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Study of structural characteristics of cellulose esters

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Abstract

In this article, structural characteristics of amorphous and crystalline domains of various cellulose triesters were studied. These triesters contained three acyl substituents having a different number of carbon atoms. To calculate the structural characteristics of amorphous esters, the Van Krevelen method of additive contributions of partial volumes of atoms and atom groups in the molar volume of amorphous polymers was used. A special correction for the molar volume of amorphous esters was made to calculate the molar volume of crystallites of cellulose esters. Based on the molar volume, also specific volume and specific gravity of amorphous and crystalline domains of cellulose triesters were found. The coincidence of calculated and experimental characteristics was shown. In addition, the correlation equations were derived, which provide predicting the structural characteristics of various cellulose esters in the amorphous and crystalline phase states.

Keywords: Triesters of Cellulose; Amorphous and Crystalline Domains; Structural Characteristics; Calculations

1. Introduction

Cellulose is the most abundant organic matter on Earth [1]. Being a renewable and inexhaustible natural raw material, cellulose is widely used for the production of various cellulosic materials, cellulose derivatives, and composites.

Structural studies have shown that cellulose is a linear, stereoregular, semicrystalline polysaccharide composed of repeating anhydroglucose units (AHUs), which are linked by chemical β-1,4-glycosidic bonds [2-4]. Segments of long cellulose chains join together in the lateral direction by hydrogen and Van-der-Waals bonds with the formation of crystallites and non-crystalline amorphous domains. The content of crystallites in natural cellulose (crystallinity degree) ranges from 50% (cellulose of herbaceous plants) to 80% (tunicate cellulose) and can be changed after physical, physicochemical, and chemical treatments [4].

Each AHU in amorphous domains of cellulose contains three accessible hydroxyl functional groups, one primary at C6 and two secondary groups at C2 and C3, which impart increased hydrophilicity to cellulose materials [2-4]. This limits the use of cellulose in such applications as the creation of waterproof materials and the production of hydrophobic fillers and reinforcements that can be compatible with hydrophobic polymers, coatings, paints, adhesives, and other hydrophobic materials.

To impart hydrophobic properties to this hydrophilic biopolymer, various methods of cellulose modification, and especially esterification with hydrophobic acyl agents, were used [7, 8]. The commercial cellulose esters, such as acetates, propionates, butyrates, and others can be applied in diverse fields such as the production of thermoplastics, electronic device housings, spectacle frames, anti-fog goggles, cigarette filters, semi-permeable and separating

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membranes, optical films, heat, and rot-resistant fabrics, self-cleaning materials, protective coatings, and other materials [7-10].

Cellulose esterification can be performed under heterogeneous and homogeneous conditions. Heterogeneous esterification proceeds in the solid phase according to the laws of topochemical reactions, namely, rapidly in amorphous domains and more slowly inside the cellulose crystallites [11]. In contrast, homogeneous esterification proceeds fairly uniformly in solvent media that swell or/and dissolve cellulose.

After esterification with various acyl agents, usually, amorphous cellulose derivatives are formed [8]. To perform the crystallization process, amorphous triesters are annealed at a high temperature exceeding their glass transition temperatures. As a result, crystalline structures of the esters can be obtained [12-15]. The supramolecular structure of cellulose esters depends on the type of acyl agent and the degree of substitution. However, the structural characteristics even of the same cellulose ester can vary significantly depending on the type of initial cellulose, reaction conditions, as well as on the accuracy of structural studies and calculations.

For example, it was found that the specific gravity (G_c) of crystallites of triacetate cellulose calculated from the parameters of the crystalline unit cell varies over a wide range, from 1.24 to 1.46 g/cm^3 [15]. For crystallites of another cellulose ester, tripropionate, a clearly unreliable G_c-value of 1.67 g/cm^3 was proposed [16], probably due to inaccuracies in determining the parameters of the crystalline unit cell. The crystalline structure of other studied esters also requires clarification, whereas the parameters of the crystalline structure of higher cellulose esters still need to be determined. In addition, little information is available on the amorphous structure of various cellulose esters.

In this study, calculating methods were used to resolve contradictions in experimental results, as well as to clarify the crystalline structures and find the structural characteristics of amorphous domains of various cellulose esters.

2. Material and methods

The various cellulose triesters were studied. Each repeating unit of these triesters contained three acyl substituents having a different number of carbon atoms, Nc (Table 1).

