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Properties of Isomers of Oxygen-Containing Cyclic Monomers

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Abstract—Structures of isomers and conformers of 1-acryloyloxymethyl-3,4-epoxycyclohexane, 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane, and 4-methylene-3,5-dioxabicyclo[5.4.0]undecane have been simulated. Properties of the *cis* and *trans* isomers upon complex formation with maleic anhydride and/or acrylonitrile have been examined by ^{1}H and ^{13}C NMR.

Keywords: monomer, cyclic isomer, quantum-chemical simulation, copolymer, oxygen-containing monomer
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Isomerism is among important factors to be considered in simulation of structures of homo- and heteroassociates of monomers; he formation of such associates in its turn influences kinetics of the radical processes, including copolymers chain growth. Rotational isomerism of vinyl monomers containing C=C–C=C or C=C–C=O fragments as well as five- or seven-membered rings has been discussed in [1–9]. However, structure of isomers of oxygen-containing cyclic monomers has not been studied in detail so far, the available contributions [10–13] are not systematic.

Cyclic monomers containing heteroatoms, epoxy group in the six-membered ring, two cycles connected via a spiro atom, and/or fused cycles are used in production of specialty polymers. The self-association and complex formation may influence the co-polymerization mechanism; however, such processes have not been studied so far. For example, in the case of *cis* and *trans* isomers of epoxyacrylate and a spiro monomer, the (co)polymerization starts with the double bond cleavage (similarly to the conventional polymerization of vinyl compounds), and the formed polymer consists of linear main chain and the side groups containing six-membered ring with the epoxy group or the oxolane cycles. The formation of hydrogen-bonded complexes of a spiro monomer with maleic anhydride or acrylonitrile may alter the polymerization mechanism to start with the ring opening and to proceed via fragmentation copoly-merization. In this case, the copolymer will contain a linear main chain and a fraction of units with cyclic side groups, partially decomposing at the total conversion above 10 wt %. The cyclohexane cycle of bicyclic ketene acetal monomer exists in the most stable *chair* conformation, similarly to cyclohexane and its derivatives [1, 2], whereas the seven-membered cycle exists in the conformations of *twist-chair* and *twist-boat*, typical of dioxepane structure [15–17]. If the condensation of two cycles does not change the hexane cycle configuration, the *twist-chair* ↔ *twist-boat* equilibrium should be retained. Then the presence of H-complex may induce the hydrogen transfer reaction resulting in the formation of additional side groups containing methyl terminal fragment which can be detected by ^{1}H NMR spectroscopy, and the main chain containing the ~C(=O)OCHC~ and ~OC(=O) CHC~ fragments.

This work aimed to simulate structures of isomers of a series of cyclic monomers and to elucidate the isomerism effect on the formation of π-H- and H-complexes and the resulting changes in the mechanism of radical binary copolymerization.

Structures of the monomers (Table 1) 1-acryloyl-oxymethyl-3,4-epoxycyclohexane [10, 11], 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane [13], and 4-methylene-3,5-dioxabicyclo[5.4.0]undecane (ketene

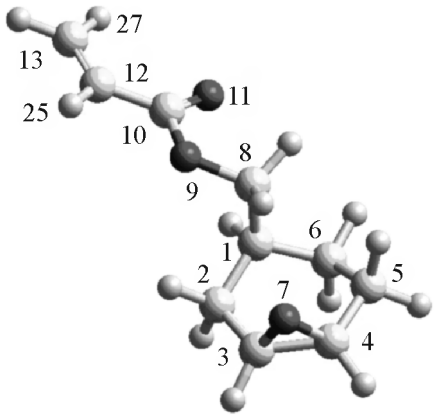


Fig. 1. General view of molecule of *cis-e-sp*-1-acryloyloxymethyl-3,4-epoxycyclohexane.

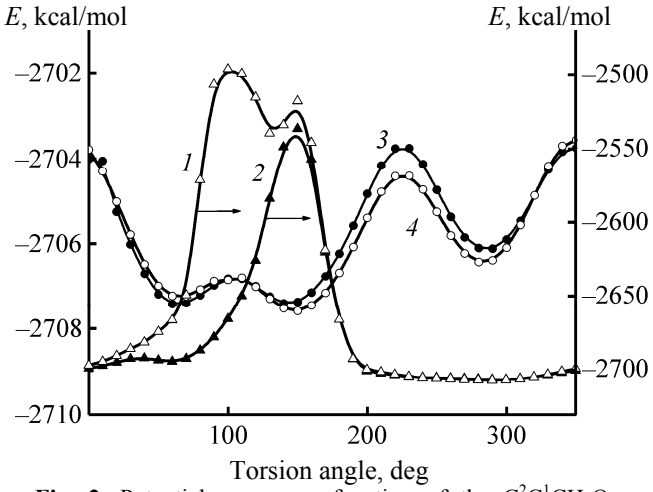


Fig. 2. Potential energy as function of the $C^2C^1CH_2O$ torsion angle for (*1*) *cis-a*, (*2*) *trans-a*, (*3*) *cis-e*, and (*4*) *trans-e* isomers of 1-acryloyloxymethyl-3,4-epoxycyclohexane.

acetal) as well as their isomers and conformers have been simulated by means of AM1 and/or HF, DFT methods.

The *cis* and *trans* isomers of the monomers as well as the copolymerization products formed in the presence of the molecular complexes of the monomers with maleic anhydride and/or acrylonitrile have been studied by ^1H and ^{13}C NMR spectroscopy. The effect of the interaction between the cycles and the substituents was studied using the formation of isomers of 1-acryloyloxymethyl-3,4-epoxycyclohexane as an example. In particular, we accounted for the presence of four axes of the internal rotation [C^1–$C(H_2)$, $C(H_2)O$, OC(=O), and C(=O)–C(=C)] in the hexane cycle substituent, resulting in the possible formation of additional rotational isomers, for example, *cis-e-sp* (Fig. 1).

