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Molecular Weight Parameters of Cellulose Nitrates Modified with Alcohols

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Abstract—We have studied molecular weight parameters of the products prepared via chemical modification of cellulose nitrates with aliphatic alcohols. Proceeding from the quantum-chemical simulation data the most probable pathways of degradation of cellulose nitrate macromolecules have been elucidated.

Keywords: cellulose nitrate, molecular weight, polydispersity coefficient, macromolecule degradation, quantum-chemical simulation

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Structure of cellulose esters and ethers produced via chemical modification of cellulose nitrates has been frequently investigated [1–7]. The data collected have revealed that generally in the course of interaction of cellulose nitrates with nucleophilic agents three types of processes occur simultaneously: reactions of nitrate groups, reactions of hydroxy groups, and polymer chains degradation via cleavage of the glycoside bonds. Reactivity of each of the reaction centers depends on their chemical surrounding, the solvent nature, the catalyst, and the attacking reagent. In the course of the interaction, the charge distribution is changed and so does the substrate reactivity.

In our previous paper [8] we described procedures to prepare cellulose nitrates chemically modified with aliphatic alcohols: ethanol, isopropanol, butanol, and amyl alcohol.

In [6] the modification of highly nitrogenated cellulose nitrate was described, the substrate empirical formula being $C_6H_7O_2(OH)_{0.87}(ONO_2)_{2.13}$ (11.56 wt % N). The chemical modification was performed in homogeneous pyridine medium; being a base, pyridine acted both as nucleophilic catalyst and as proton acceptor [9].

The experimental data reported in [8] allowed arranging aliphatic alcohols in series according to their reactivity in the nucleophilic substitution reactions: $C_5H_{11}OH < (CH_3)_2CHOH < C_4H_9OH < C_2H_5OH$. It was demonstrated that in the course of modification the following processes occurred simultaneously: substitution of the nitrate groups with the alkoxy ones, hydrolysis, glucopyranose ring opening, and the main chain degradation to form soluble organic products. The structure of elementary units appearing via substitution of the nitrate groups with the alkoxy ones was confirmed by IR and ^{1}H NMR spectroscopy data.

In all cases, the intrinsic viscosity of the products solutions in acetone was lower than that of the initial cellulose nitrate solutions, thus demonstrating the decrease in the polymer molecular mass. The intrinsic viscosity reflected exclusively the relative change of the viscosity-average molecular mass, providing no information on the molecular weight distribution of the macromolecules. In order to fill in the gap, in this work we applied the gel permeation chromatography (enabling fractioning macromolecules with respect to their molecular mass) to elucidate the molecular weight parameters of the mixed esters of cellulose.

Table 1. Molecular weight parameters as determined with polystyrene standards

Run no.	Compound	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
1	$C_6H_7O_2(OH)_{0.87}(ONO_2)_{2.13}$	5398	25428	148418	4.71
2	$C_6H_7O_2(OH)_{1.39}(C_2H_5O)_{2.21}(ONO_2)_{0.1}$	894	1891	6619	2.11
3	$C_6H_7O_2(OH)_{1.6}(i\text{-}C_3H_7O)_1(ONO_2)_{0.5}$	1041	2307	5592	2.215
4	$C_6H_7O_2(OH)_{1.1}(C_4H_9O)_{2.01}(ONO_2)_{0.22}$	1298	4192	13644	3.227
5	$C_6H_7O_2(OH)_{1.4}(C_2H_5O)_{1.93}(ONO_2)_{0.25}$	1322	4219	13782	3.191

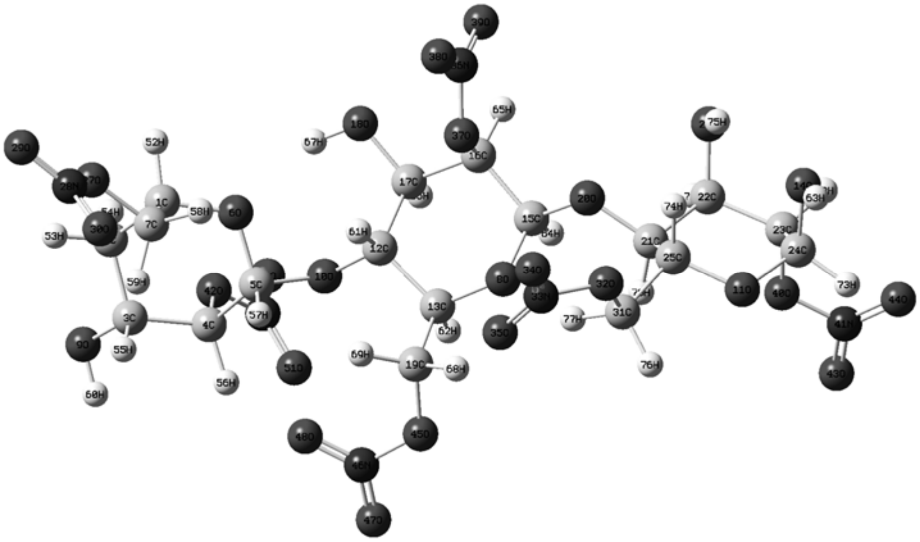
The ultimate goal of this work consisted in investigation of the alcohols reactivity in the processes of backbone degradation of cellulose nitrate.

