

QUASI-AROMATIC NATURE OF THE TAUTOMERIC UNITS OF SOME MALEIC ANHYDRIDE COPOLYMERS

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ABSTRACT

As a result of simultaneous joint transformations of repeating succinic anhydride (*an*) and adjacent vinyl chloride (or vinyl acetate) units the tautomeric enol (*en*) and dienol (*den*) derivatives having quasi-aromatic character are formed. The *en* and *den* units include high-energy ensembles C–O–H···Cl (or C–O–H···O) which take part in the cooperative interactions with nucleophilic reagents such as dimethyl formamide, NaNO₂, NaN₃ and others. Experimental assessment of the structure and reactivity of tautomeric units (IR, electron, ¹H and ¹³C NMR spectroscopy) is found to be consistent with the results of quantum-chemical (GAUSSIAN, B3LYP/6-31G(d); ADF, BP86/TZ2P) calculations. High energy transition state ensembles [^{δ+}C–O–H···Cl][#] (or [^{δ+}C–O–H···O][#]) appear to be the reaction centers of their interactions with DMF, NaNO₂, NaN₃ while reactions with the cyclic ethers (tetrahydrofuran, 1,4-dioxane) proceed *via* oxonium compounds.

Keywords: *Quasi-aromatic ensembles; skeletal rearrangements; cooperative interactions; tautomeric units; maleic anhydride copolymers; quantum-chemical modeling*

1. INTRODUCTION

It is since the 1970-s a great number of maleic anhydride (MA) copolymers and products of their chemical modification have been used in production of various coatings, as additives in the oil processing and its transport. They happen to be convenient initial products for synthesis of new copolymers which are used as active biologic substances, enzyme carriers, pore-forming materials, lubricants and other materials [1–4].

The long-term absence of the comprehensive and exhaustive knowledge of the structure and chemical properties of MA copolymers restrained the researches. That's why one could find an inadequate estimate of some MA copolymers properties in the literature. So contrary to the customary concept of the structure and reactivity of macromolecules of MA copolymers we have detected their ability to form charge-transfer complexes (CTC) with various reagents, this ability to be the effect of cyclohydride-enol tautomerism (CAET) which was unknown up to our work [5]. Triadic prototropic tautomerism includes several types with participation of C–N–O, C–C–N, N–C–N and C–C–C atoms and only two types with participation of C–C–O atoms, one of which is classical keto-enol and the other – the CAET. The consequence of the CAET is a skeletal rearrangement with the formation of nonlinear four-centered molecular (NFM) ensembles in the enol (*en*) and dienol (*den*) units of the macromolecules. It is the NFM ensembles that predetermine their unique behavior in compliance with the "substrate-reagent" type cooperative interactions, the reagents acting the role of chemical probes [6]. The use of the latter for probing of the *en* and *den* units to predict chemical behavior of the macromolecules is practically important for investigation of complex chemical and biological ensembles.

High affinity of MA copolymers to water and other substances and different solvents, on the one hand restricts their usage but, on the other hand, it allows one to employ their reactivity for development of new methods of chemical modification. Such approach allows us to develop the ways of improvement of MA copolymers by modification using various substances and solvents too. Cyclic ethers such as tetrahydrofuran (THF) and 1,4-dioxane are not only the solvents of the MA copolymers but they happen to be specific reagents. It is known that the rings of THF can be broken under influence of various catalysts, six-member 1,4-dioxane cycles easily form peroxides [7, 8]. That's why using the cyclic ethers as modifying agents of MA copolymers is of scientific and commercial interest.

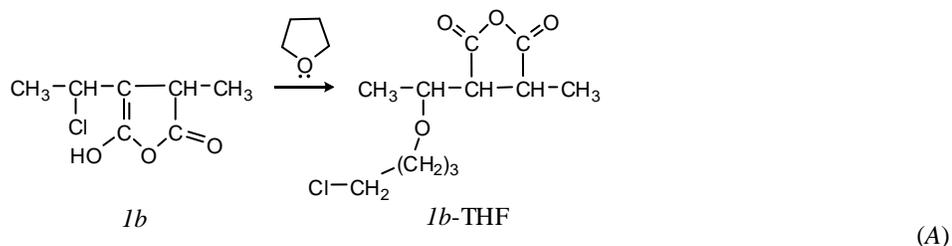
The aim of this paper is to survey our previous work to reveal the unconventional reactivity and the structure of vinyl chloride and vinyl acetate binary MA copolymers by means of the characteristics of their cooperative interactions with DMF, tetrahydrofuran and other nucleophiles by experimental and theoretical (quantum-chemical) methods. Such an approach will make it possible to solve many problems of MA copolymers *a priori*.