The potential energy (E) minima observed for the *cis-e* isomers at the $C^2C^1CH_2O$ angles of approximately 60°, 150°, and 280° possss the energy barrier (ΔE) not exceeding 16 kJ/mol (Fig. 2, curves *3* and *4*). In the case of the isomers with *cis-a* location of the substituent the energy barrier was much higher, the potential energy being ≈750 and ≈850 kJ/mol (Fig. 2, curve *1*); the *trans-a* isomer energy was ≈710 kJ/mol (Fig. 2, curve *2*).

The rotation around the C(=O)–O bond resulted in a deep minimum with the energy of ≈210 kJ/mol [10]. This resulted from the hindrance to rotation as a consequence of $O^{11}\cdots H^{14}(-C^1)$ and $O^{11}\cdots H^{22}(-C^6)$ hydrogen bonds formation between the carbonyl oxygen and the protons of the hexane cycle in the *e* and *a* forms, their length being 2.58 and 2.60 Å (*cis* isomer) and 2.44 and 2.42 Å (*trans* isomer), respectively. The rotation around the C^{10}–C^{12} bond revealed two potential energy minimums with the barrier values of 9.2 and 6.3 kJ/mol, corresponding to the O=C–C=C torsion angle of 0° and 180° (Fig. 3) in the *syn-peri* (*sp*) and *anti-peri* (*ap*) planar form of the substituent, the first state being somewhat more populated (Table 2).

Table 1. Simulated parameters of the monomers

Monomer	$-H^0_{298}$, kJ/mol	Ionization potential, eV	Electron affinity, eV	Dipole moment, D
8-Methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane	665.3	9.80	–0.95	0.80
Ketene acetal (*chair*)	406.0	9.28	–1.78	2.04
Ketene acetal (*boat*)	385.6	9.21	–1.23	2.44

In those forms of 1-acryloyloxymethyl-3,4-epoxycyclohexane we observed the interaction between the ether and the carbonyl oxygen atoms with protons of the vinyl groups and the formation of the following hydrogen bonds: $O^9\cdots H^{25}(-C^{12})$ (2.50 Å) and $O^{11}\cdots H^{27}(-C^{13})$ (2.64 Å) in the *sp* form and $O^9\cdots H^{27}$ (2.48 Å) and $O^{11}\cdots H^{25}$ (2.72 Å) in the *ap* form.

Basing on the computations of the substituent rotational isomerism (Figs. 2 and 3), four isomeric structures of 1-acryloyloxymethyl-3,4-epoxycyclohexane were optimized (Fig. 4) with the $C^2C^1C(H_2)O$ angle of 144°, 149°, 293°, and 291° for the *trans-e, cis-e*, *trans-a*, and *cis-a* forms, respectively [10]. Furthermore, the appearance of the stable conformers corresponding to the hindered *sp* and *ap* forms with the difference in the formation energy of about 2.5 kJ/mol was possible upon cooling due to the rotation around the C(=O)–C(=C) bond (Table 2).

The difference between the computed formation enthalpies of the *cis* and *trans* isomers was 0.4 kJ/mol in the case of the equatorial conformers and 1.3 kJ/mol in the case of the axial conformers. Their ratio as calculated using Eq. (1) [14] was 0.45 : 0.55 (Table 2), the *e* conformers prevailing (66 mol % in total).

$$N_1/N_2 = e^{-\Delta H_2/RT}/e^{-\Delta H_1/RT}, \quad (1)$$

where N_1 and N_2 standing for the molar fractions and ΔH_1 and ΔH_2 being the enthalpy of formation of the corresponding isomer.

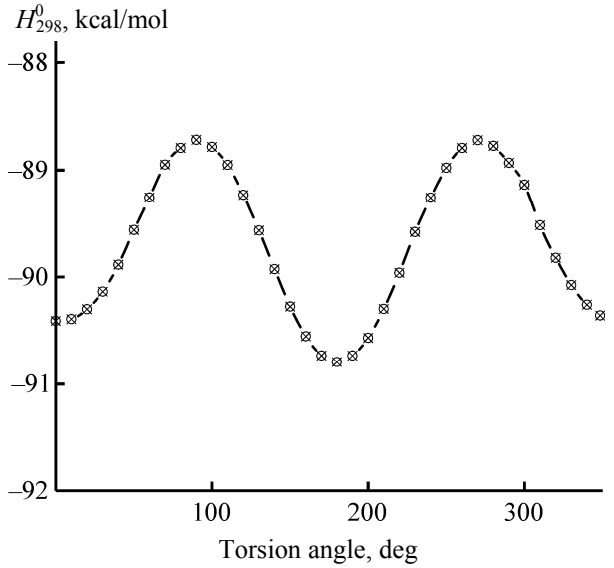


Fig. 3. Standard heat of formation as function of the C=C–C=O torsion angle for the *cis* and *trans* isomers of 1-acryloyloxymethyl-3,4-epoxtcyclohexane.

^{13}C NMR spectra of 1-acryloyloxymethyl-3,4-epoxycyclohexane (Table 3) contained pairs of signals of the C^3 and C^4 atoms of the oxirane ring, corresponding to the *cis* and *trans* isomers. The equal intensity of the signals pointed to the equal amount of the isomers, close to their calculated ratio (Table 2).

