

Influence of the Substitution Degrees on the Optical Properties of Cellulose Acetates

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ABSTRACT: Cellulose acetates with different substitution degrees possess a set of properties that makes them highly suitable for optical applications. This article discusses some of these properties, namely refractivity, dielectric properties, and transmittance. The contribution of the ratio between the molar refraction, which is proportional to the induced dipole moment, and the molar volume for the different atoms present in the studied polymers to the optical properties was investigated. The study illustrates the importance of such structural and compositional characteristics in tailoring some specific optical applications. Furthermore, optical transmission has been investigated in the 200–1000 nm range. To obtain the

optical parameters, the approach proposed by Tauc for amorphous semiconductors has been used because of the similarity of the absorption edges. The values of pseudo-gap energy ranged between 3.44 and 4.70 eV, whereas those of Urbach energy were modified in the 18–37 meV range. All parameters determined have been related to the influence of the substitution degrees and of the synthesis condition. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1751–1757, 2010

Key words: polysaccharide; refractive index; dielectric properties; transparency

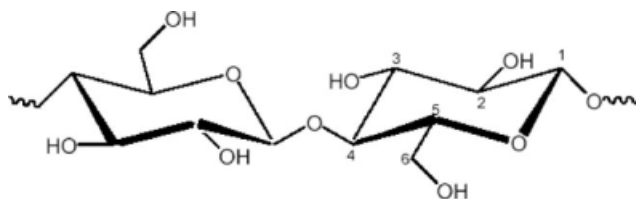
INTRODUCTION

Cellulose is a naturally abundant polymer used in a variety of applications. However, its use is limited by its poor solubility in various solvents, which is primarily due to the hydrogen bonds between the hydroxyl groups on the anhydroglucose chain. The natural abundance and biodegradability of cellulose, together with its ability to provide unique (solution and end-use) properties through derivatization have made cellulosic polymers attractive for a wide range of applications, including, among others, textile fibers, molding powder sheets, and optical membranes. Typical applications and research areas of polymeric biomaterials include tissue replacement, tissue augmentation, tissue support, and drug delivery. In many cases, the body needs only the temporary presence of a device/biomaterial in which instantly biodegradable and certain partially biodegradable polymeric materials are better alternatives than the biostable ones.¹ To this end, various cellulose derivatives have been synthesized for the diversification of their characteristics. Cellulose acetates (CA) are cellulose esters partially substituted at the

C-2, -3, and -6 positions of the anhydroglucopyranose residue (Scheme 1).

They can be easily molded into different forms, such as membranes, fibers, and spheres. To conjugate the mechanical properties of the polymer with the intrinsic properties of CA, hybrid organic/inorganic materials have been prepared.² The obtained composite materials present³ many intrinsic advantages, such as low cost, availability, biodegradability, and easy handling. On the other hand, the modern technology makes possible to manufacture from the existing suitable polymeric materials different optical cellulosic components for a wide variety of applications, such as spectacle lenses, contact lenses, intraocular lenses, consumer products, instrumentations, etc. In native form, cellulosic materials have been widely used in the manufacture of optical products, such as hard contact lenses, because of their excellent clarity, good wettability, and high gas permeability. Generally, CA are not used for corrective lenses but are occasionally used for plane lenses. High optical transparency, high moisture absorption, and low dimensional stability characterize this derivative of cellulose.^{2,4} Recent researches describe different processes for obtaining membranes in biomedical applications requiring optical and dielectric properties by utilizing CA in different complex forms. Thus, CA have been widely used for dialysis membranes, e.g. in artificial kidneys, membranes in plasmapheresis, and as drug delivery matrices for

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Scheme 1 Chemical structure of cellulose.

controlled release.^{5–7} Mention should be made of the researches on the integration of CA, onto silicon wafers by the standard microfabrication process, to add filtration capability on the chip. The membranes are biocompatible, showing good structural integrity and good adhesion to the substrate.^{8,9} Moreover, cellulose acetate membranes are recommended for different applications that require superior clarity, e.g. for optical sensors.¹⁰ Furthermore, a pH-sensitive membrane, consisting of a polyester support covered with a thin layer of cellulose onto which a pH indicator was covalently immobilized has been developed.¹¹

