Secondary Mechanical Relaxations in Amorphous Cellulose

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ABSTRACT: Amorphous cellulose exhibits two mechanical relaxation processes, so-called γ and β, below its glass transition temperature T_g. Though much work has already been published on the subject, the origin of these relaxations is still uncertain, especially because most of the dynamic mechanical data were obtained at constant frequency and mixed together with dielectric data. In order to reach more definitive answers, two main approaches were taken in this work, namely (i) the use of a low-frequency mechanical spectroscopic technique and (ii) the comparison with data of different polysaccharides, having different lateral groups and different intramolecular links along the main chain. In addition, preliminary molecular modeling based on molecular mechanics was performed on isolated chains in vacuum. The work is focused on dried cellulose, to minimize the effect of relaxation overlap, which becomes negligible for moisture content lower than 2%. The results show that the γ process occurs without cooperativity and confirm its origin in the rotation of primary hydroxyl groups. In fact, in contrast with the β relaxation, its activation energy does not involve significant entropic contribution, and molecular modeling suggests that the rotation of those lateral groups does not lead to conformational change in the rest of the chain (no cooperativity). The activation energy of the β relaxation involves an entropy contribution that varies with the water content.

Introduction

As is well-known,[1] depending mainly on the time−temperature scale at which they are studied, amorphous polymers exhibit viscoelastic behavior involving different molecular motions, with very different dynamics. These dynamics can be summarized as follows: at low temperatures, or short times, the molecular mobility is generally considered as localized and leads to a macroscopic mechanical or dielectric behavior, so-called secondary relaxations. These motions are often described as rotations of lateral groups (and referred to as γ, δ, etc. at decreasing temperature) or as motions of main chain segments (such as crankshaft movements, for instance) and assumed to correspond to the so-called β relaxation in most of the cases.[2] They are assumed to occur in regions of the materials where the mobility is easier, so-called "islands of mobility"[3,4] or more recently "quasi point defects".[5−7] At longer times or higher temperatures, the glass−rubber transition leads to a very large change in the mechanical properties, with specific dynamics not discussed here.

Secondary relaxations involve thermally activated localized motions that can be more or less cooperative. However, the concept of cooperativity implies a nonzero entropy in the total free energy cost of the conformational transition.[8−12] Thus, the relaxation time must be characterized by evaluating the enthalpy and the entropy contributions to the total energy barrier. Most studies on secondary relaxations have been performed with synthetic amorphous polymers. Relatively few attempts have been reported for natural polymers, such as polysaccharides, despite their great abundance and importance for human life. For example, cellulose is widely used in textile and paper industries. As with other polymers, it exhibits a classical viscoelastic behavior together with a high sensitivity to moisture (comparable to most polyamides, for instance). This is due to its high content of hydroxyl groups able to form hydrogen bonds with either neighboring units of the same macromolecule, or with neighboring chains or water molecules. Mechanical spectroscopy data obtained on amorphous cellulose[13−16] reveal two secondary relaxations, referred to here as γ_{cell} and β_{cell}, that are dependent on the water content. The molecular interpretation of these secondary relaxations is still a matter of controversy.[13−15,17] On the basis of the comparison of mechanical and dielectric behavior of polysaccharides, with different chemical architectures, such as cellulose, dextran, pullulan, and amylose, some authors[13] have postulated that the γ_{cell} relaxation is associated with the localized motion of hydroxymethyl groups (see Figures 1 and 2). The β_{cell} relaxation would involve motion of hydroxymethyl groups in interaction with water molecules.[13] According to other authors,[17,18] the β_{cell} relaxation process should be associated with localized motions of the main chain segments. There are several ways to reach a more definitive answer about the molecular origin of relaxation processes in polymers: for example, (i) decreasing the frequency in dynamic mechanical measurements (and so the temperature at which these relaxations occur), as it allows better separation of relaxations that have close activation energies and that overlap,[19] (ii) performing spectrometric measurements on several polymers having small differences, as for instance, different lateral groups, if these groups are suspected to play a role in the process studied,[2] and (iii) modeling the molecular motion, which is assumed to be at the origin of the relaxation process. However, molecular modeling is generally used to determine the global minimum conformation, and only a few works are concerned with the study of conformational changes. In the solid phase, the more stable conformation should correspond to the crystalline state, and disordered systems have energies much higher. For this reason, motions in the crystalline state are generally limited to very small groups of atoms. But if the polymer studied is amorphous (in the glassy state), it is globally out of equilibrium, and transitions may occur

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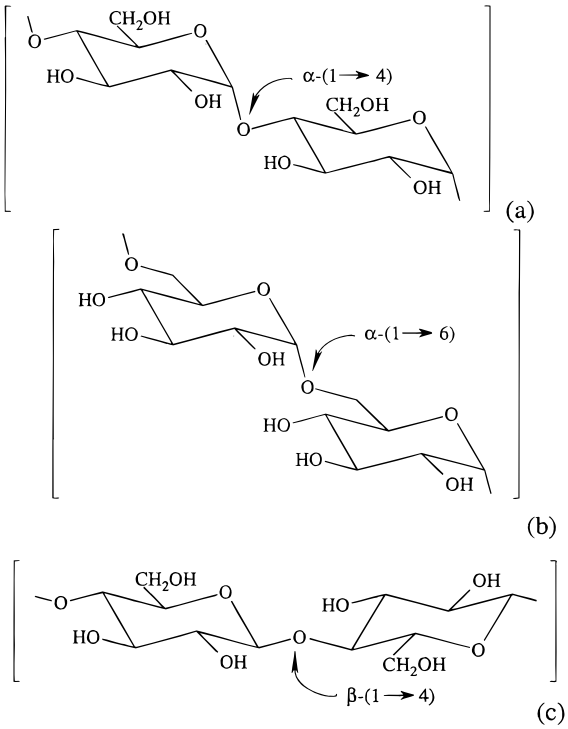

Figure 1. Chemical structure of (a) amylose, (b) dextran, and (c) cellulose.