The C^1, C^2, C^5, and C^6 atoms of the hexane cycle resonated as 8 signals of equal intensity at 32.9–

Table 2. Thermodynamic parameters and dipole moments of isomers and conformers of 1-acryloyloxymethyl-3,4-epoxycyclohexane

Configuration of the cycles and the substituent[a]	$-H^0_{298}$, kJ/mol	S^0_{298}, J mol^{-1} K^{-1}	μ, D	$\Delta H_{sp\text{-}ap}$, kJ/mol	Amount of the conformers, mole fraction
cis-e-sp	–380.6	389.9	1.23	1.6	0.35
cis-e-ap	–379.0	376.1	1.09		
trans-e-sp	–380.2	348.1	3.38	1.9	0.31
trans-e-ap	–378.3	375.7	3.88		
cis-a-sp	–378.0	388.7	1.54	1.6	0.19
cis-a-ap	–376.4	388,7	1.64		
trans-a-sp	–377.0	375.7	2.72	2.0	0.15
trans-a-ap	–375.0	375.7	3.01		
ΔH_{e-a} 2.6 (*cis*-), 2.8 (*trans*-)					

[a] Locations of the epoxy and the cyclohexane rings, of the substituent (*e*—equatorial, *a*—axial), and of the C=C and C=O bonds (*sp*—*syn-peri*-, *ap*—*anti-peri*-planar) are stated.

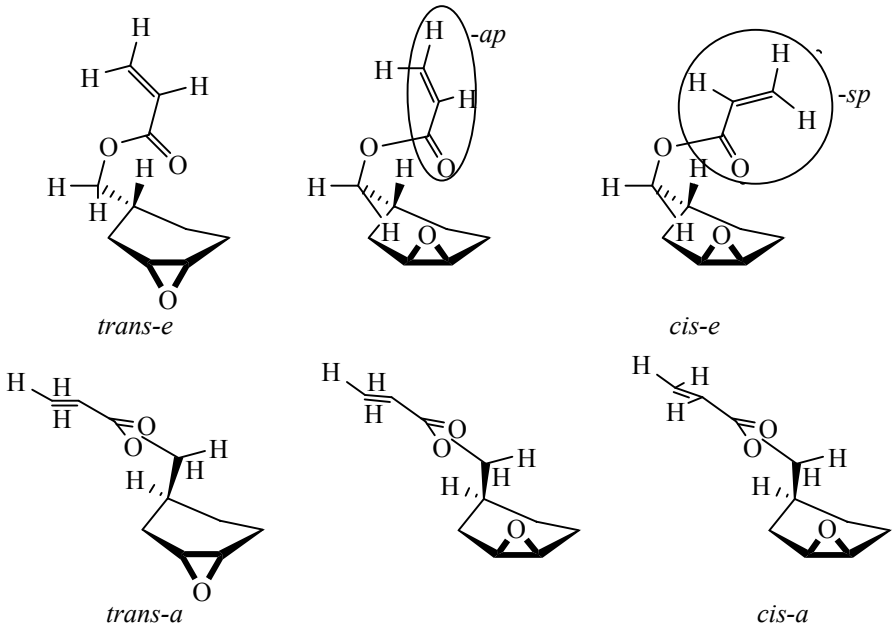


Fig. 4. Optimized structures of isomers and conformers of 1-acryloyloxymethyl-3,4-epoxycyclohexane.

21.7 ppm. The doublet signal of the C^8 atom of the methylene group was assigned to the *a* and *e* conformers. The pointed duplication of the C^3, C^4, and C^8 signals led to the presence of two and four doublets of signals of epoxy and CH_2O groups, respectively, in the ^1H NMR spectrum. Carbon atoms in the C(=O)–CH=CH_2 fragment gave singlet signals, thus confirming the free rotation around the C^{10}–C^{12} bond at ≈293 K.

A molecule of the spiro-*ortho*-carbonate contains two chiral carbon atoms: the spiro one (C^5) and the one linked to the methyl group (C^8) [2]; therefore, four chiral isomers of this compound can exist. The simulation showed that two types of the isomers can be separated: the *anti*-spiro and the *syn*-spiro ones (Fig. 5) [2].

Besides methyl group, the cycle of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane contains a double bond substituent. The cycle is planar, and the configuration of the cycle with methyl substituent corresponded to the *semi-chair*. Enthalpies of formation of the isomers were practically the same, equal to –664.9 kJ/mol. The ^{13}C NMR spectrum of the monomer contained two pairs of signals at 66.06, 66.30 and 73.70, 73.77 ppm (CH_2 group) along with pairs of signals at 17.07 and 17.77 ppm (CH_3), 80.07 and 80.19 ppm ($C^{10}H_2$), 135.53 and 136.46 ppm (=C^2), and 152.89 and 152.00 ppm (C^5). The signals

Table 3. Parameters of ^1H and ^{13}C NMR spectra of 1-acryloyloxymethyl-3,4-epoxycyclohexane

Group	δ_H, ppm	Group	δ_H, ppm	Group	δ_C, ppm	Group	δ_C, ppm
=CH_2	6.40–6.30			C(O)O	166.19	C^3	51.50
	5.92–5.85	C^2H_2	1.90–1.60				51.01
=CH	6.22–6.07			=CH_2	130.91	C^2	32.91
							30.33
CH_2O	4.06–3.90	C^5H_2	1.60–1.25	=CH	129.26	C^1	28.76
							27.70
C^4H	3.16–3.02	C^6H_2	1.25–0.95	OCH_2	68.90	C^5	25.12
C^3H					68.78		24.24
C^1H	2.15–2.05			C^4	52.48	C^6	23.58
					52.26		21.72