The most important parameters involved in the formation of CA membranes, among which special mention should be made of the nature of cellulose and of the substitution degree of CA, nature and composition of the casting solvent mixture, and temperature have been studied^{12–15} in great detail. Therefore, one of the most important roles in CA applications is the control of the balance between the refractive index of the substructures for obtaining the expected optical properties, known as depending on the molar volume and molar refraction of the polymer repeating units. Accurate values of the specific refractive index increment, $\frac{dn}{dc}$, of CA in solution should be determined to obtain the weight average molecular weight, M_w , through light scattering and for the estimation of the molecular weight distribution by size exclusion chromatography (SEC). Furthermore, the preferential adsorption of solvents in study of CA in mixed solvents can be determined by this parameter. The specific refractive index increments depend on the refractivity and content of components.^{16–18} In many applications, knowledge of the optical properties before the manufacturing of complex membranes is necessary.

In some previous articles,^{19–22} the homogeneous hydrolysis of highly acetylated cellulose was studied in the presence or absence of a hydrocarbon (toluene, benzene), in addition to acetic acid and water, on using sulphuric acid as a catalyst. The conformational behavior and the unperturbed dimensions of CA with different substitution degrees were investigated by viscometry and interferometry in 2-methoxyethanol and acetone/water solvent mixtures. The influence of concentration and

temperature on coil densities and dimensions as well as that of solvent mixtures composition on the solution properties were discussed.²³ Furthermore, rheology results show a sol-gel behavior, a case in which the specific properties are modified as a function of solvent mixture compositions. Gelation occurs as a result of nonsolvents-induced polymer aggregation and macromolecular associate formation.²⁴ In the present paper, the structural characteristics of cellulose acetate membranes were discussed in correlation with their optical properties. The influence of the substitution degree on the refractive index or dielectric constants, specific refractive index increments and optical transmission are analyzed for obtaining materials with potential applications.

EXPERIMENTAL

Materials

Cellulose acetate with different substitution degrees and number average molecular weight around 40,000 was synthesized from cellulose with outstanding porosity characteristics (Buckeye Cellulose Corporation, Memphis, TN), in conventional media (acetic acid/water) (CA_{1.88}, CA_{1.90}, CA_{2.21} samples), and in acetic acid/water/benzene system (CA_{1.73} sample), using the compositions presented in Table I, as described in detail elsewhere.^{19,20}

Modification of the hydrolysis bath composition was realized for obtaining cellulose acetate with different substitution degrees, different substitutions of hydroxyl groups on primary carbon atoms (C₆), and also on secondary positions (C₂ and C₃). The localizations of acetyl groups determine differences in supramolecular structures of samples.²⁵

MEASUREMENTS

The refractive index of cellulose acetate, n_2 , was measured with an Abbé refractometer at 25°C, whereas the specific refractive index increments, before $((dn/dc)_u)$ and after $((dn/dc)_\mu)$ establishing dialysis equilibrium, in acetone/water solvent mixtures, were measured in the standard way on a Zeiss interferometer at 25°C and at 436 nm wavelength. Equilibrium dialysis was performed in a dialyzer with a total volume of about 15 mL. Before use, the semipermeable cellophane membrane was conditioned in each of the solvent mixtures. Dialysis equilibrium was obtained within 6 h. The solvent systems were selected as a function of the substitution degrees of cellulose acetate, which dictated²³ the solubility of the solvent mixtures in the different domains.

The theoretical values of the refractive index were determined with the eq. (1) proposed by Lorenz-

TABLE I
Hydrolysis Conditions of Cellulose Acetates in Homogeneous Systems^{19,20}

Code ^a	Temperature (°C)	Time (h)	Composition (wt. %)			H ₂ SO ₄ (wt. %)
			Acetic acid	Water	Benzene	
CA _{1.73}	60	24	57	8	35	10
CA _{1.88}	40	19 (phase 1) 20 (phase 2)	90	10 (phase 1) 20 (phase 2)	–	10
CA _{1.90}	40	35	90	10	–	10
CA _{2.21}	40	63	98	2	–	10

