of polymers increases and, for the PDMS-A polymer containing 40 mol.% of such units, the flow becomes non-Newtonian and corresponds to the behavior of a pseudoplastic fluid.

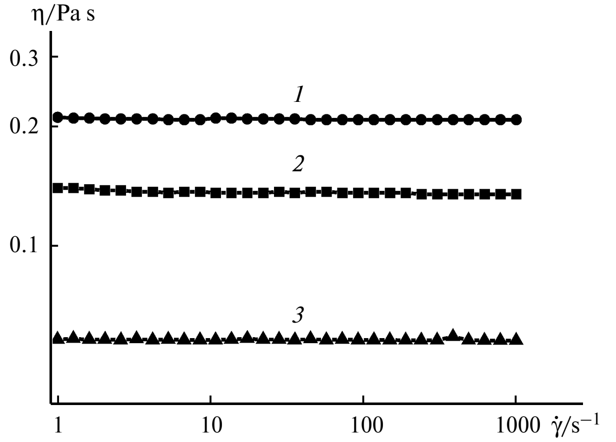

Fig. 6. Flow curves for the PDMS-E-4-7.7 (*1*), PDMS-E-6-1.7 (*2*), and PDMS-E-5-1.6 (*3*) samples.

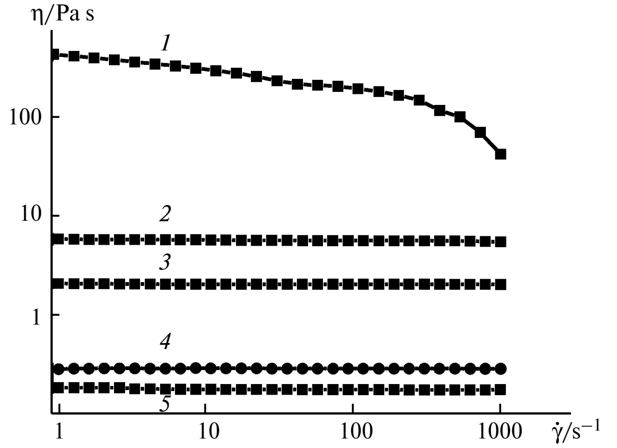

Fig. 7. Flow curves for the PDMS-A-3-40 (*1*), PDMS-A-3-16.6 (*2*), PDMS-A-2-6.5 (*3*), PDMS-A-5-2.5 (*4*), and PDMS-A-6-0.9 (*5*) samples.

Figure 8 shows the flow curves for PDMS-A with different M_n values. The most of given polymers are Newtonian fluids; the deviation from the Newtonian behavior is observed for polymers with high M_n at which even the unmodified PDMS is a pseudoplastic fluid.[17]

The presence of modifying units containing ester or carboxyl groups in the PDMS macromolecules contemplates different levels of intermolecular interaction characterized by the energy of activation of viscous flow E_a. The E_a value is determined from the temperature dependence of η according to the Arrhenius equation:

$$\eta = Ae^{E_a/RT},$$

where A is the preexponential factor, R is the gas constant, and T is temperature, K. To calculate E_a, the

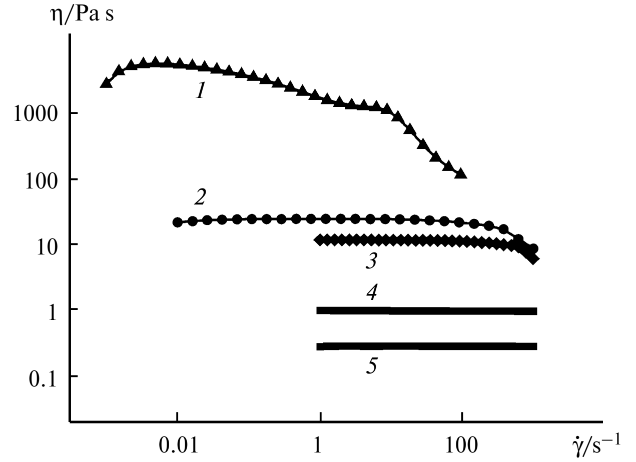

Fig. 8. Flow curves for the PDMS-A-30-0.6 (*1*), PDMS-A-14-2.6 (*2*), PDMS-A-14-0.2 (*3*), PDMS-A-10-0.5 (*4*), and PDMS-A-5-2.5 (*5*) samples.

flow curves for the polymers (Fig. 9) in a temperature range from 20 to 100 °C were obtained.

As Fig. 9 shows, for the PDMS-E and PDMS-A samples containing 7.7 and 6.5 mol.% of modifying units, respectively, the flow at all temperatures is Newtonian. In PDMS-A-40 (40 mol.% of modifying units), the viscosity decreases with an increase in the shear rate, but at 100 °C we failed to achieve a steady flow due to a slow increase in the viscosity. It appears that, above 80 °C, the polymer undergoes structuring analogous to that observed in the modified PDMSs.[5—7] The specific nature of structuring in PDMSs containing modifying units requires additional study. Figure 10 exemplifies the temperature dependences of η for some polymers in the Arrhenius equation coordinates. Since all dependences are straight lines, one can calculate the E_a values by the slope. It is seen from Fig. 13 that, with an increase in the content of modifying units in the macromolecule, the E_a value increases, which suggests an increase in the intermolecular interaction. It also follows from Fig. 13 that the E_a value for PDMS with modifying units containing ester groups is lower than that for the analogous polymers with carboxyl groups in the modifying unit.