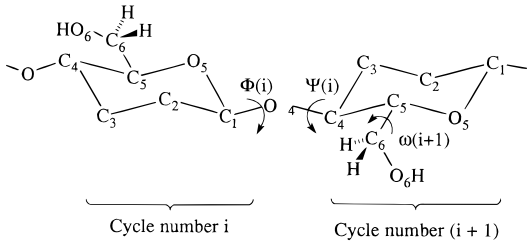

Figure 2. Schematic representation of a cellulose repeat unit including the definition of different torsion angles. Secondary hydroxyl groups are omitted for the sake of clarity.

by a hopping process between local minima having more or less the same energy. Such work is difficult to perform using molecular dynamics, due to the huge number of calculation steps required to pass through the energy barrier between the two minima considered. Though the molecular architecture of cellulose is rather complicated, and so molecular modeling difficult to achieve, preliminary calculations were performed on single chains in vacuum, in order to get a deeper understanding of such processes and also to visualize the molecular motions and their possible cooperativity.

In the present work, mechanical measurements were carried out on amorphous cellulose and dextran and qualitative and simple molecular modeling was performed to better analyze the molecular origin of the γ_{cell} relaxation.

I. Experimental Section

I.1. Sample Preparation. Samples of cellulose, from Buckeye, with an average degree of polymerization $\overline{DP}$ of 600, were dissolved in monohydrate *N*-methylmorpholine *N*-oxide (NMMO) with a cellulose concentration of 10% w/w. Then the solution, which is solid at room temperature, was extruded at 363 K (90 °C) and precipitated in anhydrous methanol in order to completely remove NMMO. In previous works,[20,21] these conditions were optimized so that no trace of NMMO could be detected by mass spectrometry. The samples were then dried 12 h at 373 K (100 °C). This process led to amorphous cellulose fibers[22] with a diameter of 0.8 mm. They were then cut to lengths of 15 mm, to perform measurements with a mechanical spectrometer working in torsional mode.

Samples of dextran, which is soluble in water, were prepared from a powder provided by Sigma (with $\overline{DP} = 1000$). Solutions containing 20% (w/w of polymer/water) were slowly evaporated at room temperature to obtain homogeneous films with a thickness of 1 mm suitable for the study of their mechanical behavior.

I.2. Mechanical Spectrometry. Dynamic mechanical measurements were carried out with a mechanical spectrometer (Mechanalyser from Metravib SA, Ecully, France)[19] operating in torsional mode at three frequencies, 1, 0.1, and 0.01 Hz, and at a heating rate of 13 K/h, starting from 100 K (−173 °C). This instrument provides the complex shear modulus $G^* = G' + iG''$. It also displays the tangent of the loss angle, $\tan \phi$ ($=G''/G'$). After each scan from 100 to 400 K (127 °C), cellulose samples were kept at 400 K (127 °C) for 1 h, except for the last treatment where the sample was kept at 400 K for 24 h. Comparable treatments were used for dextran (see "Results" and Figures 4 and 5 for more details). Each thermal treatment removed a certain amount of water, which was determined by gravimetry. The average relaxation time τ was determined as a function of temperature T using the relationship $\omega\tau = 1$, where ω is the angular frequency and T is the temperature for which G'' passes through a maximum.

I.3. Moisture Content Measurements. The moisture content was determined using a reference sample located close to the analyzed sample inside the spectrometer. Thus, it was submitted to the same thermal treatments as for the sample on which the dynamic mechanical measurements were carried out. After each scan, this reference sample was weighed.

I.4. Molecular Modeling. In principle, conformational sampling necessary to efficiently explore the multidimensional potential energy surface of large molecules (and to find the global minimum) can be performed by molecular mechanics (energy minimization), Monte Carlo calculations, and molecular or stochastic dynamics.[23] Molecular dynamics has severe limitations, as only short times, at best on the order of nanoseconds, can be simulated. Thus, unreasonably high temperatures are needed to cross energy barriers.[24] The molecular mechanics technique has been chosen for the present study, because it allows subsequent variation of sugar ring geometry (contrary to Monte Carlo methods), and adiabatic mapping, and has been shown to be a very powerful technique for the evaluation of the energy barriers between different stable or metastable conformations.[23]

Conformational changes in cellulose depend upon rotations around single bonds. The recommendations and symbols proposed by the Commission on Nomenclature are used throughout this paper.[25] As a consequence of the chemical structure of carbohydrates (hydroxylated rings linked together by two or three single bonds; see Figures 1 and 2), the torsion angles Φ and Ψ along the glycosidic linkages are the principal degrees of freedom that describe the general shape of the polymer whereas the torsion angles ω describe the orientation of the hydroxymethyl pendant groups. Different random-coil conformations of isolated cellulose oligomers of 10 and 20 residues were used as starting coordinates. These conformations were generated by randomly assigning [Φ, Ψ] values of energy minima of the disaccharide model compound according to the respective Boltzmann populations at 300 K. Each oligomer thus generated was then geometrically optimized.[26] The rotation around each torsion angle $\omega(i) = O5(i) - C5(i) - C6(i) - O6(i)$, where i refers to the unit number of the chain, were then systematically studied. Plots of the energy versus $\omega(i)$ were calculated step by step by rotating the primary hydroxyl groups each time by 5° over the whole angular range. For each so-generated conformation, the energy was minimized by allowing the Cartesian coordinates of each atom to vary, except those defining the studied torsion angle. In this procedure, 600 steps of the conjugate gradient method were used. Energy evaluation was made using the empirical method CHARMm[27] interfaced in Quanta graphical software