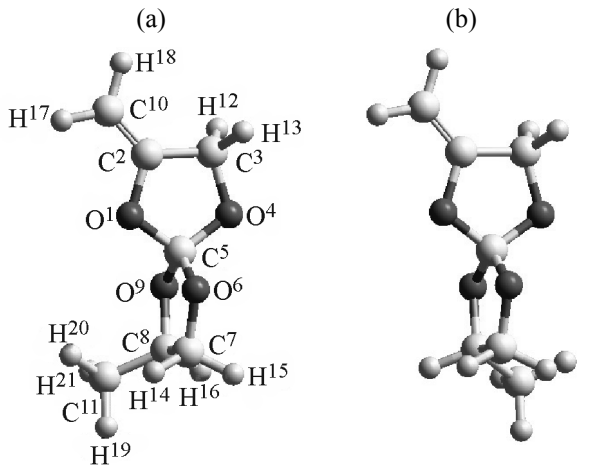


Fig. 5. General view of molecules of (a) *anti*-spiro and (b) *syn*-spiro isomers of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane.

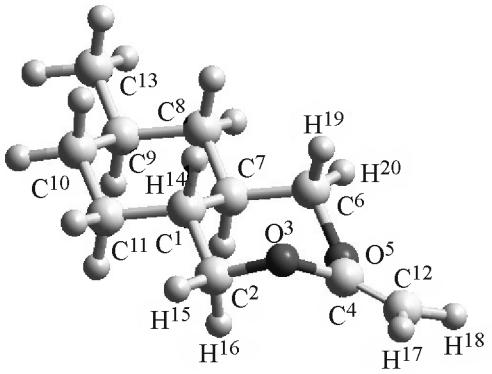


Fig. 6. General view of molecule of 9-methyl-4-methylene-3,5-dioxabicyclo[5.4.0]undecane.

assignment was confirmed by the DEPT experiment. Duplication of the signals of the CH and CH_2 groups evidenced that the monomer existed as mixture of two isomers in the 1 : 1 ratio, differing in the spatial location of substituents.

The presence of fused aliphatic cycles, substituents, and heteroatoms in the molecule of 4-methylene-3,5-dioxabicyclo[5.4.0]undecane (Fig. 6) significantly enriches the diversity of the possible stable isomers and conformers (Fig. 7); elucidation of their equilibrium is important for further discussion. The formation of *cis* and *trans* isomers is possible [2] taking into account that cyclohexane and its derivatives exist in the *chair* form [1, 2] whereas the seven-membered cycle can exist in the *twist-chair* and *twist-boat* forms [15–17]. The simulation data (Table 4) revealed that heats of formation of the *trans* and *cis* isomers of the ketene acetal differed by 8.3 kJ/mol (the *twist-chair* form of the dioxepane cycle) or by 4.0 kJ/mol (the *twist-boat* form). Those data (Table 4) evidenced the prevalence of the fraction of the *trans* isomers, especially for the *twist-chair* dioxepane cycle; the ΔH value for those forms was close to that for *trans* and *cis* bicyclo[4.4.0]decane (11.3 kJ/mol), the latter molecule consisting of two cyclohexane rings in the *chair* conformation (11.3 kJ/mol) [2].

The ketene acetal conformers with the *twist-boat* dioxepane cycle have close H^0_{298} values, due to the low

Table 4. Simulated formation enthalpy and dipole moment of 4-methylene-3,5-dioxabicyclo[5.4.0]undecane as function of the cycle shape and the substituent location

Cycles shape and the substituent location	$-H^0_{298}$, kJ/mol	The conformer fraction, mol %	μ, D	ΔH^a, kJ/mol
twist-chair-trans-e	406.0	64.3	2.03	5.9
twist-chair-trans-a	400.1	15.5	2.03	
twist-chair-cis-e	397.7	8.7	1.87	5.9
twist-chair-cis-a	391.8	2.2	1.90	
twist-boat-trans-e	395.6	5.3	2.24	5.9
twist-boat-trans-a	389.7	1.3	2.25	
twist-boat-cis-e	391.6	2.1	2.45	6.0
twist-boat-cis-a	385.6	0.5	2.44	

[a] Difference between heats of formation of the two conformers.