^a Subscripts denote the substitution degrees, DS

Lorentz.^{26,27} Furthermore, the specific refractive index increments in acetone/water of the studied samples were determined using the eq. (2), with the refractive index from eq. (1)²⁸:

$$R_u = V_u \times (n_2^2 - 1)/(n_2^2 + 2) \quad (1)$$

$$\frac{dn}{dc} = \bar{v}_2 [(n_2^2 - 1)/(n_2^2 + 2) - (n_1^2 - 1)/(n_1^2 + 2)] \times (n_1^2 + 2)^2 / 6 \times n_1 \quad (2)$$

where \bar{v}_2 is the partial specific volume of CA in solution, which can be approximated by the specific volume of the polymer in solid state, $v_2 = V_u/m_0$, m_0 being the molar mass, n_1 is the refractive index of acetone/water solvent mixtures at different compositions, n_2 is the refractive index of CA, and V_u and R_u are the molar volume and molar refractivity, respectively, expressed by eqs. (3) and (4):

$$V_u = \sum_i a_i \times V_i \quad (3)$$

$$R_u = \sum_i a_i \times R_i \quad (4)$$

where V_i and R_i are the group contributions, and a_i is the number of groups i in the repeating unit.

Transmittance of cellulose acetate with different substitution degree films was recorded in 200–1000 nm wavelengths on a SPECORD 200 Analytik-Jena spectrophotometer. The used membranes were prepared from cellulose acetate solutions of 3 g/dL concentration in 2-methoxyethanol. The polymer solutions were cast on a glass plate and solidified initially by slow drying in saturated atmosphere of the used solvent, and finally under vacuum, at 30°C. The CA membranes thus prepared were subjected to transmittance investigations.

RESULTS AND DISCUSSION

Refractive index and specific refractive index

The key features of the CA used in optical applications are the refractive index and the specific refrac-

tive index increment. These properties are the effects of atomic polarizability and are characterized by the dipole moment per unit volume induced by the electromagnetic field.²⁹ Theoretical study offers the possibility to calculate the refractive index of a polymeric compound from the contribution of the individual atoms. In the current investigation, the refractive index of CA was determined by eq. (1) in which the molar refraction, R_u , and the molar volume, V_u , were calculated using eqs. (3) and (4), whereas the increments of various substructures, R_i and V_i , were taken from the literature²⁹ (Table II). R_u , V_u , and n_2 results are illustrated in Table III.

The theoretical values of the CA refractive index decrease with the increase of the substitution degrees and correspond to transparent materials (Table III). These data are slightly different from those provided in literature, which indicated a refractive index range between 1.47 and 1.49, but are closed to our experimental evaluations. Thus, the experimental value of n_2 for all CA samples is 1.472, within the experimental errors of about ± 0.03 % and it is close to the theoretical value, 1.468.

Similarly, with the refractive index, the dielectric constant depends on the chemical structure and on the polarization mechanisms. The magnitude of the dielectric constant is dependent on the ability of the polarizable units present in a polymer to orient themselves fast enough to keep up with the oscillations of an alternating electric field. At optical frequencies (around 10^{14} Hz), only the lowest mass species, the electrons, are efficiently polarized. At lower frequencies, the atomic polarization of the nuclei that move more slowly contribute to the dielectric constant. The contribution of each polarization mode to the dielectric constant is expressed in eq. (5):

$$\epsilon = \epsilon_{\text{electronic}} + \epsilon_{\text{atomic}} + \epsilon_{\text{dipolar}} \quad (5)$$

where $\epsilon_{\text{electronic}}$ is the dielectric constant corresponding to electronic polarization at optical frequencies (10^{15} Hz); ϵ_{atomic} is the dielectric constant corresponding to atomic polarization at lower frequencies (10^{12} Hz); $\epsilon_{\text{dipolar}}$ is the dielectric constant

TABLE II
Increments of Various R_i and V_i Substructures

Increment	R_i (cm ³ /g)	V_i (cm ³)	R_i/V_i
—CH ₂ —	4.504	15.528	0.290
=CH—	3.412	8.085	0.422
—CO ₂ CH ₃	12.189	48.559	0.251
—OH	2.439	12.203	0.200
—O— (ether)	1.625	9.052	0.180

corresponding to the dipolar polarization occurring at microwave (10⁹ Hz). In solid state, alignment of the permanent dipoles requires considerably more time than electronic or atomic polarization, occurring at microwave (10⁹ Hz) or at lower frequencies. At optical frequencies, when only electronic polarization occurs, the dielectric constants, $\epsilon_{\text{electronic}}$, from Table III were determined using Maxwell's relationship, which assumes knowledge of the refractive indices, according to eq. (6):

$$\epsilon_{\text{electronic}} = n_2^2 \quad (6)$$

Moreover, the dielectric constants slightly decrease with increasing the substitution degrees, being useful for certain applications that require a lower polarizability for the cellulose acetate compounds.