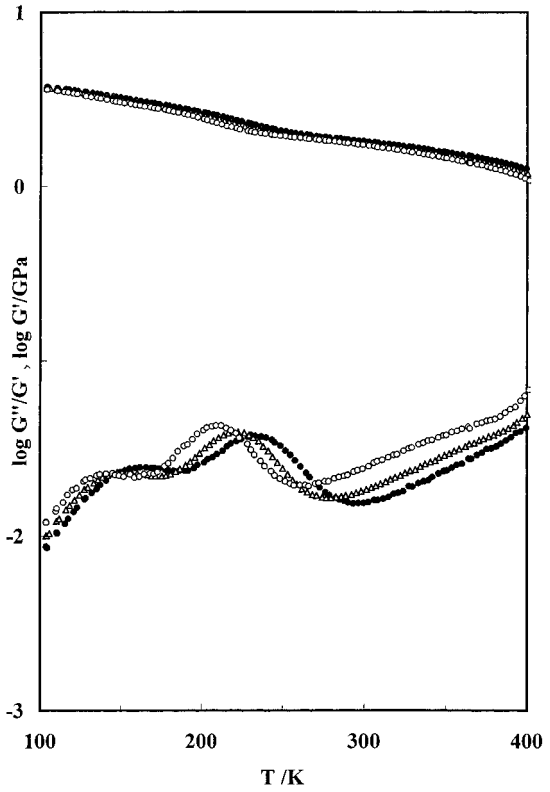

Figure 3. Dynamic mechanical data for amorphous cellulose versus temperature: log(G'/GPa) (top) and log(tan ϕ), referred to as G''/G' (bottom): (●) 1 Hz; (△) 0.1 Hz; (○): 0.01 Hz.

(Molecular Simulations) using a force-field appropriate for carbohydrates.[28] The dielectric constant of the vacuum was chosen throughout all the simulations, and as a preliminary attempt, isolated chains in vacuum were considered. The relative population of each minimum corresponding to a metastable conformer j, P_j, is given by the Boltzmann distribution:

$$P_j = \frac{\exp\left[-\frac{E_{\mathrm{rel}\,j}}{kT}\right]}{\sum_j^n \exp\left[-\frac{E_{\mathrm{rel}\,j}}{kT}\right]} \quad (1)$$

with k the Boltzmann constant, E_{relj} the relative potential energy of the conformer number j, and n the total number of metastable or stable conformers.

All calculations were carried out on Silicon Graphics Indigo 2 and Sun Sparc 2 workstations. Molecular drawings were performed using Quanta.

II. Results and Discussion

II.1. Mechanical Analysis of the Secondary Relaxations. (a) Experimental Data for Cellulose. The study of cellulose by mechanical spectrometry shows the existence of two relaxation processes. Figure 3 shows the log of the real part of the shear modulus, G', as well as the log of tan ϕ versus temperature, for three frequencies, 0.01, 0.1, and 1 Hz. Figure 4 shows the evolution of log(tan ϕ) for varying water content. Table 1 displays the water content of cellulose for each experiment. With water content below 2% (plots b to e), two secondary relaxation peaks γ_{cell} and β_{cell} are observed. The peak position and intensity vary with the water content. At first, the low-temperature relaxation γ_{cell} appears at a constant temperature of 150 K and its amplitude increases as the moisture content

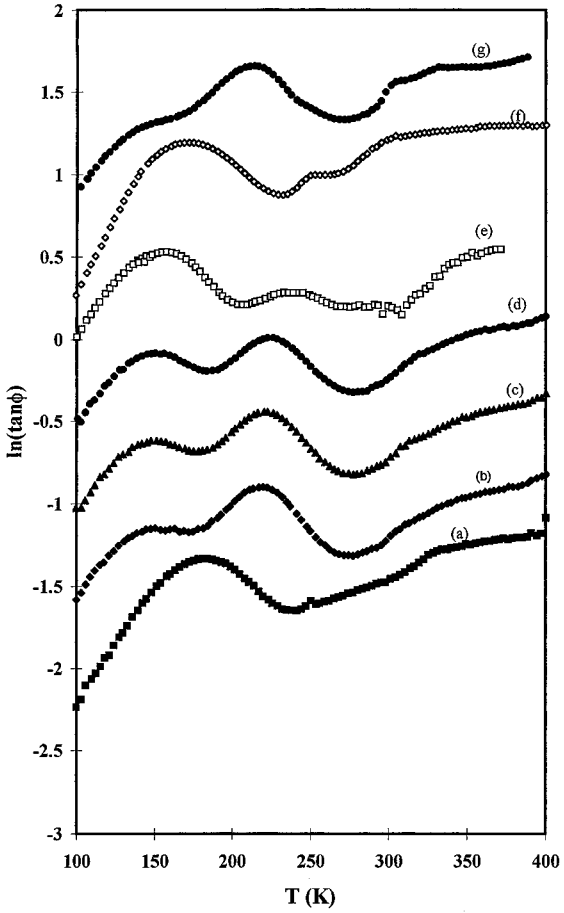

Figure 4. Dynamic mechanical data at 0.1 Hz for cellulose, log(tan ϕ) versus temperature: (a) before treatment; (b) after (a) + 1 h at 400 K; (c) after (b) + 1 h at 400 K; (d) after (c) + 1 h at 400 K; (e) after (d) + 24 h at 400 K; (f) after (e) following a stay in humid atmosphere; (g) after (f) + 1 h at 400 K. Each curve is shifted by one decade from the previous one, (a) being the reference.