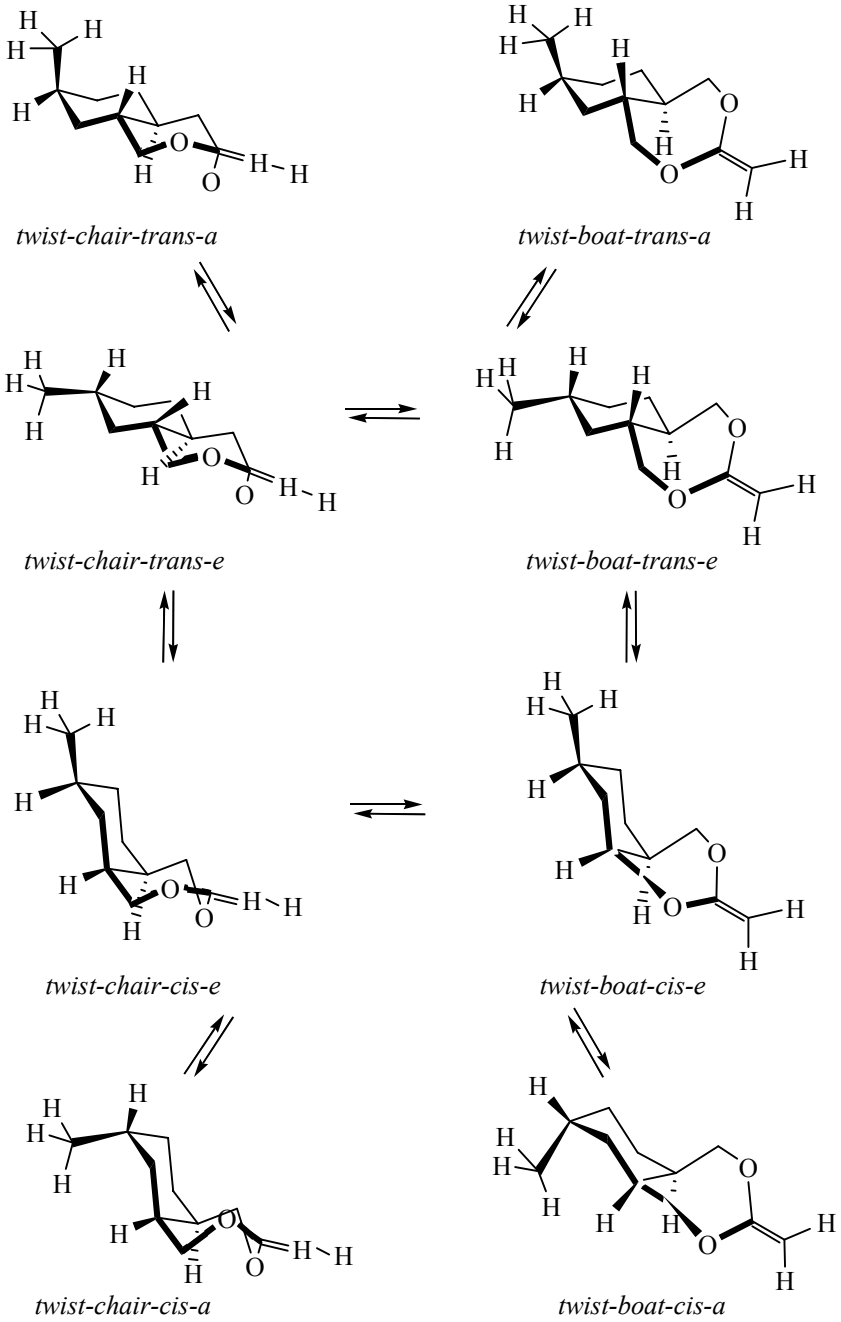


Fig. 7. Optimized structures of the *trans* and *cis* isomers with axial and equatorial location of the substituent in the ketene acetal monomer simulated via AM1 method.

barrier of the conformations conversion and the possibility of free *trans* ↔ *cis* transformation via the pseudo rotation, as was demonstrated for the *twist-boat* dioxepane conformation. The difference in heats of formation of the *twist-chair* and *twist-boat* forms was 6.1 (*cis* isomer) and 10.9 (*trans* isomer) kJ/mol, well coinciding with the corresponding data for cycloheptane (10.0 kJ/mol [15]).

The H^0_{298} values difference for the *e* and *a* conformers of the ketene acetal remained practically equal (≈6.0 kJ/mol), coinciding with that for the *e* and *a* conformers of methylcyclohexane (5.9 kJ/mol, our data; 7.1 kJ/mol [18]; 6.5±0.9 kJ/mol [19]). The fraction of the ketene acetal conformer with the *twist-chair* dioxepane cycle (Table 4 and Fig. 6) was 91%. The *trans* isomer with the *twist-chair* seven-membered

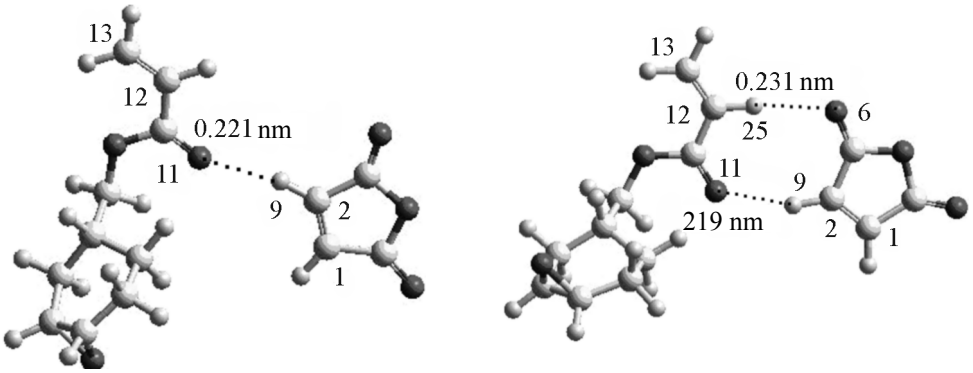


Fig. 8. General view of the complex between 1-acryloyloxymethyl-3,4-epoxycyclohexane with maleic anhydride.

ring and *e*-located methyl group was the most thermodynamically favorable, its fraction being 64% [20].

The optimized values of the bond and torsion angles in cyclohexane ring of the ketene acetal were 111.3° and 54°, close to those obtained by the molecular mechanics simulation (111.4° and 54.8° [15]) or in the experiment (112° and 55.2° [2]); these results confirmed the validity of the AM1 calculations for the cyclic compounds. According to the simulation, the methylcyclopropane fragment in the ketene acetal was practically neutral, the total charge being 0.009 *e*. The charges of the O^3–C^4(=$C^{12}H_2$)–O^5 fragment and the oxygen atom adjacent to the C^2H_2 and C^6H_2 groups equaled –0.363 and +0.372 *e*, practically neutralizing one another. Hence, the cyclohexane ring containing no polar substituents and multiple bonds could affect the ketene acetal reactivity in radical reactions exclusively via the steric hindrance.