The specific refractive index increments of CA in acetone/water solvent mixtures were determined by Lorenz-Lorentz equation (eq. (1)) with the refractive index of polymers from Table III and the refractive index of acetone/water solvent mixtures from Table IV. The partial specific volume, \bar{v}_2 , was approximated by the specific volume of the polymer in solid state, $v_2 = V_u/m_0$, where the m_0 values are presented in Table III.

Table IV shows the theoretical results for specific refractive index increments, together with the experimental data obtained both before, $(dn/dc)_u$, and after, $(dn/dc)_v$, establishing dialysis equilibrium, and further used²³ in the evaluation of preferential adsorption in the cellulose acetate/acetone/water ternary system. The experimental values recorded for these samples before establishing dialysis equilibrium, at wavelength 436 nm, agree very well with those calculated by the Lorenz-Lorentz equation.

Low discrepancies can be caused if using the specific volume v_2 of solid polymers instead of \bar{v}_2 in eq. (2). It can be also seen from Table IV that the specific refractive index increments decrease with increasing the acetone content, being not affected with modification of the substitution degree.

These studies indicated that some properties of polymeric compounds attained before the preparation process. Therefore, one of the extremely important roles in cellulose acetate applications is the control of the balance between the refractive index of the substructures, for obtaining the desired optical properties.

Optical transmission

Typical transmission spectra of the CA investigated over the whole measured range are shown in Figure 1.

For all samples, the transmission spectra start in the ultraviolet domain, for CA_{1.73} the wavelength being lower than that for the CA with higher substitution degrees. Furthermore, at higher wavelengths, the transmission spectra are different depending on cellulose acetate substitution degrees and synthesis conditions. The level of transmission, of about 90% at DS = 1.73, is distinctly lower at higher substitution degrees. However, the CA_{2.21} sample, with a higher substitution degree, evidences a higher value. This sample is characterized by a substitution of hydroxyl groups at the primary carbon atom (C₆) and also, in secondary positions (C₂ and C₃), generating modification of supramolecular structure, comparatively with other studied samples from Table I where the substitution takes place preponderantly at primary carbon atom. Furthermore, experimental data were obtained for films prepared by evaporation of the CA solutions in 2-methoxyethanol. According to previous investigations concerning the solution properties,²³ surface and interfacial properties by contact angle method and atomic force microscopy,²⁴ a special behavior was observed for this sample. Generally, it is known that CA that have small substitution degrees are soluble in water.^{30,31} This phenomena is attributed to disruption of the intra- and intermolecular hydrogen bonding within cellulose system on the introduction of small

TABLE III
Molar Weights of the Structural Units, m_0 , Molar Refraction, R_u , Molar Volume, V_u , and Theoretical Values of the Refractive Index, n_2 , and Dielectric Constant, $\epsilon_{\text{electronic}}$ for Cellulose Acetates with Different Substitution Degrees

Sample	m_0	R_u , cm ³ /g	V_u , cm ³	R_u/V_u	n_2	$\epsilon_{\text{electronic}}$
CA _{1.73}	234.66	68.498	246.273	0.278	1.468	2.155
CA _{1.88}	240.96	69.961	251.727	0.278	1.468	2.155
CA _{1.90}	241.80	70.156	252.455	0.278	1.468	2.155
CA _{2.21}	254.82	73.178	263.725	0.277	1.467	2.152

TABLE IV
Volume Fraction of Acetone in Acetone/Water Solvent Mixtures, ϕ_1 , Refractive Index of Solvent Mixtures, n_1 , Theoretical Values of the Specific Refractive Index Increments Obtained from the Lorentz-Lorentz Equation, (dn/dc) , and Experimental Values of the Specific Refractive Index Increments Obtained Before $((dn/dc)_u)$ and After $((dn/dc)_a)$ Establishing Dialysis Equilibrium