The experimental data collected in Table 1 demonstrate that in all cases the studied interaction was accompanied with the pronounced degradation of the macromolecules: that was reflected in the decrease of both $\bar{M}_n$ and $\bar{M}_w$ values. The weight-average molecular mass of the starting cellulose nitrate was 25428 (polystyrene equivalent), significantly higher than that of any of the alcohol-modified samples.

In the course of the degradation process, the molecular mass of the sample became more uniform: polydispersity index of the modified products (2.2–3.2) was much less than that of the initial cellulose nitrate (4.7). The polydispersity index of the samples modified with ethanol or isopropanol was lower than those treated with butanol- or pentanol. The lower polydispersity of a polymer means a lesser dispersion of its properties across the sample and therefore more stable technology and utilitarian properties. Noteworthily, $\bar{M}_w$ of the products of cellulose nitrate interaction with butanol or amyl alcohol was somewhat higher than that of the other products.

The random degradation of polymer chains (with equal probability of the cleavage of all the macromolecule bonds) should have led to a polydispersity of 2. However, in the studied cases, the degradation was likely not random. Firstly, traces of the gel fraction were found in sample no. 5, with molecular mass of 1400000. Secondly, molecular mass distribution of the sample was bimodal: besides the basic peak with maximum at $\bar{M}_w$ of 1778, the additional maximum with $\bar{M}_w$ of 56234 was observed.

To find the reactive site attacked in the course of the degradation process as a function of the reacting species, we performed quantum-chemical simulation of cellulose dinitrate (see Experimental). The structure of the conformer with the lowest energy is shown in the figure, the Mulliken charges are compiled in Table 2.



Structure of cellulose dinitrate conformer.

Table 2. Mulliken atomic charges in cellulose dinitrate molecule as calculated by the AM1 method

Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
^{1}C	0.043970	^{21}C	–0.027903	^{41}N	0.659147	^{61}H	0.139653
^{2}C	–0.192589	^{22}C	0.029985	^{42}O	–0.228937	^{62}H	0.121500
^{3}C	0.040904	^{23}C	–0.025170	^{43}O	–0.278751	^{63}H	0.238526
^{4}C	–0.036829	^{24}C	0.127541	^{44}O	–0.356212	^{64}H	0.106845
^{5}C	0.139487	^{25}C	0.020450	^{45}O	–0.241778	^{65}H	0.174159
^{6}O	–0.299647	^{26}O	–0.288836	^{46}N	0.662010	^{66}H	0.108872
^{7}C	–0.057762	^{27}O	–0.258238	^{47}O	–0.270197	^{67}H	0.240573
^{8}O	–0.302596	^{28}N	0.659822	^{48}O	–0.403137	^{68}H	0.174722
^{9}O	–0.294575	^{29}O	–0.282727	^{49}N	0.663575	^{69}H	0.129528
^{10}O	–0.272803	^{30}O	–0.356505	^{50}O	–0.289720	^{70}H	0.127254
^{11}O	–0.293031	^{31}C	–0.024767	^{51}O	–0.358935	^{71}H	0.138604
^{12}C	–0.027345	^{32}O	–0.251437	^{52}H	0.155019	^{72}H	0.163667
^{13}C	0.006809	^{33}N	0.665619	^{53}H	0.129112	^{73}H	0.146507
^{14}O	–0.352222	^{34}O	–0.282042	^{54}H	0.138740	^{74}H	0.134573
^{15}C	0.154828	^{35}O	–0.386829	^{55}H	0.091361	^{75}H	0.227220
^{16}C	0.007948	^{36}N	0.669740	^{56}H	0.165854	^{76}H	0.130280
^{17}C	0.016081	^{37}O	–0.238660	^{57}H	0.108711	^{77}H	0.151211
^{18}O	–0.316086	^{38}O	–0.293923	^{58}H	0.124839		
^{19}C	–0.028334	^{39}O	–0.340617	^{59}H	0.105571		
^{20}O	–0.237871	^{40}O	–0.255760	^{60}H	0.211951		

Electrophilic and nucleophilic properties of a molecule are determined by the sign of LUMO (relative energy of the lowest unoccupied orbital). If LUMO is negative, the reagent is electrophilic, whereas in the opposite case it acts as a nucleophile. The approximately zero energy of LUMO reflects the dual (both electrophilic and nucleophilic) properties of the reactant. In the case of cellulose nitrate the respective value was –0.7763 eV. The highest absolute value of the negative charge corresponded to oxygen atoms, thus determining the most probable site of electrophilic attack; the highest positive charges were located at atoms of carbon and nitrogen, making them probable sites of reactions with nucleophiles.