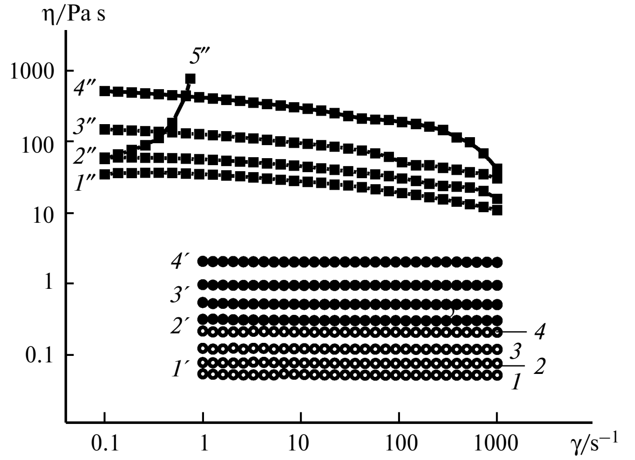

Fig. 9. Flow curves for the PDMS-E-4-7.7 (*1—4*), PDMS-A-2-6.5 (*1′—5′*) and PDMS-A-3-40 (*1′′—5′′*) samples at 20 (*1, 1′*), 40 (*2, 2′*), 60 (*3, 3′*), 80 (*4, 4′*), and 100 °C (*5′*).

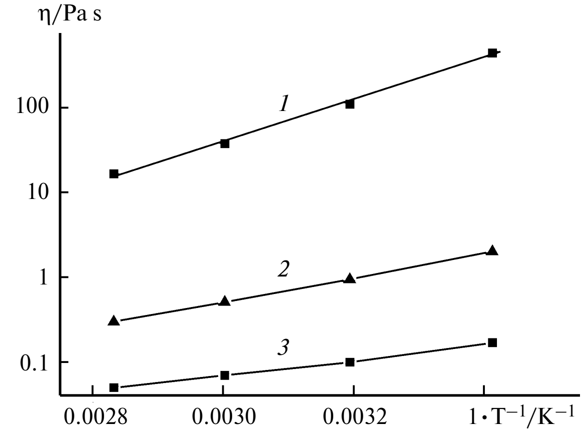

Fig. 10. Temperature dependences of the viscosity in the Arrhenius equation coordinates for the PDMS-A-3-40 (*1*), PDMS-A-2-6.5 (*2*), and PDMS-A-6-0.9 (*3*) samples.

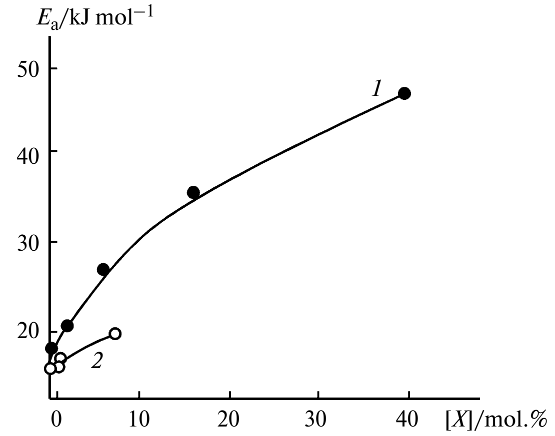

Fig. 11. E_a value as a function of the content of modifying units (*X*) in the PDMS-A (*1*) and PDMS-E (*2*) polymers.

Thus, the introduction of modifying units containing ester or carboxyl groups into the backbone of the PDMS macromolecules increases the level of the intermolecular interaction, which is manifested in the increase in the E_a value upon an increase in the content of such units. The most of modified PDMS are characterized by the Newtonian flow and, only at a high content of modifying units or high molecular weight, the flow becomes non-Newtonian.

Rheological properties of 10-carboxydecyl and *tert*-butyl decanoate telechelic PDMS. The flow of 10-carboxydecyl or *tert*-butyl decanoate PDMS derivatives as for PDMS with modifying units statistically distr-

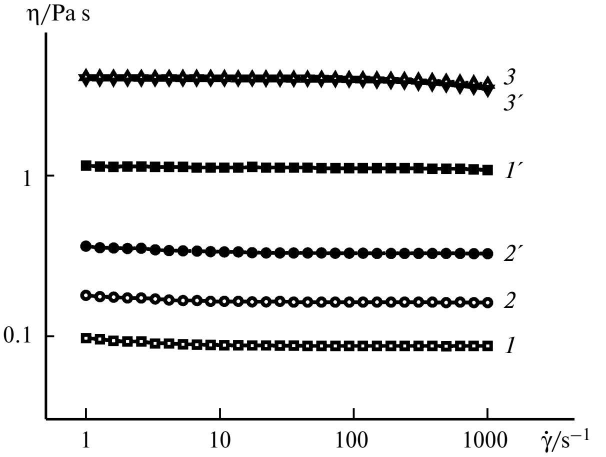

Fig. 12. Flow curves for the *tert*-butyl decanoate PDMS-E-3 (*1*), PDMS-E-5 (*2*), and PDMS-E-17 (*3*) and the 10-carboxydecyl telechelic PDMS-A-2 (*1′*), PDMS-A-5 (*2′*), and PDMS-A-16 (*3′*).

ibuted over the backbone is Newtonian in nature (Fig. 12).