2. EXPERIMENTAL

The synthesis of the vinyl chloride-maleic anhydride (VCMA) copolymer and its identification are described in [5] and those of vinyl acetate-maleic anhydride (VAMA) copolymer – in [9]. Intermolecular and cooperative reactions with nucleophilic reagents (DMF, NaNO₂, NaN₃ etc.) are describe in [10–12] in detail, and those with THF and 1,4-dioxane – in [13].

Mathematical modeling of the copolymers microstructure [10] allowed us to construct the formulae of low molecular analogues (LMA) of the repeating units of macromolecules (Fig. 1) in order to carry out the quantum chemical computations.

Estimation of the possibility of the reaction between THF and LMA *1b* was carried out by means of quantum-chemical modeling of their interaction:



The calculations were carried out by the Hybrid method of the Density Functional B3LYP with the exchange functional of Becke B3 [14], and the correlative functional Lee, Yang and Parr (LYP) [15]. For all the atoms the 6-311+G(2d,p) full-electron basic set with diffuse and polarization functions was used which turned out to be the best from the point of view of accuracy and efficiency. All calculations were carried out by means of the standard package of the GAUSSIAN'03W program [16]. The polarization continuum method (PCM) for modeling in acetonitrile medium was used in the GAUSSIAN program. The stationary character was confirmed by the absence of imaginary vibration frequencies. Dissociation energies of the calculated molecules were corrected taking into account the zero-vibration energy and reduced to the standard conditions (298.15 K, 1 atm) using thermal amendment for enthalpy and free energy. The carbon atoms rehybridization leading to new tautomeric ensembles (Fig. 1)



was carried out using the natural bond orbital method [17]. On the other hand the selected molecules and the complexes were also studied using the ADF program (Amsterdam Density Functional) [18, 19]. We have used the BP86/TZ2P+ functional [20]. Two different DFT methods were used to evaluate whether CAET could in principle occur. These methods are based on the density functional theory with both comparable functionals and basis sets. Despite the fact that both programs use different basis functions (GAUSS and Slater) the symbasis of the tautomeric ensembles series stability, obtained by both programs, designates a reliable description of the processes (B).

The IR spectra were recorded on the Nicolet 5700 IR Fourier-transform spectrophotometer (Thermo Electron, USA), ¹H and ¹³C NMR spectra were obtained on the Bruker Avance AV 300 NMR spectrometer (Bruker, Germany) with an operating frequency of 300 MHz at 25 °C in d₆-acetone and DMSO (10 mass. %) [13].

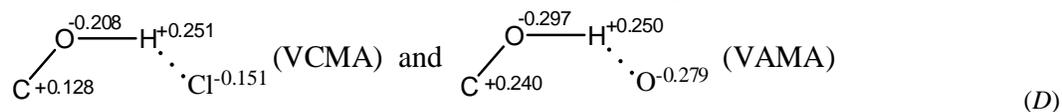
Thermal analysis of the samples was carried out on the differential scanning calorimeter DSC 204 Phoenix (NETZSCH, Bavaria/Germany) in helium atmosphere (0–200 °C) and in the oxidizing one (air, 25–500 °C) at 10 degrees per minute heating rate.

To prevent the hydrolysis of the succinic anhydride rings the experiments were carried out under conditions excluding contact with atmospheric moisture.

3. RESULTS AND DISCUSSION

3.1. Quasi-aromatic ensembles as the centers of unconventional reactivity

The *en* and *den* quasi-aromatic ensembles as the result of the CAET in the VCMA and VAMA macromolecules contain the NFM structures of the horseshoe shape (Fig. 1) with alternating charges calculated by NBO approach:



which predetermine their unique behavior in relation to many nucleophilic reagents (DMF, NaNO₂, NaN₃, THF, 1,4-dioxane etc.) [9–11]. Fig. 1 demonstrates the LMA of the copolymers tautomeric units in question.