decreases. The evolution of the β_{cell} relaxation is different from that of the γ_{cell}: it shifts to higher temperatures after each thermal treatment, which removes water. Simultaneously, its amplitude decreases. A plot of log(τ) versus $1/T$ is linear for both relaxations. Thus, in a first approach in which the overlap of the two relaxations is not taken into account, we can describe the variation of $\tau_{\gamma_{cell}}$ and $\tau_{\beta_{cell}}$ by the Arrhenius equation as

$$\tau_{\gamma_{cell}} = \tau_{0\gamma_{cell}} \exp\left[\frac{E_{\gamma_{cell}}}{RT}\right] \quad (2)$$

$$\tau_{\beta_{cell}} = \tau_{0\beta_{cell}} \exp\left[\frac{E_{\beta_{cell}}}{RT}\right] \quad (3)$$

where $E_{\gamma_{cell}}$ and $E_{\beta_{cell}}$ are the apparent activation energies and $\tau_{0\gamma_{cell}}$ and $\tau_{0\beta_{cell}}$ the preexponential factors of the $\tau_{\gamma_{cell}}$ and $\tau_{\beta_{cell}}$ relaxation times, respectively. $E_{\gamma_{cell}}$ is found to be independent of the thermal treatments and close to 38 kJ/mol. $\tau_{0\gamma_{cell}}$ is on the order of 10^{-12} s. $E_{\beta_{cell}}$ slightly increases after each thermal treatment and reaches 85 kJ/mol for the anhydrous sample. Simultaneously, $\tau_{0\beta_{cell}}$ becomes shorter and is on the order of 10^{-20} s for anhydrous cellulose. For cellulose having 6% water, only one relaxation appears, as shown in Figure 4. This peak is clearly discernible and is wider than the γ_{cell} and β_{cell} peaks for samples having less

Table 1. Activation Energy and Entropy and Preexponential Factor from Fit of γ_{cell} and β_{cell} for Different Moisture Contents[29]

curve of Figure 4	moisture content/w/w %	$\langle E_{\gamma_{cell}}\rangle$/ kJ·mol^{-1}	$\tau_{0\gamma_{cell}}$/s	$\langle E_{\beta_{cell}}\rangle$/ kJ·mol^{-1}	$\tau_{0\beta_{cell}}$/s	T of β_{cell}/K	ΔS of β_{cell}/ J·mol^{-1}·K^{-1}
a	6	34	9×10^{-13}	60	5×10^{-17}	190	64
b	2	34	9×10^{-13}	84	3.3×10^{-20}	223	119
c	1	34	9×10^{-13}	84	4×10^{-20}	224	123
d	0.5	34	9×10^{-13}	84	4.4×10^{-20}	227	123
e	0	36	10^{-12}	85	5×10^{-20}	230	123

water. Its average E and τ_0 were determined and are of 60 kJ/mol and 10^{-14} s, respectively. In fact, it seems that this unique peak results from the merging of the two previous ones at increasing moisture content.[29] It is worthy to note that this evolution of the γ_{cell} and β_{cell} processes in the amorphous cellulose is reversible. This was confirmed by rehydrating an anhydrous sample obtained after all these thermal treatments. This sample (plot f of Figure 4) shows the behavior already observed for the raw material containing 6% water. A further heat treatment (as for curve b) leads to a similar result, shown by curve g. Thus, as expected, it is clear that the molecular mobility of amorphous cellulose is drastically influenced by its moisture content. The following results focus on dried cellulose, so that it is possible to neglect the effect of overlap and so to determine accurately the activation energy and preexponential factor for the two relaxations. However, it is interesting to point out that our data (G', G'', and tan ϕ) can be fitted by assuming that the activation energy follows a Gaussian distribution (see, for a complete discussion, refs 30 and 31). Over the entire moisture range investigated here, the distribution half-width was found to be 7 kJ/mol for γ_{cell} and 10 kJ/mol forβ_{cell}.[29] Activation energies and preexponential factors are summarized in Table 1.

(b) Enthalpy and Entropy Contributions for the γ_{cell} Process Activation Energy. According to most works on sub-T_g relaxations (see, for example, ref 2), the γ_{cell} and β_{cell} processes should be due to localized motions of groups of atoms or of molecular segments. In particular, local regions containing the smallest group capable of reorientation should produce the γ_{cell} relaxation peak and local regions containing larger groups should produce the β_{cell} relaxation peak. The preexponential and apparent activation energy parameters provide information about the nature of the motions involved in the relaxation processes. Since $\langle E_{\gamma_{cell}}\rangle$ is relatively small and $\tau_{0\gamma_{cell}}$ is close to the Debye time $\tau_D = 10^{-13}$ s ($=2\pi h/kT$ at room temperature), the motions associated with the γ_{cell} relaxation may be considered to be localized and noncooperative.[2]

As discussed many times in the past (see for instance ref 8), the Eyring theory[32] can be used to describe the relaxation time τ as follows:

$$\tau = \frac{2\pi h}{kT} \exp\left[\frac{-\Delta S}{R}\right] \exp\left[\frac{\Delta H}{RT}\right] \tag{4}$$

with ΔS and ΔH the entropy and enthalpy contributions of the free activation energy of a thermoactivated motion, k the Boltzmann constant, and h the Planck constant. On the other hand, the apparent activation energy E corresponds to the derivative of $\ln(\tau)$ versus $1/T$:

$$E = R\frac{\mathrm{d}(\ln(\tau))}{\mathrm{d}(1/T)} \tag{5}$$

Thus from eqs 4 and 5, if $\Delta S = 0$, E becomes

$$E = \Delta H + RT \tag{6}$$

and is, in fact, very close to ΔH.