As seen from Table 2, of the carbon atoms of glucopyranose ring, C^2 atoms in positions 1 and 4 are the most reactive towards electrophiles, the interaction being accompanied with degradation of the polymer chain. Electrophilic attack of $C^{7,19,31}$ at position 6 (accompanied with nitrate groups substitution) is less probable. The least probable is the attack of C^4 at position 2 (substitution of nitrate groups as well).

According to the quantum-chemical simulation, the highest positive charge in cellulose nitrate molecule was located on the nitrogen atoms of the nitrate groups; therefore, they should be the most reactive towards nucleophiles. Of other reactive sites, nucleophilic attack at $C^{5,15,24}$ (positions 1 and 4) were the most probable, that reaction leading to cellulose nitrate degradation. Atoms of $C^{1,3,17,22,25}$, corresponding to the carbon atoms C^3 and C^5 of the end groups, were less reactive under conditions of nucleophilic attack. Nucleophilic attack at those reaction sites led to substitution of hydroxy groups and opening of

Table 3. Mulliken atomic charges as computed by the AM1 method

Ethanol		Isopropanol		Butanol		*n*-Pentanol	
atom	charge	atom	charge	atom	charge	atom	charge
			Alcohol				
^{1}C	–0.214895	^{1}C	–0.209139	^{1}C	–0.158302	^{1}C	0.158188
^{2}C	–0.019298	^{2}C	0.027610	^{2}C	–0.019428	^{2}C	–0.019281
^{3}O	–0.329538	^{3}C	–0.249840	^{3}C	–0.158811	^{3}C	–0.157938
		^{4}O	–0.329027	^{4}C	–0.209997	^{4}C	–0.158083
				^{5}O	–0.32909	^{5}C	–0.210027
						^{6}O	–0.328958
			Alcohol in the presence of pyridine				
^{1}C	–0.220427	^{1}C	–0.214610	^{1}C	–0.164613	^{1}C	–0.164588
^{2}C	–0.021810	^{2}C	0.027189	^{2}C	–0.021007	^{2}C	–0.021112
^{3}O	–0.361380	^{3}C	–0.249272	^{3}C	–0.159095	^{3}C	–0.157935
		^{4}O	–0.360652	^{4}C	–0.213396	^{4}C	–0.160894
				^{5}O	–0.359884	^{5}C	–0.213178
						^{6}O	–0.359814

glucopyranose rings, respectively. The least reactivity in reaction with nucleophiles was found in the C^{16} atoms in the position 2.

Depending on the catalyst nature, alcohols may participate in both above-discussed reaction types: electrophilic attack with proton of the hydroxy group and the formation of adducts via the oxygen atom. Quantum-chemical simulation allowed determination of the reactivity type of alcohols. The simulations were performed for pure alcohols and for alcohols in the presence of pyridine. The Mulliken charges at atoms of the aliphatic alcohols are given in Table 3.

As seen from LUMO energy (~3.5 eV), the alcohols were weak nucleophiles. In the presence of pyridine, the charges were redistributed, and the negative charge at oxygen atoms of the alcohols hydroxy groups was up by 0.3–0.4. The most negative charge was found in the case of ethanol; therefore, that alcohol should be the most reactive in nucleophilic substitution of nitrate groups of cellulose ester, and the degradation of the polymer chains should be the most intense in the case of ethanol. Acidity of alcohols (in particular, the ability towards dissociation of the O–H bond) decreases with higher molecular mass and with more branched hydrocarbon chain, due to positive inductive effect of alkyl substituents.

The quantum-chemical simulation data coincided with the experimental data. In the course of cellulose nitrate interaction with the alcohols, four types of reactions occurred: substitution of nitrate groups with the alkoxy ones, hydrolysis, glucopyranose ring opening, and macromolecules chain degradation.

To conclude, basing of molecular mass distribution of the prepared products of cellulose nitrate modification with aliphatic alcohols, we concluded that the products parameters were governed by the interaction conditions as well as by the nucleophile basicity. By changing the nucleophile basicity, the depolymerization depth could be regulated.

EXPERIMENTAL

Initial and alcohol-modified samples of cellulose nitrates were analyzed with the Viscotec GPC max VE-2001 chromatograph with tetrahydrofuran as solvent.

For the initial cellulose nitrate and the prepared derivatives (50°C, 6 h), we determined the numberaverage $\bar{M}_n$, weight-average $\bar{M}_w$, z-average $\bar{M}_z$ molecular weights as well as the polydispersity index $\bar{M}_w/\bar{M}_n$.

Full optimization of the studied molecules geometry was carried out without symmetry restrictions using the AM1 semiempirical method. Analysis of normal oscillations confirmed the conformity of the optimized structure to the energy minimum at the potential energy surface. The simulation was performed using GAUSSIAN 09 software [10].

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