Sample	(ϕ_1)	n_1	dn/dc [eq. (2)]	$(dn/dc)_u$ (exp.)	$(dn/dc)_a$ (exp.)
CA _{1.73}	0.75	1.352	0.104	0.100	0.141
	0.80	1.353	0.102	0.096	0.149
	0.85	1.355	0.101	0.088	0.147
CA _{1.88}	0.75	1.352	0.103	0.083	0.131
	0.80	1.353	0.102	0.115	0.167
	0.85	1.355	0.101	0.103	0.168
CA _{1.90}	0.75	1.352	0.103	0.429	0.458
	0.80	1.353	0.102	0.139	0.171
	0.85	1.355	0.101	0.060	0.138
CA _{2.21}	0.85	1.355	0.099	0.085	0.113
	0.90	1.356	0.098	0.098	0.173
	0.95	1.358	0.097	0.113	0.113

number of acetyl groups.³¹ With increasing substitution degrees, CA become insoluble in water but show good solubility in a variety of organic solvents, which interact differently with hydroxyl and acetyl groups from CA. Thus, properties of cellulose acetate films depend on their chemical structure, involving different substitution degrees and positions of acetyl groups along the chain, as well as the history of the films prepared from 2-methoxyethanol solutions. From this reason, it is difficult to control or characterize properties of CA. Concretely, as shown in previous article,²³ the highest flexibility was obtained for CA_{2.21} macromolecular chains in unperturbed state, indicating a lower density, which may influence the transmittance.

To obtain the absorption coefficient, α , from transmission data, expression (7) has been used:

$$\alpha = (1/d) \times \ln(1/\text{Transmission}) \quad (7)$$

where d is film thickness.

Generally, for a typical amorphous semiconductor, three domains are evident in the variation of the absorption coefficient versus photon energy. The first region describes the optical absorption generated by defects appearing at energy lower than the optical gap. This energy, E_T , describes the defect states and is rather sensitive to the structural properties of the materials. In the second region, absorption at photon energy below the optical gap depends exponentially on the photon energy, which defines Urbach energy. In the third region, the absorption coefficient due to interband transition near the band-gap describes the optical gap energy E_G in amorphous semiconductors.

From our data, the absorption edge and Tauc plots are represented in Figures 2 and 3, respectively, as a function of photon energy.

The shape of all edges is very similar to the behavior proposed by Tauc for a typical amorphous semiconductor,³²⁻³⁴ although the level of absorption is lower than for amorphous, inorganic thin films. These results agree with other literature data, which assume that a lower absorption in polymer materials is due to a lower degree of bonding delocalization.^{35,36} Each of the absorption edges from Figure 2 exhibits two different exponential regions with different slopes and a saturation region for higher energy. The exponential parts are described by relation (8):

$$\alpha = \alpha_0 \times \exp(E/A) \quad (8)$$

where α_0 is a constant and E is the photon energy.

Parameter A becomes either E_U in the high-energy exponential region, or E_T - in the low-energy exponential region of the absorption coefficient. For all investigated CA, the absorption edges have been

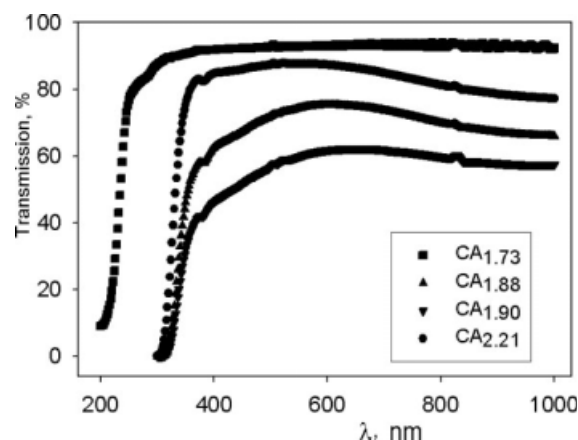


Figure 1 Typical overall transmission spectra of CA with different substitution degrees.

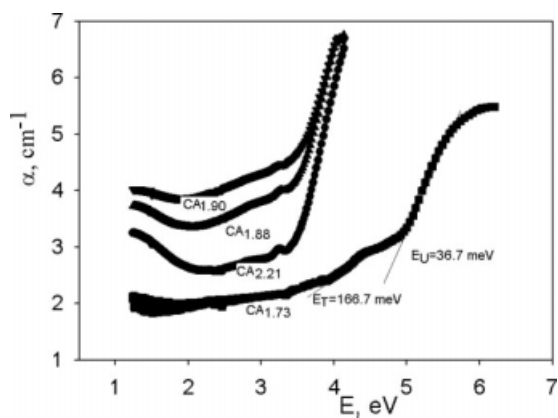


Figure 2 Absorption coefficient of CA with different substitution degrees.

found to follow the Tauc power law [eq. (9)] in the range over which the photon energy is higher than E_G :

$$(\alpha \times E)^{1/2} = B \times (E - E_G) \quad (9)$$

where B is a constant.