According to Starkweather,[8,12] the apparent activation energy of a relaxation appearing at temperature T and frequency f can be written as a function of its apparent activation entropy ΔS:

$$E = RT[1 + \ln(kT/2\pi hf)] + T\Delta S \tag{7}$$

For a relaxation for which ΔS is close to zero, E varies linearly with T at a given frequency f. For the γ_{cell} relaxation of amorphous cellulose, ΔS is found to be negligible for all values of the water content (i.e., $\tau_{0\gamma_{cell}}$ is close to the Debye time). Thus, the activation energy of the relaxation γ_{cell} is essentially due to an enthalpy contribution.

(c) Enthalpy and Entropy Contributions for the β_{cell} Process Activation Energy. We observe that the average apparent activation energy $\langle E_{\beta_{cell}}\rangle$ increases when the water content decreases in the cellulose and reaches 85 kJ/mol for the anhydrous sample (Table 1). Simultaneously, the preexponential time $\tau_{0\beta_{cell}}$ decreases and is on the order of 10^{-20} s for anhydrous cellulose. The width of the energy distribution is about 10 kJ/mol. This value is higher than the width found for the γ_{cell} relaxation (7 kJ/mol).[29] The short preexponential time, combined with a high apparent activation energy for the β_{cell} relaxation can be analyzed as previously discussed using eq 7. It appears that the entropy contribution $T\Delta$S for the β_{cell} process is not negligible compared to the enthalpy term. $T\Delta S$ increases as the water content decreases. Values of ΔS for different values of water content are collected in Table 1.

(d) Comparison with Dextran. Figure 5 shows the dynamic mechanical thermogram of dextran containing different moisture contents (see Table 2). Samples containing more than 3% water show only one secondary relaxation peak with a maximum of tan(ϕ) around 4×10^{-2}. Below 3% water an additional peak is discernible. This low-temperature relaxation, referred to as γ_{dex}, appears at 130 K at 0.1 Hz. Its amplitude is small (10^{-2}) compared to the other relaxation referred to as β_{dex}, which appears at 250 K at 0.1 Hz. The apparent activation energies, $E_{\gamma_{dex}}$ and $E_{\beta_{dex}}$, and the preexponential times, $\tau_{0\gamma_{dex}}$ and $\tau_{0\beta_{dex}}$, were measured for the dried sample. $E_{\gamma_{dex}} = 50$ kJ/mol and $\tau_{0\gamma_{dex}}$ is extremely short, on the order of 10^{-21} s. $E_{\beta_{dex}} = 87$ kJ/mol, and $\tau_{0\beta_{dex}}$ is on the order of 10^{-19}s. $E_{\beta_{dex}}$ increases and $\tau_{0\beta_{dex}}$ becomes shorter at decreasing moisture content (see Table 2). Figure 6 shows that these data are in agreement with those available in the literature.[13,15]

II.2. Molecular Origin of the Cellulose γ Mechanical Relaxation. Such relaxation is often associated with the motion of lateral groups. Cellulose has two kinds of lateral groups, (i) the hydroxymethyl groups (CH_2OH) and (ii) the secondary hydroxyl groups (OH). The γ relaxation of cellulose could be associated

Table 2. Mechanical Secondary Relaxations in Dextran

curve of Figure 5	water content/w/w %	$T_{\gamma_{dex}}$/K	$E_{\gamma_{dex}}$/ kJ·mol^{-1}	$\tau_{0\gamma_{dex}}$/s	$T_{\beta_{dex}}$/K	$E_{\beta_{dex}}$/ kJ·mol^{-1}	$\tau_{0\beta_{dex}}$/s
a	9.0				152	48.5	3.6×10^{-17}
b	7.5				185	64	1.4×10^{-18}
c	7.0				189	64.5	4×10^{-18}
d	4.5				194	64.5	9.6×10^{-18}
e	3.5				202	80.5	3.5×10^{-22}
f	3.0				208	70	4.3×10^{-18}
g	2.0	130	60	1.3×10^{-17}	225	79	9.7×10^{-19}
h	1.0	125	52	3.5×10^{-22}	231	83	2.9×10^{-19}
i	0.5	128	53	2×10^{-22}	238	83	10^{-19}
j	0	128	56	10^{-22}	242	83	2×10^{-19}