The increase in M_n of polymer results in an increase in the viscosity; in the case of PDMS-A at low viscosity the η value is always higher than that for the PDMS-E homologs and, at high molecular weights, the effect of the nature of terminal groups on η is neutralized and its value depends on the type of modifying units.

To calculate the E_a values, the flow curves for telechelics in a temperature range from 20 to 80 °C were obtained. At higher temperatures, these compounds as well as the polymers with statistically distributed modifying units with carboxyl groups are characterized by a slow increase in the viscosity.

Figure 13 exemplifies the flow curves for PDMS-E and PDMS-A with identical M_n values at different temperatures. It is seen that the polymer flow is Newtonian at all temperatures.

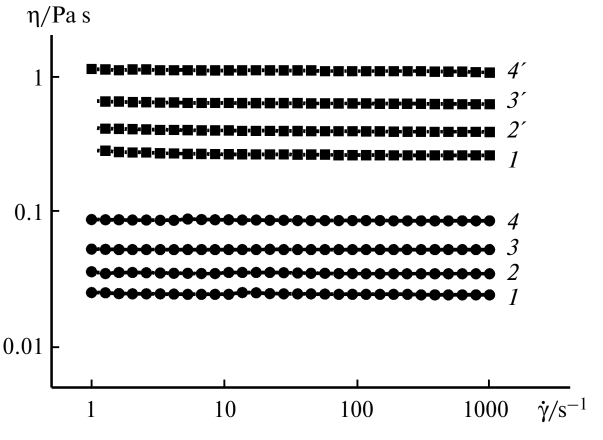

Fig. 13. Flow curves for PDMS-E-3 (*1—4*) and PDMS-A-2 (*1′—4′*) at 20 (*1, 1′*), 40 (*2, 2′*), 60 (*3, 3′*), and 80 °C (*4, 4′*).

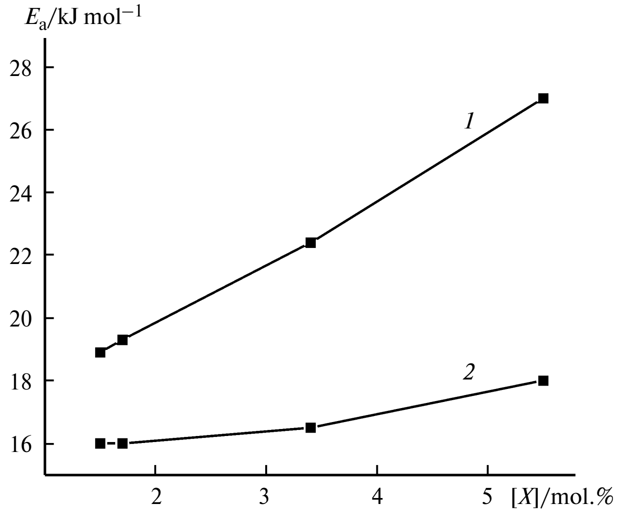

Fig. 14. E_a value as a function of the content of modifying units (*X*) for the PDMS-A (*1*) and PDMS-E (*2*) samples.

The temperature dependences of viscosity in the Arrhenius equation coordinates are straight lines, which allows one to determine the energy of activation of viscous flow E_a by the slope angle of this line. It is seen from Fig. 14 that the E_a value for PDMS-E slightly changes with an increase in the portion of modifying units, while this effect for PDMS-A is much more pronounced.

It should be noted that, although the viscosities of PDMS-E-17 and PDMS-A-16 having close contents of modifying units are almost identical (see Fig. 12), the E_a values for these polymers are different.

Thus, the introduction of modifying units into PDMSs containing ester or carboxyl groups in the decyl substituent at the silicon atom strengthens the intermolecular interaction, which is manifested in the increase in the E_a value with an increase in the portion of such units. The most of modified PDMSs are characterized by the Newtonian flow, i.e., a slight amount of polar substituents has a weak effect on the specificity of the siloxane chain and, only at their high content (in the case of carboxyl-containing PDMSs), the flow becomes non-Newtonian. The presence of terminal modifying units in the PDMS macromolecule results in an increase in the E_a value and the viscosity is governed to a greater degree by the molecular weight of the polymer rather than the presence of polar fragments. The specific feature of modified PDMSs containing chain distributed 10-carboxydecyl and *tert*-butyl decanoate substituents is structuring being manifested in the viscosity increase at temperatures above 80 °C. To clarify features of this process, further studies are required.

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