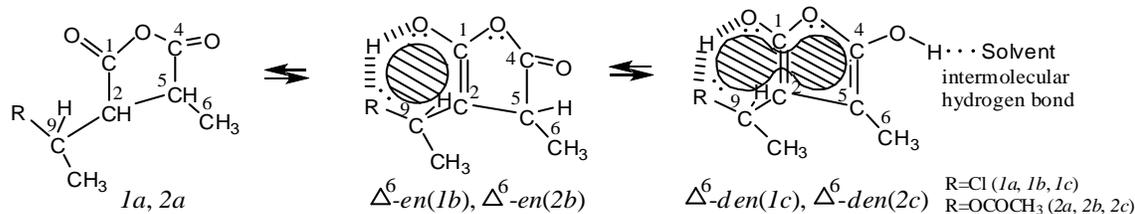


Figure 1. Cycloahydride-enol tautomers of the LMA of the VCMA and VAMA copolymers: 3-(1-chloroethyl)-4-methyl-dihydrofuran-2,5-dione – the LMA of the an VCMA tautomer (1a); 4-(1-chloroethyl)-5-hydroxy-3-methylfuran-2(3H)-one – the LMA of the en VCMA tautomer (1b); 3-(1-chloroethyl)-4-methylfuran-2,5-diol – the LMA of the den VCMA tautomer (1c); 1-(4-methyl-2,5-dioxotetrahydrofuran-3-yl)ethyl acetate – the LMA of the an VAMA tautomer (2a); 1-(2-hydroxy-4-methyl-5-oxo-4,5-dihydrofuran-3-yl)ethyl acetate – the LMA of the en VAMA tautomer (2b); 1-(2,5-dihydroxy-4-methylfuran-3-yl)ethyl acetate – the LMA of the den VAMA tautomer (2c).

The *en* and *den* quasi-aromatic ensembles in the macromolecules are formed as a result of the intramolecular hydrogen bond (intra HB) formation with the simultaneous tautomerism which is accompanied by delocalization of the electron density inside the six-member Δ^6 -*en* or adjacent six- and five-member Δ^6 -*den* rings [21]. The six-member rings with two *p*-electrons of the $^1\text{C}=\text{C}$ π -bond and two *p*-electrons of oxygen of the hydroxyl groups and two ones of Cl atoms together with two «electron holes» participate in the electron density delocalization of the Δ^6 -*en* ensembles. Similar delocalization in the VAMA takes place, oxygen atoms of the OCOCH_3 groups acting the part of Cl in the VCMA. Fig. 1 shows this process as an example of the tautomerism of the LMA 1a, 1b, 1c and 2a, 2b, 2c chosen for quantum-chemical calculations. The quasi-aromaticity of the *en* and *den* ensembles decreases the energy of the system due to the conjugation (Fig. 1) additionally.

Thus, the intermolecular bond, the intra HB formation and appearance of the conjugation which is realized in the quasi-aromatic state in the Δ^6 -*en* and Δ^6 -*den* ensembles are the mainspring of the CAET.

A stable hydrogen bond is being formed preceding the closure of the Δ^6 cycles [22], so a rehybridization of the ^1C , ^2C , ^4C and ^5C carbon atoms in stereo chemically favorable units from tetrahedral (C_{sp^3}) to trigonal (C_{sp^2}) configurations takes place: $1a \rightleftharpoons 1b \rightleftharpoons 1c$ and $2a \rightleftharpoons 2b \rightleftharpoons 2c$ (Fig. 1). This follows from the results of the quantum-chemical modeling of the *an*, *en* and *den* tautomer structures using the natural bond orbital method: the ^2C carbon atom is $\text{C}_{\text{sp}^{3.4}}$ in the *an* units and the same carbon atom is $\text{C}_{\text{sp}^{1.96}}$ in the *en* units. Moreover as a result of the modeling of the *en* and *den* tautomers pure *p*-type orbitals appear [23].

The experimental NMR spectra of the VCMA copolymers indicate the presence of the *an*, *en* and *den* tautomers. Comparison of these spectra of the VCMA copolymers where signals of hydroxyl protons and aromatic carbon atoms have been found with NMR spectra of the 1a, 1b and 1c calculated (Fig. 2, Table 1) testifies to the correctness of the LMA choice.

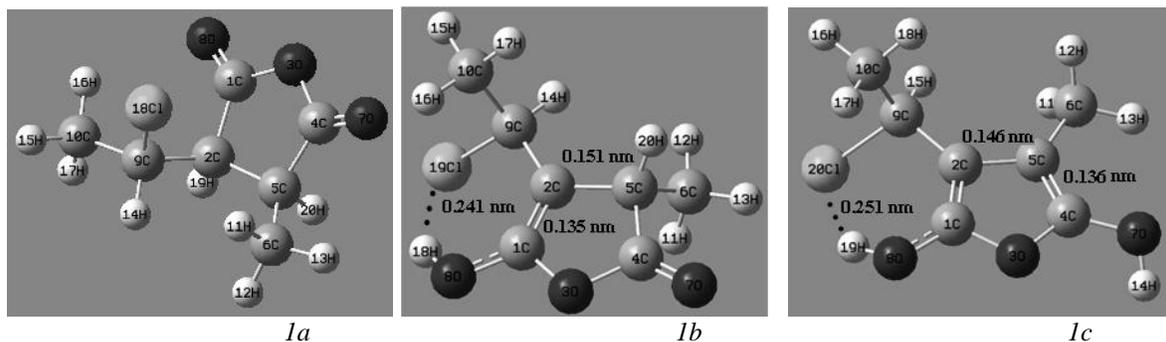


Figure 2. Low molecular analogues of the *an*, *en* and *den* VCMA tautomers (GAUSSIAN, B3LYP/6-31G(d)).