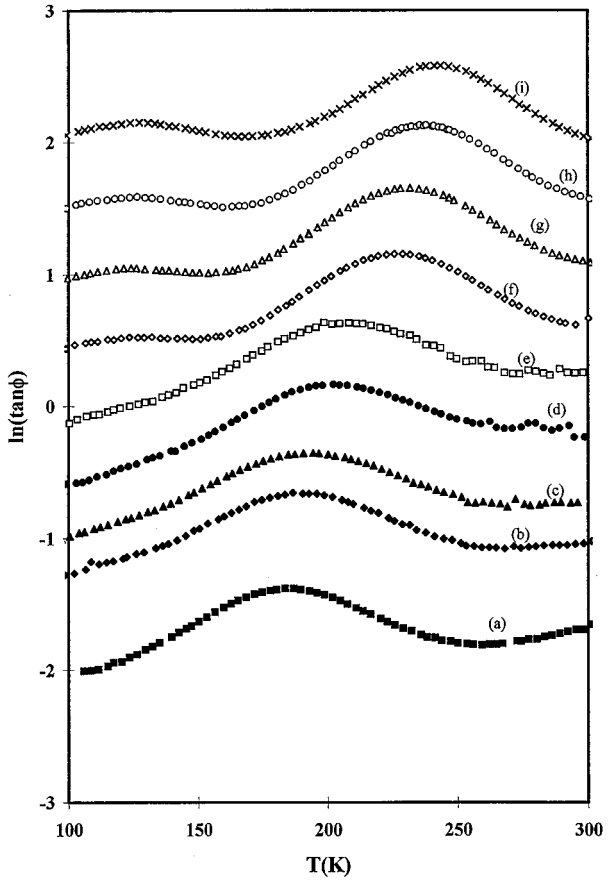

Figure 5. Dynamic mechanical data at 0.1 Hz for dextran, log(tan ϕ) versus temperature: (a) before treatment; (b) after (a) + 1.5 h at 310 K; (c) after (b) + 2.5 h at 310 K; (d) after (c) + 2 h at 340 K; (e) after (d) + 2 h at 350 K; (f) after (e) + 2 h at 400 K; (g) after (f) + 2 h at 400 K; (h) after (g) + 2 h at 400 K; (i) after (h) + 24 h at 400 K. Each curve is shifted by one decade from the first one, (a) being the reference.

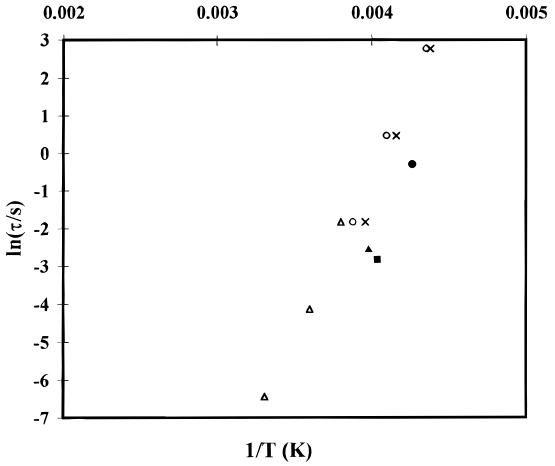

Figure 6. Variation of ln(τ) versus 1/T. Comparison of β secondary relaxation in cellulose, amylose, and dextran: (○) β_{cell} (our data); (×) β_{dex} (our data); (●) cellulose;[14] (■) amylose;[13] (▲) dextran (mechanical data);[13] (△) dextran (dielectric data).[15]

with the rotation of the CH_2OH and/or of the OH. In fact, the only group involved in the mechanical relaxation should be CH_2OH because mass transfer by rotation of OH around the C−OH axis is extremely small and therefore is not likely to produce a relaxation feature. Furthermore, in the dielectric study, the motion of OH around the C−OH axis should be clearly discernible, as the dipole moments of both primary and secondary OH groups are similar. To test these assumptions, i.e., that (i) the γ mechanical relaxation of cellulose results from local motions of lateral groups and (ii) the contribution of OH groups is negligible compared to the contribution of the CH_2OH groups, two different approaches have been conducted. We have compared our data with those obtained with other polysaccharides (dextran,[13,15] amylose,[13,15] pullulan[15]) by mechanical spectrometry. All of them are made of glucose rings but either the nature of the glycosidic linkage is different from the $\beta(1 \rightarrow 4)$ linkages present in cellulose or their side groups are different (see Figure 1). Preliminary molecular modeling has been performed to compare calculated data with experiments and also to visualize the molecular motions and their eventual cooperativity.

(a) Mechanical Analyses of Other Polysaccharides. It has been shown that polysaccharides having CH_2OH side groups display γ secondary mechanical relaxation whose characteristics are similar to those of the γ_{cell} mechanical relaxation of cellulose.[13,14,16] In contrast, dextran, which contains only secondary hydroxyl groups, exhibits a very weak γ_{dex} relaxation, with very different characteristics (see Figure 5, Table 2, and ref 13). Though the origin of γ_{dex} still remains unknown, from such data it can be assumed that the γ_{cell} relaxation of amorphous cellulose is essentially associated with rotational motions of CH_2OH groups.

(b) Molecular Modeling: Rotation of the Hydroxymethyl Groups. Calculations were performed using the procedure described in the Experimental Section. 5 random conformations of a 10 residue cellulose chain and 4 of a 20 residue cellulose chain were studied. For each of the 130 hydroxymethyl groups considered, three typical ω values were determined, corresponding either to a local energy minimum or at least to an inflection on the curve $E(\omega)$. Referred to as ω_1, ω_2, and ω_3, they correspond to a decreasing probability of occupation, P_1, P_2, and P_3 calculated according to eq 1. In Table 3, only the hydroxymethyl groups having at least two stable positions are reported, i.e., 23 among 130.

The calculated data show that each residue displays a specific energy profile. For example, parts a and b of

Table 3. Modeling of the Rotation of Hydroxymethyl Groups in Random Coil Conformations of Cellulose Oligomers[a]

ω_1/deg	ω_2/deg	no. of conformers	E_{rel}/kJ·mol^{-1}	P_1/ %	P_2/%	ΔE/kJ·mol^{-1}
53 ± 2.9	170 ± 3.5	9	7 ± 0.8	92 ± 1.7	8 ± 1.7	41 ± 6
60 ± 2.5	325 ± 5	6	3.3 ± 1.4	72 ± 6.6	27 ± 6.7	24 ± 4.3
190	50	2	5	77	20	42
318 ± 6.7	55 ± 4	4	3 ± 0.4	76 ± 2.5	24 ± 2.5	28 ± 7.5
313	166	2	6.4	91	8	51

[a] E_{rel} is the difference between the two lowest minima. ΔE is the energy barrier between these two minima.