Table 1 The studied cellulose esters

Esters of cellulose	Abbreviation	M	Nc
Triacetate	TAC	288	6
Tripropionate	TPC	330	9
Tributyrate	TBC	372	12
Trivalerate	TVC	414	15
Trihexanoate	THC	456	18
Trienanthate	TEC	498	21

To calculate the molar volumes ($V_{m,a}$) of amorphous esters, the Van Krevelen method of additive contributions of partial volumes of atoms and atom groups in the volume of polymers was used [17]. The molar volumes ($V_{m,c}$) of the crystallites were also calculated. The obtained results were compared with data on $V_{m,c}$ found from the volumes (V_c) of unit cells [12-15] as follows:

$$V_{m,c} = A\, V_c/k \quad (1)$$

Where A is the Avogadro number, and *k* is the number of repeating units in the unit cell.

If V_c is expressed in nm^3, and $V_{m,c}$ in cm^3/mol, then

$$V_{m,c} = 602.2 V_c/k \quad (2)$$

Then, also specific volume, $V_s = V_m/M$, and specific gravity, $G = M/V_m$ can be calculated, where M is the molecular mass of the repeating unit of the cellulose ester.

3. Results and discussion

Using the Van Krevelen method, the partial molar volume ($V_{m,sk}$ = 83.1 cm^3/mol) of the skeleton of an anhydroglucose unit, AGU (Figure 1) was calculated.

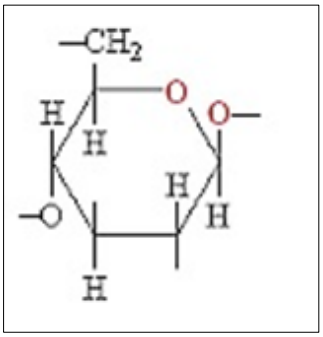
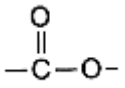


Figure 1 Skeleton of AHU

Then the partial volumes of groups present in substituents of amorphous glassy esters were found (Table 2).

Table 2 Partial volumes of groups ($V_{m,g}$) of acyl substituents

Group	$V_{m,g}$, cm^3/mol
-CH_2-	15.85
-CH_3	23.9
	23.0

For example, TBC consists skeleton of AGU, six CH_2-groups, and three CH_3-and COO- groups. Summing up the contributions of partial volumes of the skeleton and all groups of tributyrate, the molar volume of amorphous TBC was calculated, $V_{m,a}$=318.9 cm^3/mol. Knowing the mole volume, the specific volume, $V_{s,a}$=0.857 cm^3/g, and specific gravity, G_a=1.17 g/cm^3, can be also found for amorphous TBC.

The results of calculations of structural characteristics of various amorphous triesters are presented in Table 3.

Table 3 Calculated structural characteristics of amorphous glassy triesters

Esters of cellulose	$V_{m,a}$, cm^3/mol	$V_{s,a}$, cm^3/g	G_a, g/cm^3
TAC	223.8	0.777	1.28
TPC	271.4	0.822	1.22
TBC	318.9	0.857	1.17
TVC	366.6	0.885	1.13
THC	414.0	0.908	1.10
TEC	461.6	0.927	1.08

After discussing the characteristics of the crystalline structure of cellulose triesters, it was concluded that the most reliable specific gravity of TAC crystallites is 1.30 g/cm^3 [15]. Reliable values of specific gravity were obtained also for crystallites of TBC (1.23 g/cm^3) and TVC (1.17 g/cm^3) (Table 4).

Table 4 Parameters of crystalline unit cell and specific gravity of crystallites of some cellulose triesters [15]

Triesters	a, nm	b, nm	c, nm	γ°	k	V_c, nm^3	$V_{m,c}$	$V_{s,c}$	G_c
TAC II	2.460	1.152	1.044	90	8	2.958	222.6	0.771	1.30
TBC	2.537	1.534	1.033	90	8	4.020	302.6	0.813	1.23
TVC	2.940	1.540	1.036	90	8	4.690	353.0	0.853	1.17

Note: $V_{m,c}$ is expressed in cm^3/vol; $V_{s,c}$ in cm^3/g, and Gc in g/cm^3

On the other hand, it was found that the structure of amorphous cellulose esters should rather be called mesomorphous since the X-ray diffraction patterns of these samples show not one diffuse scattering characteristic of completely amorphous substances, but at least two pronounced peaks [18, 19]. A model of the mesomorphous structure of cellulose esters was proposed [18]. According to this model, the substituted AHUs form layers with an approximately constant distance (ca 0.4 nm) between these layers, However, in the layer planes, the distance between substituted AHUs increases directly proportional to the Nc: d (nm) = 0.55 + 0.06 Nc. Based on this model it is possible to calculate the values of specific gravity of the mesomorphous unit cell for various triesters (Table 5), which were the same as those calculated for amorphous esters by the Van Krevelen method (Table 3).