In the NMR ^{13}C spectrum of the 1a compound there are signals of the aliphatic (^2C , ^5C , ^6C , ^9C , ^{10}C) and carbonyl (^1C , ^4C) carbon atoms. The NMR ^{13}C spectrum of the 1b has signals of the aliphatic (^5C , ^6C , ^9C , ^{10}C) and carbonyl (^1C , ^4C) carbon atoms and a signal of the trigonal carbon atoms (^2C in Fig. 2) which is attributed to the enol units.

They appear as a result of the skeletal rearrangements $an \rightleftharpoons en$. In calculated NMR ^{13}C spectra of the *den* VCMA tautomers (1c) there are signals of the carbon atoms in the region of 105-156 ppm which can be referred to the aromatic carbons (Fig. 2, Table 1).

Table 1. Calculated chemical shifts of the 1a, 1b and 1c compounds (see Fig. 2) and experimental ones of the corresponding VCMA copolymer units.

Signal assignment	1a δ , ppm		1b δ , ppm		1c δ , ppm	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
$^{13}\text{C}(1)$	160-180 (region E)	178.19 $^1\text{C}=\text{O}$	160-180 (region E)	165.88 close to $^1\text{C}=\text{O}$	120-150 (region D)	156.38 $^1\text{C-Ar}$
$^{13}\text{C}(2)$	50-70 (region B)	56.82 $^2\text{CH-CHCl}$	90-120 (olefinic carbon atoms region)	93.18 $=^2\text{C-CHCl}$	90-120 (olefinic carbon atoms region)	105.64 $=^2\text{C-CHCl}$
$^{13}\text{C}(4)$	160-180 (region E)	181.54 $^4\text{C}=\text{O}$	160-180 (region E)	181.54 $^4\text{C}=\text{O}$	120-150 (region D)	151.54 $^4\text{C-Ar}$
$^{13}\text{C}(5)$	10-50 (region A)	44.52 $^5\text{CH-CH}_3$	10-50 (region A)	48.43 $^5\text{CH-CH}_3$	90-120 (olefinic carbon atoms region)	100.00 $=^5\text{C-CH}_3$

Earlier the quantum-chemical assessment of the geometry and energy of the LMA of VAMA repeating units (2a, 2b and 2c) was carried out [9]. Adjacent six- and five-member rings are located in one plane. The $\text{O}-^9\text{C}-^2\text{C}$ angle is equal to 116° , i.e. the ^9C atom is sooner trigonal than tetragonal and it provides the coplanarity of the rings (Fig. 1). The $\text{H}\cdots\text{O}$ distance in the 2b compound is 0.171 nm and in the 2c compound it equals to 0.191 nm which is less than the sum of the van der Waals radii of the corresponding atoms (0.25 nm).

Thus the results of the quantum-chemical calculations of the geometry of the *en* and *den* VAMA tautomers [9] and those of the calculated chemical shifts denote probability of the trigonal carbon atoms. The presence of the trigonal carbon atoms in the VCMA and VAMA macromolecules is confirmed experimentally: signals of the OH protons are registered in the ^1H NMR spectra of the VCMA and VAMA copolymers whose appearance is possible only at the trigonal carbons ^1C and ^4C (Fig. 1, Fig. 2) [24]. Signals of the aromatic carbon atoms are registered in the ^{13}C NMR spectra of the copolymers (Fig. 3) [9]. The A and B regions have signals of the aliphatic carbon atoms; signals of the ^{13}C carbonyl groups are registered in the D region and those of aromatic carbon atoms – in the region E.