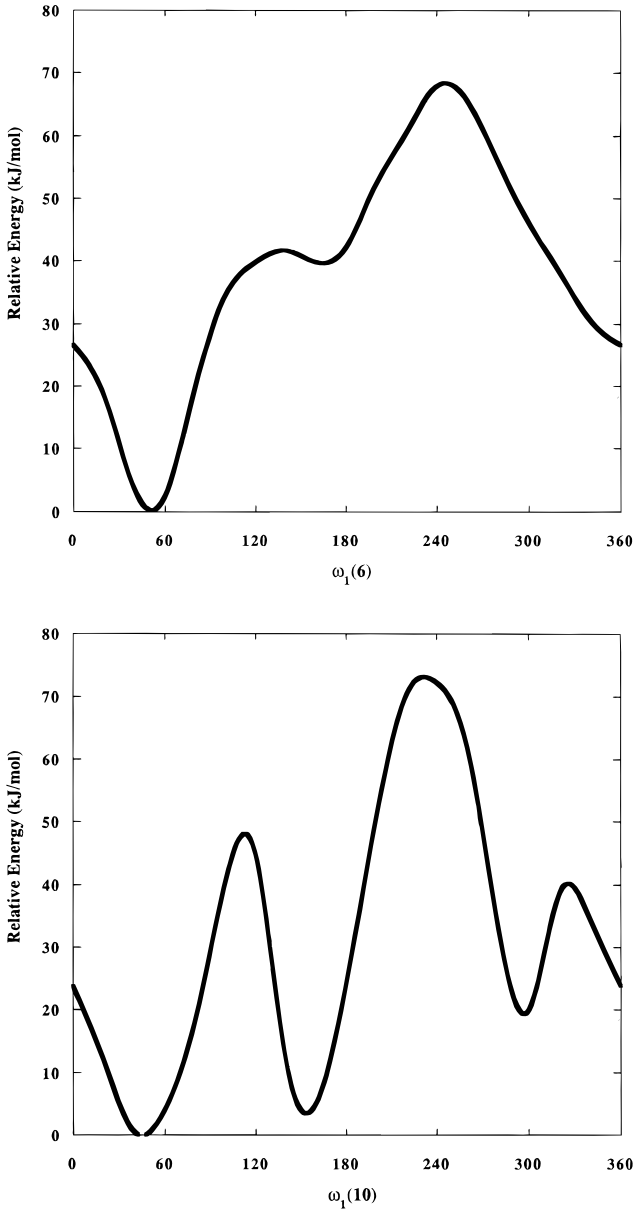

Figure 7. Variation of the energy E versus ω of a molecule of amorphous cellulose for two extreme cases: (a) only one stable position, *gt*; (b) nearly same probability of occupation for the two positions *gt* and *tg*.

Figure 7 show the energy profiles of two different residues. The principal explanation for these differences is that the intramolecular environment of each hydroxymethyl group varies along the chain. The hydroxymethyl groups experience different intramolecular interactions, such as Van der Waals and electrostatic interactions (i.e., hydrogen bonds) with other units. Evidence for the influence of the neighboring units is seen from the comparison with calculations on an isolated glucose molecule. Two inequivalent conformers for a glucose unit are predicted by the

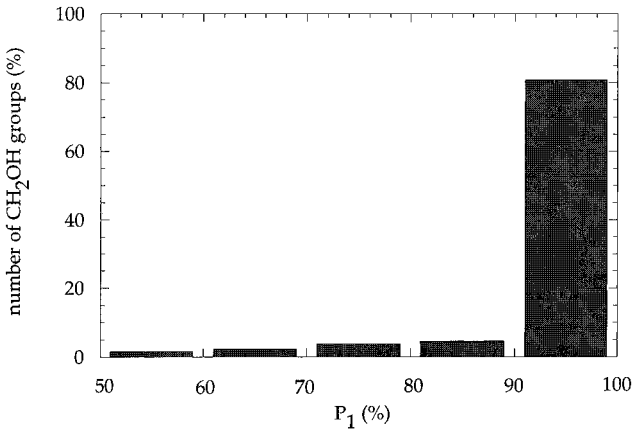

Figure 8. Histogram giving the probability of occupation of the more stable position of hydroxymethyl groups (see text for details).

CHARMm force-field for $\omega_1 = 55°$ and $\omega = 320°$. Furthermore, there is a slight change in the slope of the energy curve at 170°, but it does not correspond to a true minimum.[33] It is generally acknowledged that three staggered conformations occur for the hydroxymethyl group.[34,35] These are referred as *gt* ($\omega_1 = 60°$ following our definition), *tg* ($\omega_1 = 180°$), and *gg* ($\omega_1 = 300°$). The results presented here show that the angles for the minima are close to these values. In fact, ω_1 obtained for oligomers are in the range 50−60°, 165−190°, and 310−330° for the *gt*, *tg*, and *gg* conformers, respectively. Furthermore, as for isolated glucose molecules, the *gt* conformer has the lowest energy in most of the cases (here 15 of 23). Using eq 1, the probability P_1 to occupy the more stable position was calculated for each of the 130 hydroxymethyl groups and is plotted in the histogram, Figure 8. Groups having a probability close to 50% can be found either in position ω_1 or ω_2, while increasing P_1 corresponds to a lower probability of occupying ω_2. Thus only 10% of the groups have a probability higher than 20% to occupy two metastable positions, i.e., to provide a contribution to the relaxation process. The energy barrier ΔE needed to jump between populated conformers is distributed between 24 and 51 kJ/mol, with an average ΔE of 40 kJ/mol. This value is consistent with the activation energy of γ_{cell} ($\langle E_{\gamma_{cell}} \rangle =$ 37 kJ/mol) and its distribution width.