Table 5 Parameters of mesomorphous unit cell and specific gravity of cellulose triesters [18]

Triesters	a , nm	b, nm	c, nm	γ°	V_c, nm^3	V_m	V_s	G
TAC	1.00	1.00	1.034	133.6	0.749	225	0.781	1.28
TPC	1.17	1.17	1.034	140.7	0.896	270	0.818	1.22
TBC	1.34	1.34	1.034	145.4	1.054	317	0.853	1.17
TVC	1.51	1.51	1.034	149.0	1.214	366	0.884	1.13
THC	1.68	1.68	1.034	151.8	1.379	415	0.910	1.10
TEC	1.86	1.86	1.034	154.7	1.529	460	0.924	1.08

Note: V_m is expressed in cm^3/vol; V_s in cm^3/g, and G in g/cm^3

Table 6 Experimental (Exp) and calculated (Cal) parameters of crystalline structure of triesters

Esters of cellulose	$V_{m,c}$, cm^3/mol		$V_{s,c}$, cm^3/g		G_c, g/cm^3	
	Exp	Cal	Exp	Cal	Exp	Cal
TAC	222	218	0.771	0.758	1.30	1.32
TPC	ur	262	ur	0.794	ur	1.26
TBC	303	307	0.813	0.826	1.23	1.21
TVC	353	354	0.853	0.855	1.17	1.17
THC	na	400	na	0.877	na	1.14
TEC	na	445	na	0.893	na	1.12

Note: ur denotes unreliable; na denotes not available

If compare the values of specific gravity for crystallites of triesters (G_c) and amorphous (or rather mesomorphous) triesters (G_a), then an average ratio $R_{av}= (\sum \frac{Gc}{Ga})/n$ = 1.034 can be obtained. Thus, to calculate the specific gravity of crystallites, the specific gravity of amorphous (mesomorphous) esters should be multiplied by R_{av}. As follows from Table 6, the calculated characteristics of the crystalline structure of cellulose triesters are close to the experimental ones.

It has been shown that the structural characteristics of cellulose triesters are linear functions of the number of carbon atoms (Nc) in three substituents contained in one repeating unit of the esters (Figures 2-5). These dependencies can be expressed by the correlation equations shown in Table 6.

Table 7 Correlation equations

Characteristics	Equation
$V_{m,a}$, cm^3/mol	$V_{m,a} = 128 + 16.0\ Nc$
$V_{m,c}$, cm^3/mol	$V_{m,c} = 126 + 15.2\ Nc$
$V_{s,a}$, cm^3/g	$V_{s,a} = 0.729 + 0.010\ Nc$
$V_{s,c}$, cm^3/g	$V_{s,c} = 0.713 + 0.009\ Nc$
G_a, g/cm^3	$G_a = 1.34 - 0.013\ Nc$
G_c, g/cm^3	$G_c = 1.39 - 0.013\ Nc$

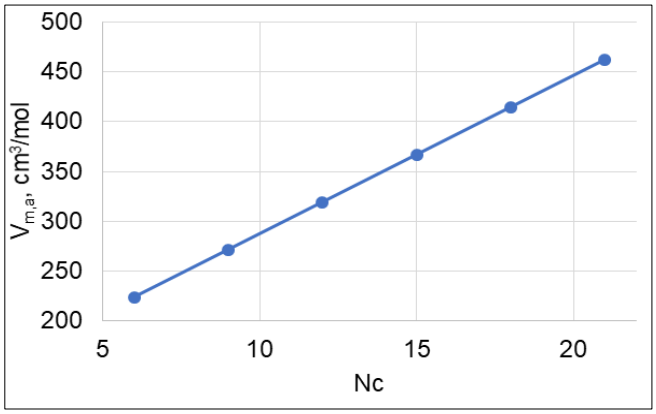


Figure 2 Linear dependence of molar volume on the number of carbon atoms in substituents for amorphous (mesomorphous) cellulose esters