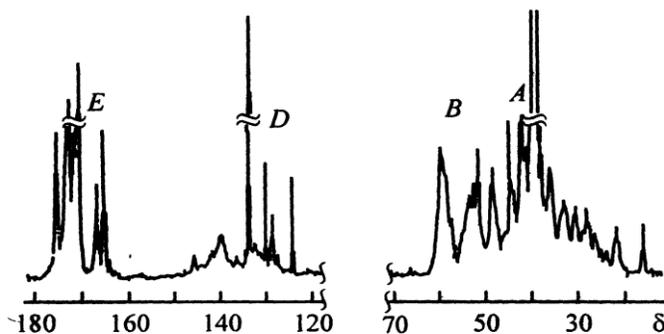
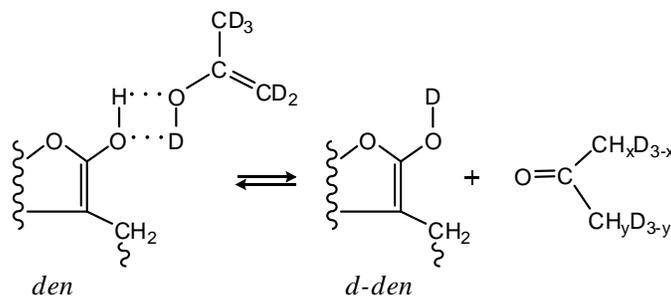


Figure 3. ^{13}C NMR spectrum of the VCMA copolymer in DMSO.

The unambiguous evidence of the hydroxyl protons presence is the reaction of deuterioexchange proceeding in the solution of VCMA in deuterioacetone:



The intensity of the OH signal decreases 4 times within 3.5 h whereas the intensity of the CH_3 groups signal increases by the same value as a result of the deuterioexchange [25].

Aromaticity can be detected by registration of the $\pi \rightarrow \pi^*$ band in the range of 250-300 nm. The electron spectra of the freshly prepared VCMA solutions contain one $\pi \rightarrow \pi^*$ absorption band B ($\lambda_{\max}=246$ nm, 1 in Fig. 4) in the Δ^6 -*en* ensembles. The quasi-aromatic state is formed in the course of time: a new band 2 (E) appears at $\lambda_{\max}=268$ nm. In the structural combination of adjacent five- and six-member rings (Δ^6 -*den*) the delocalization of ten-electron density proceeds as a result of the quasi-aromatic system being formed (Fig. 1, Fig. 4) [26]. As a structural molecular ensemble Δ^6 -*den* can be compared with the molecule of 2,3-benzofuran. Really the spectrum becomes similar to that of the 2,3-benzofuran in heptane solution in several days. In electron spectrum of the VAMA solutions in DMF there is a band at $\lambda_{\max}=264$ nm. The intensity of this band grows within 8 days and then slowly falls down due to the processes of formation and destruction of quasi-aromatic ensembles in the copolymer solution [9]. The IR spectra of the VAMA films containing remnants of DMSO as a high boiling solvent have strong absorption bands $\nu_{C=C}$ (1660-1680 cm^{-1}) and ν_{O-H} (3450 cm^{-1} , wide) and weaker bands $\nu_{C=O}$ (1870-1720 cm^{-1}). The IR spectra of the VAMA films free from DMSO [27] contain strong $\nu_{C=O}$ bands. The same picture is observed for the VCMA films [28].

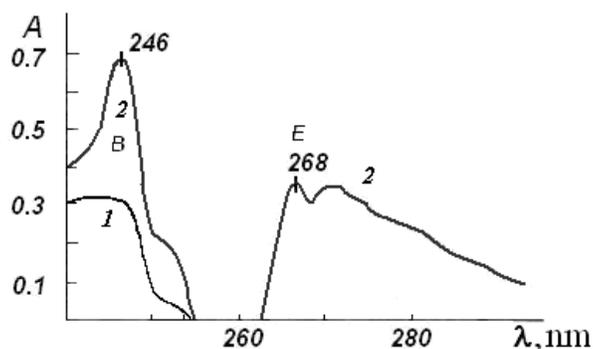


Figure 4. Electron absorption spectra of the freshly prepared VCMA solution $3.34 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ in dioxane (1) and that of the same solution in 4 (2) days.

Finally, earlier we have synthesized the well known chloromethylsuccinic anhydride (4-(chloromethyl)dihydrofuran-2,5-dione) [29, 30] from itaconic anhydride to be used as an available (alternative) low molecular model compound. Chemical behavior of the chloromethylsuccinic anhydride has shown that it undergoes the CAET as well [31]: the IR spectrum contains absorption bands due to the stretching vibrations of the OH and the C=C groups. In the ^1H NMR spectrum in deuterioacetone the signals of the OH protons of the enol tautomers have been registered [31]. It is interesting to note that an enol tautomer of 3-(methoxycarbonyl)-2*H*-pyran-2,4-(3*H*)-dione was obtained both in solution and in solid state, which according to B3LYP/6-31G** calculations is 7.7 kcal/mol more stable. This enol is an enol derivative of the cyclic anhydride [32].