Despite the different nature of the above-described donor molecules and the different ways of approaching the partner, their interaction with maleic anhydride or acrylonitrile (acceptor) yielded the H-complexes with fairly close length of the H···O bond, the C–H···O angle value, and the charges at the interacting atoms. The shortest H···O distance and the higher charges separation resulted in the highest heat of the complex formation. In particular, the *trans*-*e* isomer with a single C–H^9···O^{11} bond (complex between 1-acryloyloxymethyl-3,4-epoxycyclohexane with maleic anhydride) possessed the heat of formation 6.1 kJ/mol, the complex containing two bonds (H^{25}···O^6 and H^9···O^{11}) showed the heat of formation 13.8 kJ/mol, and the complex of the =C^5 and O^7 groups with maleic anhydride showed the 11.9 kJ/mol heat release [11]. The strongest interaction involving the carbonyl group of the 1-acryloyloxymethyl-3,4-epoxycyclohexane substituent with CH group of maleic anhydride possibly resulted from the high negative charge at the O^{11} carbonyl atom (≈–0.35 *e*) as well as the possibility of additional withdrawing of electron density from the O^9C^{10}(=O^{11})–C^{12}H=CH_2 group. That was confirmed by the increase in the positive charge at the C^{10} atom by 0.015 *e* and decrease in the negative charge at the O^9 atom by 0.006 *e* upon the complex formation. The formation of two complexes of the *cis*-*e* isomers, analogous to the complex between 1-acryloyl-oxymethyl-3,4-epoxycyclohexane with maleic anhydride, occurred without any hindrance, and the corresponding –Δ*H* values were close (Figs. 8 and 9).

However, the mutual influence of the oxirane ring and the carbonyl group in *cis*-*e*-1-acryloyloxymethyl-3,4-epoxycyclohexane form resulted in the formation of the complex with maleic anhydride via the C^2–H^9 and C^{10}=O^{11} bonds of the donor exclusively involving the vinyl group proton, the heat of formation of such complex with two hydrogen bonds being up to 18.2 kJ/mol [11]. In the cases of polar cyclic monomers the cyclic structures containing two or three hydrogen bonds were found (self-associates of the ketene acetal and 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]-nonane as well as their complexes with maleic anhydride and acrylonitrile) via the π-interaction, but their heat of formation was somewhat lower than that of 1-acryloyloxymethyl-3,4-epoxy-cyclohexane com-plex containing a single hydrogen bond.

Analysis of ^{1}H NMR spectra of the prepared polymers showed that complexation of the cyclic monomers in the reaction mixture influenced the radical process mechanism. In particular, the spectrum of copolymer of 8-methyl-2-methylene-1,4,6,9-tetra-oxaspiro[4.4]nonane with maleic anhydride isolated at

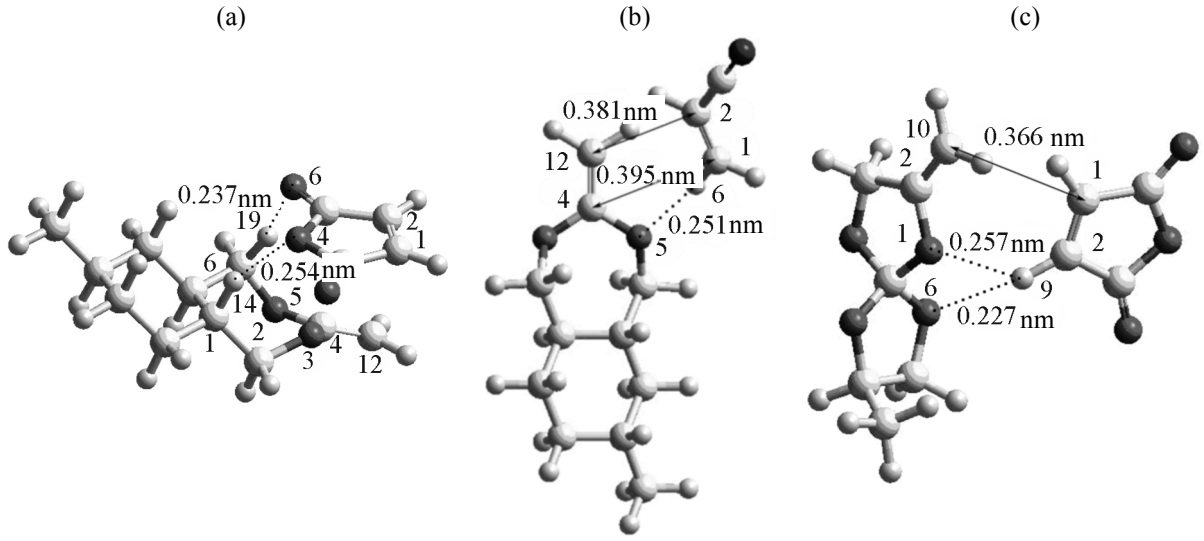


Fig. 9. General view of the complexes between (a) 4-methylene-3,5-dioxabicyclo[5.4.0]undecane and maleic anhydride, (b) 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane and acrylonitrile, and (c) 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]-nonane with maleic anhydride.