Thus, the dependence plotted in Figure 3 was used to obtain the Tauc optical energy gap E_G . The approach is typical for amorphous semiconductors, but it has been also applied to polymer films.³⁷

The values of the obtained optical parameters for cellulose acetate (Figures 2 and 3) are presented in Table V. Looking at the presented optical parameters, one may observe that all types of CA are transparent, i.e. the energy gap E_G values are higher than 3.26 eV.

Moreover, the values of E_G decrease with increasing the substitution degrees. Nevertheless, the E_G value for sample CA_{2.21} possesses a higher value. Increasing of chain flexibility determines an increase of transparency expressed by the E_G value, the

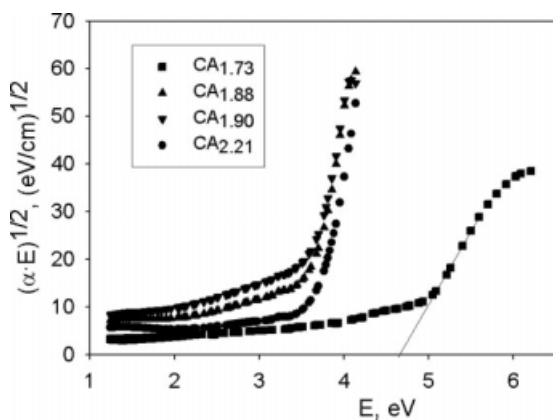


Figure 3 Tauc dependence of CA with different substitution degrees.

TABLE V
Optical Parameters of Cellulose Acetate with Different Substitution Degrees

Sample	d (μm)	E_T (meV)	E_U (meV)	E_G (eV)
CA _{1.73}	100	166.7	36.7	4.70
CA _{1.88}	110	131.2	19.6	3.55
CA _{1.90}	99	121.6	20.5	3.44
CA _{2.21}	105	46.1	18.3	3.67

reason being the same as the above-specified one, for transmission spectra. On the other hand, the substitution degrees influenced the E_U and E_T values. Thus, the E_T energies for samples with higher substitution degrees are lower. Furthermore, the E_U energies are lower with increasing of substitution degrees. These two parameters are related to the localized state induced by the polymer atomic structures. Such possible structure defects, like break, abbreviation, or torsion of the polymer chains seem to be responsible for the low-energy absorption described by the E_T parameter.

CONCLUSIONS

One of the extremely important roles in cellulose acetate applications is the control balance between the refractive indexes of the substructures for obtaining the desired optical properties. Thus, for multiple applications, knowledge on the optical properties before the preparation process is necessary.

This article evaluates the cellulose acetate optical properties from the theoretical and experimental data of the refractive index and specific refractive index increment in acetone/water solvent mixtures at 25°C. It is observed that the ratio of molar refraction (proportional to the induced dipole moment) to molar volume for the different atoms present in the studied samples is reflected in the variation of the refractive index and specific refractive index increment. The theoretical values of the refractive index and the specific refractive index increment of CA are slightly different from the experimental values; they correspond to transparent materials. These values decrease easily with increasing the substitution degrees. Furthermore, theoretical data of the dielectric constants at visible wavelength confirm the lower polarizability of these samples.

On the other hand, CA appear as very interesting materials because of their transmittance properties. These flexible membranes are transparent, with transmission between 60%, at high substitution degree, and 95%, respectively, at small substitution degree, over the whole visible spectral range. One of them, CA_{2.21}, possesses higher transmittance, explained by the different substitution of hydroxyl

groups at primary carbon atom (C_6) and also, in secondary positions (C_2 and C_3). In addition to this, the historic of the films preparation influences the supramolecular structures of the studied samples. The absorption edges of the investigated samples were similar to the typical edge for amorphous semiconductors, allowing obtaining of optical parameters. Increasing the substitution degrees generally caused a decrease of the energy gap, with the exception of the $CA_{2,21}$ sample, but all samples can be considered transparent materials, with E_G values greater than 3.26 eV. Furthermore, the Urbach energy, E_U , and the optical absorption by defects, E_T , which are related to the localized state induced by the polymer atomic structures, show a decrease with increasing the substitution degrees. Such possible structure defects, like break, abbreviation, or torsion of the polymer chains seem to be responsible for the low-energy absorption described by parameter E_T .

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