Good correlation of the results of various instrumental methods of the CAET investigation invited us to use a noninstrumental one to describe these processes. The mutual transitions of the tautomeric forms may be considered from the point of view of their relative thermodynamic stability. Comparison of the calculated thermodynamic characteristics of the *an*, *en* and *den* (1*a*, 1*b*, 1*c* and 2*a*, 2*b*, 2*c* LMA) has shown that the ΔG values of the 1*c* (-12 kcal/mol) and 2*c* (-18 kcal/mol) model compounds are higher than the same characteristics of the rest LMA. As it should be expected, the stability of all model compounds in solution is higher than that in vacuum. As expected the ΔG values of the 2*a*, 2*b* and 2*c* compounds decrease in the series:

$$2c \text{ (-18 kcal/mol)} > 2b \text{ (-16 kcal/mol)} > 2a \text{ (-9 kcal/mol)}.$$

The assessment of the relative stability of the *an*, *en* and *den* VCMA tautomers by mathematical modeling has been investigated earlier [10, 24, 26].

3.2. Cooperative interactions of quasi-aromatic ensembles with nucleophilic reagents

Unique reactivity of the VCMA and VAMA copolymers towards various nucleophilic reagents is due to the quasi-aromatic ensembles formed in their macromolecules. All the *en* and *den* VCMA and VAMA tautomers contain NFM ensembles (*D*) of the horseshoe shape which react with the DMF molecules of the same shape acting the role of a chemical probe. It is the NFM ensembles of these units in accordance with their geometric and electrostatic complementarities which interact with the NFM ensembles of DMF molecules forming the CTC in the long run.

The VCMA copolymer solution in DMF becomes slightly pink and two new overlapping bands at $\lambda_{\max}=534$ and 560 nm are registered. Absorbance of the band at 560 nm reaches the maximum in several hours and remains constant within 5 days *ca* (Fig. 5).

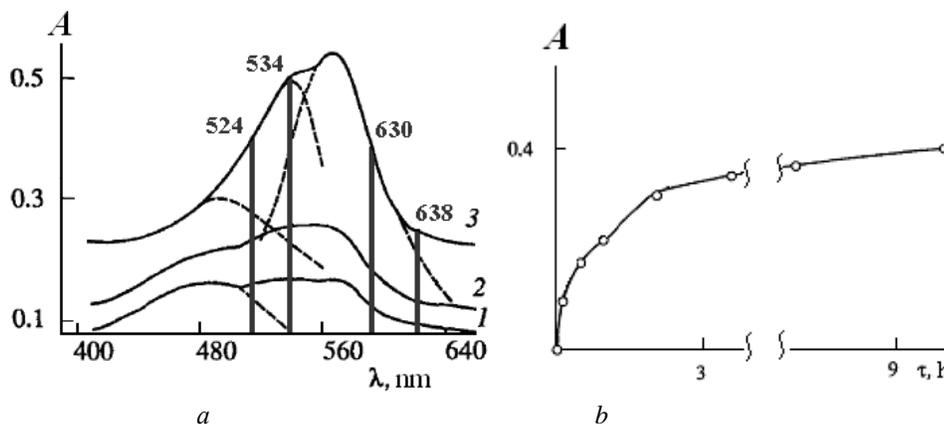


Figure 5. Electron absorption spectra of the VCMA solution in DMF ($l=1$ cm, $c=4 \cdot 10^{-2}$ mol/L) in 3 (1), 30 (2) and 120 min (3) after mixing (a). Absorbance of the 560 nm band of the same solution (b). The calculated values of λ_{\max} are 524, 534, 630 and 638 nm (GAUSSIAN).

The quantum-chemical analysis of the electron density distribution in the CTC allows us to represent the shape of the HOMO-1 and HOMO-2 and the LUMO molecular orbitals in the $1c \cdots \text{DMF}$ complex. Both the experimental electron spectra of the copolymer solutions [11] and the calculated one of the LMA [23] contain a number of identical bands due to the transitions from the occupied onto free energy levels [6]. Fig. 6 shows the electron density distribution in the CTC structure $1c \cdots \text{DMF}$ and Table 2 shows the calculated (GAUSSIAN) wavelength values of the electron spectrum of this structure and the assignment of the single-electron energy levels. The $\lambda_{\max} = 524$ band is due to the transition from HOMO-3 level where the unshared electron pairs of Cl_p are settled onto the LUMO where the electron density (the *den* fragment ring) is distributed. The $\lambda_{\max} = 534$ nm band is a consequence of the HOMO-2 \rightarrow LUMO transition which is associated with the electron density distributed on the DMF molecule. The $\lambda_{\max} = 630$ and 638 nm bands correspond to the change in the electron distribution in the *den* fragment (HOMO-1 \rightarrow LUMO and HOMO \rightarrow LUMO transitions, Fig. 6, Table 2). Discrepancy of the calculated and experimental λ_{\max} values by 40-70 nm is apparently due to unforeseen intramolecular and intermolecular interactions (the calculated length of H-bond between DMF and *en*, *den* is equal about 1.64 Å).