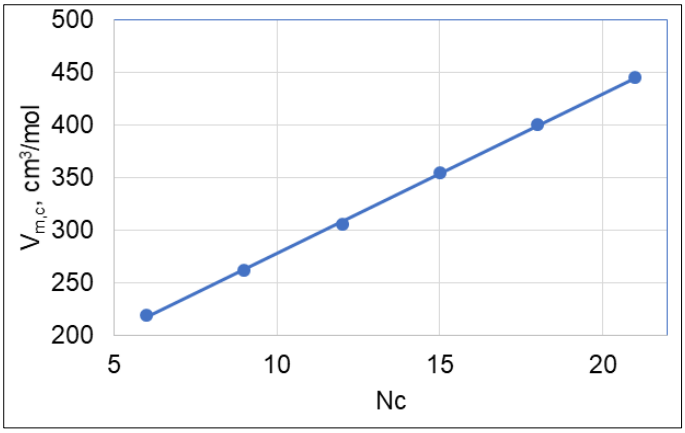


Figure 3 Linear dependence of molar volume on the number of carbon atoms in substituents for crystallites of cellulose esters

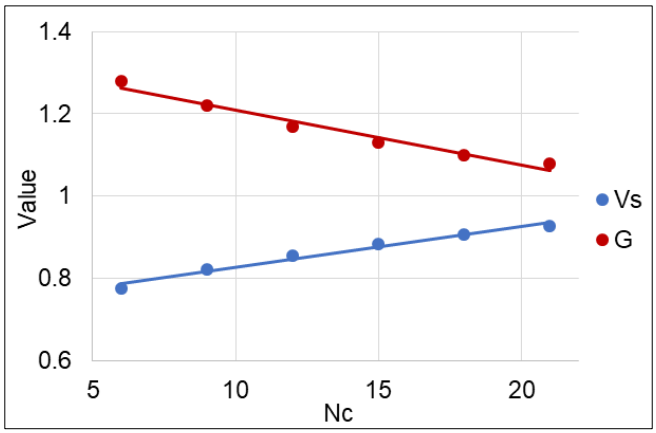


Figure 4 Linear dependences of specific volume and specific gravity on the number of carbon atoms in substituents for amorphous (mesomorphous) cellulose esters

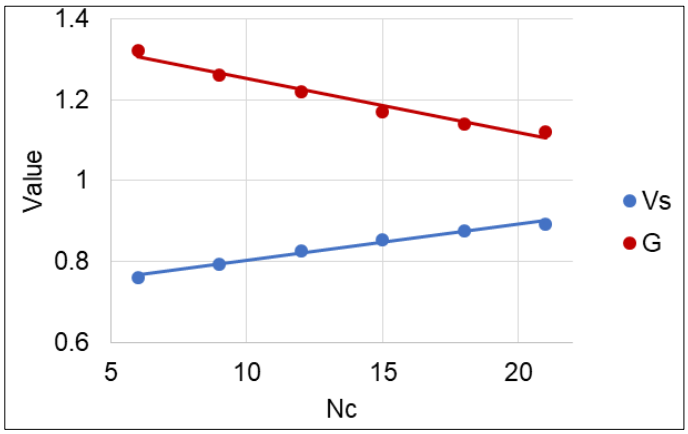


Figure 5 Linear dependences of specific volume and specific gravity on the number of carbon atoms in substituents for crystallites of cellulose esters

The correlation equations presented in Table 5 provide predicting the structural characteristics of various cellulose esters in the amorphous and crystalline phase states.

4. Conclusion

Structural characteristics of amorphous and crystalline domains of various cellulose triesters were studied. These triesters contained three acyl substituents having a different number of carbon atoms, from 6 to 21. It was found that the structure of amorphous cellulose esters should be considered mesomorphous. To calculate the structural characteristics of amorphous (or rather mesomorphous) esters, the Van Krevelen method of additive contributions of partial volumes of atoms and groups in the volume of amorphous polymers was used. Using a special correction of the molar volume of mesomorphous esters, the molar volume of crystallites of cellulose esters was found. Based on the molar volume, also specific volume and specific gravity of mesomorphous and crystalline domains of cellulose triesters were calculated. The coincidence of calculated and experimental characteristics was shown. It has been found that the structural characteristics of cellulose triesters are linear functions of the number of carbon atoms in three substituents contained in one repeating unit of the esters. These dependencies can be expressed by correlation equations, which provide predicting the structural characteristics of various cellulose esters in the mesomorphous and crystalline phase states.

Compliance with ethical standards

Disclosure of conflict of interest

The author of this paper hereby declares that there is no conflict of interest

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