This technique allows the position of each atom of the chain to be determined for each step of the calculation. As an example, Figure 9 shows the superposition of the molecular drawing of the two metastable conformations, which corresponds to the two energy minima of Figure 7b. It is of interest to notice that the rotation of the hydroxymethyl group does not produce any significant change in the global conformation of the chain. This can be estimated from the extremely low value (0.002 Å) of the root mean square deviation of Cartesian coordinates of the heavy atoms in the superimposed chains (excluding the O6 of the rotating group). This confirms that such motion can occur without cooperat-

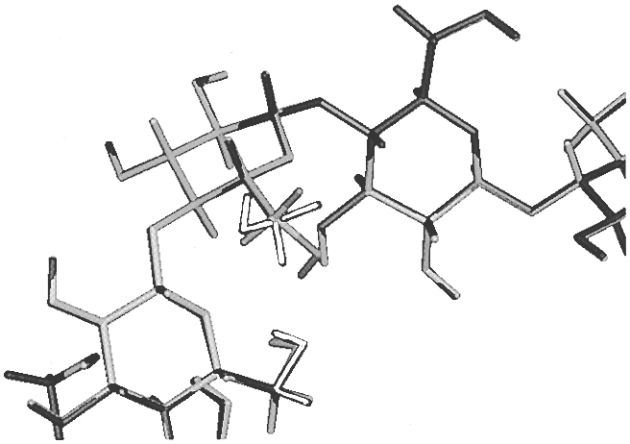

Figure 9. Superposition of the schematic representation of the two stable conformations corresponding to Figure 7b.

ivity. We can also assume that intermolecular interactions play a minor role, supporting the use of a simplified model to describe these molecular motions.

Recalling that moisture decreases the γ_{cell} relaxation intensity, this could be due to the change of hydrogen bond interactions in the presence of water molecules distributed along the cellulose macromolecules. A possible consequence could be a decrease of the number of hydroxymethyl groups able to relax if the energy difference between minima increases due to the presence of water molecules.

II.3. Molecular Origin of the β_{cell} Relaxation. As for the study of γ_{cell}, it is of interest to compare the β mechanical relaxation process of different polysaccharides. Dextran exhibits a β mechanical relaxation that also changes with water content. In Figure 6, $\ln(\tau)$ is plotted versus $(1/T)$ for our experimental data for cellulose and dextran. Data obtained by Bradley and Carr[13] from mechanical measurements on dried amylose have been added, together with data obtained by several authors from mechanical measurements[14,15] and also dielectric spectroscopy.[15] Our results are in good agreement with those already published. Moreover, all of these β relaxations have similar characteristics. Their relaxation times depend on the water content of samples. According to Heijboer,[2,36,37] the apparent activation energies are too high (and $\tau_{0\beta}$ too short compared to the Debye time) to ascertain that only lateral groups are responsible for these relaxations and it is clear that these processes could not correspond to the glass transition. Thus, they should be associated with localized motions of the main chain.

We have previously observed that the activation entropy is nonzero for the β relaxation. The origin of the activation entropy of the β relaxation can be found either in intramolecular interactions or in intermolecular interactions, as it is difficult to imagine that the rotation of a main chain segment can occur without any contribution from their first neighbors. More probably, in fact, the two effects have to be considered. However, the only way to determine the value and the origin of the entropy contribution would be to perform molecular modeling and dynamics calculations, so as to model the thermoactivated motion.

Conclusion

The γ and β mechanical secondary relaxations of amorphous cellulose were characterized by mechanical spectrometry. It appears that the activation energy of the γ mechanical process is mainly enthalpy. In contrast, the very low preexponential time $\tau_{0\beta}$ of the β mechanical process ($\approx 10^{-20}$ s) indicates a large entropy contribution.

It can be concluded that the γ process corresponds to isolated motions occurring without cooperativity. The comparison of mechanical analyses of cellulose with other polysaccharides (dextran, amylose) confirms that the γ relaxation of cellulose results from the rotation of CH_2OH groups. In fact, dextran, which does not have such lateral groups, exhibits a very weak γ mechanical relaxation with abnormally high activation energy, the origin of which is still not understood. In order to better characterize the motion of CH_2OH groups, preliminary molecular modeling based on molecular mechanics was performed. Calculations are consistent with the well agreed idea that the rotation of CH_2OH around the C5−C6 axis is probably at the origin of the γ mechanical relaxation process of cellulose. From several sets of calculations, it has been determined that less than 10% of CH_2OH groups can relax between two metastable positions having close energy levels. The average energy barrier was found to be 40 kJ/mol with a distribution width of about 10 kJ/mol, which is consistent with mechanical spectroscopy data. Finally, comparison between stable conformations shows that the rotation of CH_2OH groups produces significant changes neither in the chain conformation nor, probably, in neighboring chains. This in turn, is consistent with the negligible activation entropy associated with the relaxation phenomenon. In addition, it indicates that in this case, calculations performed on isolated chains are sufficient to give information on the molecular motion involved in the relaxation process.

In contrast, the very low preexponential time and the relatively high apparent activation energy of the β mechanical relaxation indicate a large entropy contribution. The values of the average activation energies and the comparison of mechanical analysis data of cellulose and other polysaccharides show that the process should involve motions of segments of the main chain. The cooperativity (which can be evaluated from the preexponential term of the Arrhenius fit of the relaxation time) associated with a relaxation process could correspond (i) to an intramolecular contribution and/or to (ii) an intermolecular contribution. In addition, this cooperativity decreases with the amount of water.

Furthermore, the question of the γ and β relaxation intensity with the water content still remains. This problem could in part, be directly related to the number of sites where the energy minina of the metastable conformers are very close, so that their probability for occupation is more or less equivalent. If the average difference between these minima is modified by the presence of a water molecule, then the intensity of the relaxation process should be modified.

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