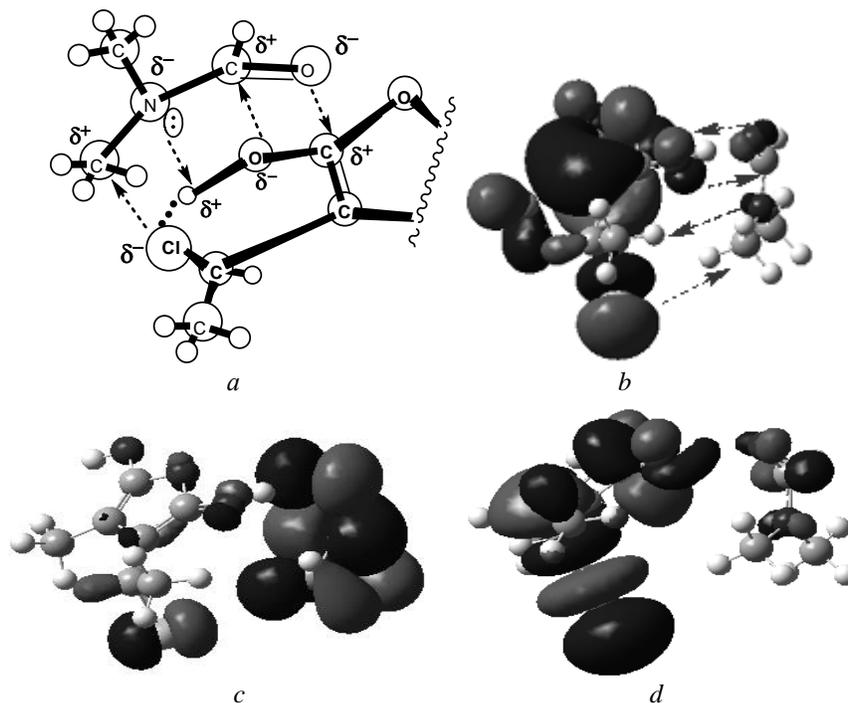
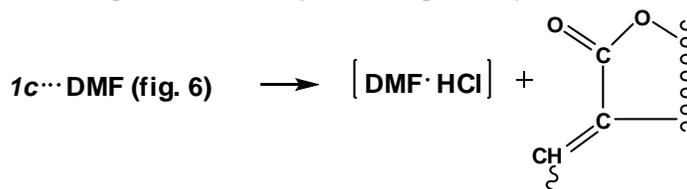


Figure 6. Scheme of formation of the $1c \cdots \text{DMF}$ CTC via four-centered mechanism (a) and the electron density distribution on the HOMO-1 (b), HOMO-2 (c) and LUMO (d) in the CTC $1c \cdots \text{DMF}$ structure.

Table 2. Calculated electronic spectrum of the $1c \cdots \text{DMF}$ complex.

Wavelength, nm	Single-electron transition	Assignment
524	(HOMO-3)→(LUMO)	$\text{Cl}_p \rightarrow \text{den}$
534	(HOMO-2)→(LUMO)	$\text{DMF} \rightarrow \text{den}$
630	(HOMO-1)→(LUMO)	$\text{den} \rightarrow \text{den}$
638	(HOMO)→(LUMO)	$\text{den} \rightarrow \text{den}$

The calculation of thermodynamic characteristics (GAUSSIAN, B3LYP/6-31G(d) and ADF, BP86/TZ2P) of the CTC $1c \cdots \text{DMF}$ formation (Fig. 6) is reported in [6]: the $\Delta H_{\text{CTC}} = -9$ kcal/mol and the $\Delta E_{\text{CTC}} = -3$ kcal/mol. Decomposition of the $1c \cdots \text{DMF}$ complex in several days is accompanied by HCl elimination [33]:



High reactivity of the MA copolymers to solvents and various substances allows one to carry out new and unexpected reactions of the copolymers. Cyclic ethers such as THF and 1,4-dioxane despite their relative stability act as specific agents of the structure and properties control of the VCMA copolymers in soft conditions [13]. The $\Delta^6\text{-en}$ VCMA units are found to react with THF and 1,4-dioxane cyclic molecules which open themselves with simultaneous grafting. The $[\text{Cl} \cdots \text{H}-\text{O}-\text{C}^{\delta+}]$ ensembles appear to be the reaction centers causing the cycles break. The former are the intermediate compounds promoting formation of the oxonium transition state (Fig. 7).