conversion of 7.5 wt % contained a multiplet at 4.13–4.08 ppm (Table 5) confirming the presence of a double bond in the OCH_2–C(=C$\underline{H}_2$)O unit of the spiro-*ortho*-carbonate. The appearance of a multiplet at 4.7–4.6 ppm evidenced the incorporation of the ketene acetal units with the preserved *exo* methylene-containing cyclic fragments in the polymer chain. The spectra of the copolymers with maleic anhydride and acrylonitrile showed strong signals at 4.8–4.0 ppm, pointing to the presence of the 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane units containing the CO–C$\underline{H}_2$–O–CO–O–C$\underline{H}_2$–-CH(CH_3)–C fragments in the chain; those units were formed in the course of copolymerization via opening of the methyl-containing ring. The methine proton signal at δ ≈ 5.1 ppm, corresponding to the OC$\underline{H}$(CH_3)CH_2, group, was negligibly weak. Methylene protons of the 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane units, not containing adjacent oxygen groups, gave a relatively narrow signal at 1.8–1.6 ppm. A signal at ≈1.4–1.2 ppm was assigned to the CH_3 group in the linear units of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro-[4.4]nonane formed via opening of both rings. Additionally, the spectra contained the weak doublets at δ ≈ 1.55, 1.52, and 1.22, 1.20 ppm corresponding to methyl groups in the preserved spirane structure and the dioxolane cycle.

The presence of self-associates or complexes formed via interaction of double bond of the *trans* isomers of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro [4.4]nonane with maleic anhydride in the reaction mixture resulted in the fragmentation polymerization via opening of double bond of the spiro monomer yielding units **I** and **II** and the formation of the linear chain fragments **IIIa** and **IIIb** in the course of further polymerization (Scheme 1).

In the cases of H-complexes of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane with maleic anhydride or with acrylonitrile, the polymerization

Scheme 1.

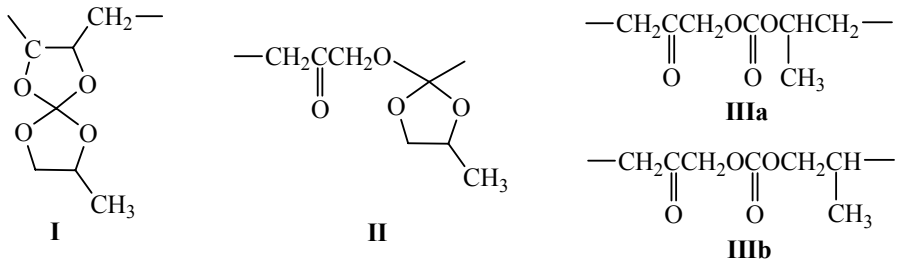


Table 5. Total content of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane units [m_1] and the fraction of its different structures in the copolymer chain as function of copolymerization conditions ([Sp–M]$_0$ denotes the fraction of the spiro monomer in the initial feed)

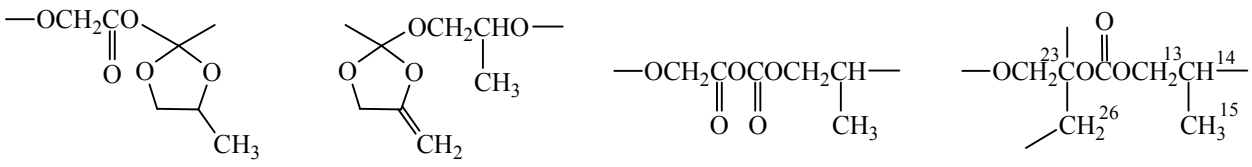
Copolymerization conditions			[m_1], mol %	Fraction of different units of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro-[4.4]nonane (mol %, with respect to the total content in the copolymer)					
[Sp–M]$_0$, mol %	T, K	conversion, wt %		**I**	**II** + **IV** + **V**	**III** + **VI**	**I** + **II** + **III**	**IV** + **V** + **VI**	**VII**
Copolymerization with maleic anhydride									
50	333	7.5	50	12	42	46	40	60	0
50	333	20.9	50	3	20	77	75	25	0
Copolymerization with acrylonitrile									
50	333	10.1	43	31	57	12	79	21	0
50	348	9.3	41	37	44	4	72	13	15
60	348	9.8	42	34	31	11	57	19	24
70	348	23.1	43	16	12	22	43	7	50
86	348	7.0	53	14	41	33	64	24	12
100	393	19.5	100	21	21	43	63	22	15

involved incorporation of units **IV** and **V** into the polymer chain; those units were further transformed into structure **VI** to give a double bond and fragments **VII** in the copolymers of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane with acrylonitrile at the conversion above 10 wt % (Scheme 2).

The fraction of spirane monomer units formed preserving the C=C bond was ≈60% relative to their total content in the copolymer of 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane with maleic anhydride at the conversion of 7.5 wt % (Table 5), decreasing to 25% at the conversion increasing to ≈21 wt %. For acrylonitrile (m_1) copolymers it was found that at conversion of 10 wt % (333 K, [m_1] = 43 mol %) the units with one closed ring prevailed in the copolymer chain, the branching reaction and the formation of structure **VII** were not observed (Table 5). With the conversion increased to 13.5 wt %, the amount of linear structures **III** and **VI** decreased by 11 mol % whereas the amount of the double bond-containing fragments **IV**, **V**, and **VI** was increased by 6 mol % due to the decreased fraction of structures **II** with a single dioxolane cycle. Increasing the polymerization temperature from 333 to 348 K (conversion of 9.3 wt %) decreased the amount of spirane structure **I** in the copolymer chain by 6 mol %, and about 15 mol % of branched structures **VII** appeared; simultaneously, the fraction of the structures with a single cycle (**II**, **IV**, and **V**) was down by 13 mol %, and the content of linear structures **III** and **VI** was down by 8 mol %.

Increasing the conversion to 23.1 wt %, other conditions being the same, decreased the fraction of spirane structure **I** and the oxolane structures **II**, **IV**, and **V** by 21 and 32 mol %, respectively (3.7 times), increasing the fraction of the linear structures **III** and **VI** by 18 mol % and that of the branched structures **VII** by 35 mol %; hence, the total fraction of the linear

Scheme 2.