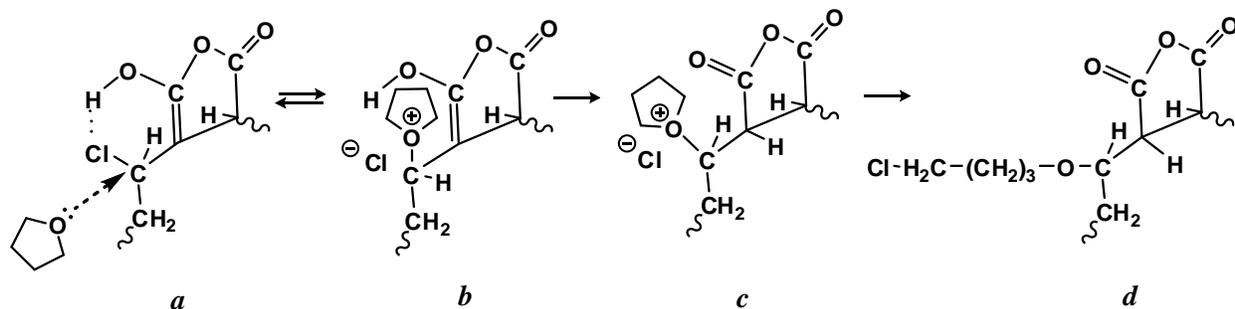


Figure 7. Probable mechanism of THF cycles grafting on the VCMA macromolecules.

Formation of the d units (Fig. 7) is favorable, the calculated $\Delta H/\Delta G$ and the ΔE values of the model reaction of the LMA ($1b$) with THF (A) both in vacuum and in solution testifies to it. In accordance with the ΔH , ΔG and ΔE values of the process (A) formation of the $1b$ -THF derivatives (its polymer analog is the d unit in Fig. 7) is favorable both in vacuum ($\Delta H = -28.8$ kcal/mol, $\Delta G = -18.8$ kcal/mol, $\Delta E = -20$ kcal/mol) and in solution ($\Delta H = -39.5$ kcal/mol, $\Delta G = -33.9$ kcal/mol, $\Delta E = -21$ kcal/mol).

The chains of the opened THF (or 1,4-dioxane) cycles grafted on the VCMA macromolecules (Fig. 7d) make them hydrophobic and promote active combustion of these samples under thermo-oxidative conditions. On the differential scanning calorimeter (DSC) curve of the original VCMA sample (helium, Fig. 7a) the endothermic effect at 65 °C caused by the adsorbed water loss is observed. It testifies to hydrophilic nature of the original nonmodified copolymers contrary to those treated by THF or 1,4-dioxane. On the DSC curves of the VCMA samples treated by THF (or 1,4-dioxane) there is no endothermic effect in that region. It testifies to hydrophobization of the initial samples of copolymers by means of methylene and Cl groups of the opened THF or 1,4-dioxane cycles.

Thus the THF and 1,4-dioxane cyclic ethers are not only good solvents of MA copolymers but they are also reagents if the CAET occurs in their macromolecules.

4. CONCLUSIONS

4.1. High reactive quasi-aromatic structures appearing in the VCMA and VAMA macromolecules as a result of the skeletal rearrangements of the tetragonal carbons (C_{sp^3} in the anhydride cycles) into trigonal (C_{sp^2} in the enol and dienol units) are experimentally ascertained. The results of quantum-chemical calculations of the corresponding low molecular analogues have confirmed the probability of the formation of the quasi-aromatic ensembles in the macromolecules of the MA binary copolymers with vinyl chloride and vinyl acetate in the enol and dienol forms.

4.2. Calculations by the density functional method allowed us to estimate the thermodynamic characteristics both of the model analogues of the *en* and *den* units and of the charge-transfer complexes of the VCMA units with DMF as a chemical probe. Characteristics of the low molecular analogues of the VCMA and VAMA copolymers units and those of the complexes of the VCMA units with DMF calculated both by the GAUSSIAN and ADF program packages were found to be close to the experiment. This method with DMF as a chemical probe can be applied for assessment of the structure and reactivity *a priori*.

4.3. The enol and dienol tautomeric units of the VCMA copolymers react with THF and 1,4-dioxane molecules to form the side hydrophobic substituents. Reactive centers in these reactions are the high-energy NFM ensembles which take part in the formation of the transition cyclic oxonium ions with their subsequent opening. Short chains of the THF (1,4-dioxane) opened cycles grafted on the VCMA macromolecules promote the hydrophobicity of the products.

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