IV **V** **VI** **VII**

8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane units was up from 19 to 72 mol % (3.8 times). Analysis of the NMR spectra showed that at the 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane units fraction of 41–55 mol % the chain structure was mainly governed by the total conversion of the monomers. The absence of signals at 6.41–6.39 ppm in the spectrum of the copolymer isolated at conversion of ≈21 wt % pointed at consumption of double bonds of maleic anhydride linear units in the course of copolymerization.

Assignment of all signals in ^{13}C NMR spectra of the copolymerization products of the ketene acetal with maleic anhydride was complicated; however, the signals at 50–40 ppm, absent in the spectra of the starting monomers, were assigned to the copolymer. The signal at 42.8 ppm and the IR $\nu_{C=O}$ absorption band at 1747 cm^{-1} corresponded to the ketene acetal units with the opened dioxepane ring. However, none of the ^{1}H NMR regions in the spectra of the co-polymerization products could be assigned to the integer number of protons, and their distribution was more complex than in the cases of the polymers formed via partial or complete opening of the oxygen-containing rings. Many narrow signals and no broadened ones in the spectrum of the isolated oligomer indicated that it was a mixture of relatively low-molecular products quite rich in methyl groups (their content being 1.4–1.5 times higher than in the starting ketene acetal). Such chain structure was possible in the case of the operation of the hydrogen transfer reactions resulting in the methyl-terminated side fragments and the fragments of ~C(=O)OCHC~ and ~OC(=O)CHC~ in the main chain. In view of that we studied in detail two regions of spectra with δ 5.0–4.9 and 2.8–2.6 ppm (corresponding to methine protons in the above-mentioned groups). As commented elsewhere [21], the characteristic signals at 2.8–2.6 ppm in combination with ^{13}C NMR data confirmed the branching reactions occurring in the course of free-radical polymerization of 2-methylene-1,3-dioxepane via 1,7- and 1,4- hydrogen transfer [21]. Hence, our results showed that similar reactions were typical of the (co)polymerization of the considered ketene acetal. Comparison of the signals intensity demonstrated that the ratio of the units with 1,7- and 1,4-branches was 1 : 4, their total content being 35 to 50 mol % in the case of the oligomer. Moreover, the double bond that could be formed via the chain termination was assigned to the broad IR absorption band at 1630 cm^{-1}. The presence of double bond in the chain of the ketene acetal copolymer with maleic anhydride allowed for interaction of the copoly-merization products with other unsaturated compounds.

To conclude, we have demonstrated that *cis* and *trans* isomers of the studied monomers can form complexes differing in the $\Delta_f H$ value and the influence on the copolymer chain growth. NMR data have confirmed the formation of oligomeric products containing seven types of the spiro monomer units. Their ratio can be controlled by altering the conversion in the copolymerization with maleic anhydride or acrylonitrile to obtain polymers differing in the chain microstructure. In particular, the UV-transparent composite material with good mechanical properties has been prepared basing on 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane polymer matrix. Such copolymers are promising components of glues with high adhesion to various materials (including Teflon), strong binders, durable coatings, and medical materials. Copolymers containing epoxy side groups and the branched ketene acetal units can be used for development of heat-resistant polymer coatings.

EXPERIMENTAL

1-Acryloyloxymethyl-3,4-epoxycyclohexane, 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane, and 9-methyl-4-methylene-3,5-dioxabicyclo[5.4.0]undecane were prepared as described elsewhere [10, 13, 22, 23]. Acrylonitrile, maleic anhydride, and the solvents were purified as described in [13].

Quantum-chemical simulation of geometry and electronic parameters of the individual molecules, self-associates, and complexes was performed using the AM1 (MOPAC7]) [24], Hartree–Fock (RHF), and density functional (DFT) {GAMESS (US) [25]} methods with the HF/6-31++G(d), B3LYP/6-31G(d), and B3LYP/6-311++G(d) [25–28] basis sets. Geometry optimization was run over all the independent parameters with the gradient rate of 0.002 (AM1) or 0.0001 (RHF and DFT); frequency analysis was performed under harmonic approximation. When applying the non-empirical methods, zero potential vibration energy (ZPVE) was computed along with the normal vibrations frequencies. The complexes configurations were identified by the absence of the imaginary frequencies in the vibration spectra. Association (or complex formation) energy) was calculated as the $\Delta E = E^{compl} - \Sigma E^{start}$ ($\Delta H = H^{compl}$ –

ΣH^{start}) difference, the ZPVE correction was used in the RHF and DFT simulations [28].

IR spectra of the solutions in CCl_4 were recorded at 4000–400 cm^{-1} (1 cm^{-1} data spacing) at 298 K using a Tensor 27 (Bruker) Fourier spectrometer equipped with 50 or 100 μm CaF_2 fluid cells; alternatively, solvent-free thin films were examined. IR spectra of the 0.015 g/mL solutions in $CHCl_3$ were recorded at 1900–1500 cm^{-1} and 2300–2150 cm^{-1} using a Specord IR-75 spectrometer equipped with 1.01–0.111 mm NaCl fluid cell.

^1H and ^{13}C NMR spectra of the solutions in $CDCl_3$ or CCl_4 were recorded with a Bruker Avance II (400 MHz) spectrometer at 298 K using TMS as internal reference and acetone-d_6 as external reference. Accuracy of the chemical shift determination was ±0.0005 ppm (^1H) and ± 0.001 ppm (^{13}C).

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