# Secondary Molecular Mobility in Amorphous Ethyl Cellulose: Aging Effects and Degree of Co-Operativity

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**ABSTRACT:** The secondary relaxations in amorphous ethyl cellulose are studied using thermally stimulated depolarization currents (TSDCs) in the temperature region from 165 °C (108 K) up to 145 °C (418 K). The influence of aging on the current peaks of the secondary relaxation is discussed, and it is concluded that some modes of motion of this mobility are aging independent, while others are affected by aging. A particular attention is focused on the discussion of the degree of co-operativity of the motional modes of the secondary relaxation. The conclusion to be driven from the obtained TSDC results is that the aging-independent motional modes, as well as those that are aging dependent, do not show any appreciable co-operative character.
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## INTRODUCTION

Several dielectric relaxation studies addressed the problem of the relaxation behavior of cellulose and related polymers.[1–7] However, the microscopic attribution of the observed relaxations, that is, the molecular interpretation of the different mobility modes, is the subject of a considerable controversy. The group of Jürgen Einfeldt, at the University of Rostock, carried out recently an interesting and extensive study on the relaxational dynamics of cellulose and related polysaccharides by dielectric relaxation spectroscopy (DRS).[8–13] It was found that these polysaccharides behave differently in the wet and in the dried states. The influence of water is so important that the presence of small residuals gives rise to the appearance of a new and strong relaxation process, called $\beta_{\mathrm{wet}}$, that vanishes on drying and reappears after rewetting.[10] For well-dried samples the conclusions of this extensive study are as follows: (1) The dominant process is observed between −120 and 0 °C, called $\beta$, and is attributed to local motions of chain segments via the glucosidic bond that connects the chain units. We noted that a co-operative character is claimed for this $\beta$-process on the basis of the low values of the Arrhenius prefactor associated to this relaxation.[5,12,14] (2) A weak and broad process appears in extremely dry samples where the $\beta_{\mathrm{wet}}$ disappears. It is detected in all polysaccharides in the frequency range of the $\beta_{\mathrm{wet}}$, that is, in the low frequency side of the $\beta$-relaxation, called $\delta$-relaxation, and its molecular origin is not clear. In some cases there is a hint that it is associated to end groups, but it can also be a shifted residual of the $\beta_{\mathrm{wet}}$.[8] (3) At higher frequencies, a broad and low

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dielectric strength process is found, called $\gamma$-relaxation. An overall consensus has not been reached on the details of the molecular interpretation of this mobility. Some authors suggest that it represents the reorientational mobility of the hydroxyl and methylol groups present in the anhydroglucose unit.[1,3] However, these internal rotations are too fast (too low activation energy) to be detected in the frequency window of DRS and cannot be so distributed (broad) as found in polysaccharides. Others associate this mobility to the ring inversion of the glucose unit, but it seems clear that this interconversion requires both a high activation energy and co-operative motion of several glucose units to occur.[7] The most likely explanation is probably that the $\gamma$-relaxation is due to cross-correlations of the side group rotations with the local main chain motions. Two important findings of this research need to be underlined: (1) all these relaxations display an Arrhenius behavior; (2) all these processes occur at sub-$T_g$ temperatures and have the features of the secondary relaxations, so that the primary or $\alpha$-relaxation (connected to the glass transition) was not observed in any cellulosic material.[8,9] The experimental technique of thermally stimulated depolarization currents (TSDCs) was also used to study the molecular mobility in polysaccharides. In ethyl cellulose, two relaxations were found,[15,16] at $\approx$70 and $\approx$110 °C. The first one was attributed to the reorientation of the ethoxy side groups, but the activation energy of 20 kJ mol$^{-1}$ reported to this relaxation is not compatible with its temperature location. The second one was attributed to space charge polarization. In the studies on pullulan and amylase,[17,18] no $\alpha$-relaxation was reported. In these TSDC studies the only relaxation detected for dried samples is observed at −130 °C (for pullulan) and −110 °C (for amylose), show an Arrhenius behavior, called $\gamma$, and is attributed to the rotation around the axis $C_5$-$C_6$ of the methylol groups attached to the $C_5$ atom in the glucose residue. The other detected relaxations, including one appearing at room temperature, are ascribed to bound water. In a recent TSDC and DRS study on cellulose,[19] three relaxations were reported. The $\gamma$ relaxation was found in TSDC and in DRS and was ascribed to local internal rotations of the methylol groups. The $\beta$-relaxation was not found in DRS and appeared in TSDC in the region between −100 and −50 °C. It was ascribed to localized co-operative motions of short sequences of the backbone, and the attribution of a co-operative character to this relaxation was justified by a very slight deviation of these modes to the Starkweather line (or zero activation entropy approximation). Finally, TSDC gave clear evidence for a relaxation with maximum intensity at $\approx$85 °C which was ascribed to the $\alpha$-relaxation. If this attribution is correct, the analysis of the corresponding relaxation peak indicates that cellulose is a very strong glass-former. This is in contradiction with the interpretation of the dielectric data by the Einfeldt group that claims the absence of the $\alpha$-relaxation in cellulosic polymers based on the fact that, in a very large volume of experimental results, no evidence was found for a dynamics with a Vogel-Fulcher temperature dependence.[8] However, it is not excluded that the relaxation observed by this research group in the temperature range between 80 and 180 °C[20] (named $\sigma$, which shows an Arrhenius behavior with activation energy of 95–110 kJ mol$^{-1}$, and was ascribed to a space charge relaxation) corresponds in fact to the glass transition relaxation. The fact that cellulosic polymers are strong glass-formers (low fragility index) should be at the origin of the observed Arrhenius behavior. The DRS signature of the $\alpha$-relaxation in amorphous ethyl cellulose is also reported in a recent study mainly devoted to the sub-$T_g$ mobility.[14] The corresponding relaxation peak appears at about 125–155 °C, but it was not analyzed in detail because of the overlapping of a dc conductivity.

Given the diversity and the complexity of the problems to be understood in relation with the slow molecular mobility in amorphous polysaccharides, we decided to perform a series of studies on these systems using the technique of TSDCs: first, because the TSDC studies on polysaccharides are relatively scarce; second, because we believe that TSDC can provide an important contribution to the elucidation of some aspects of this molecular mobility that are not yet understood. TSDC and DRS are dielectric-related techniques. The power of the DRS technique arises from its isothermal nature and, above all, from its wide frequency range. Oppositely, TSDC is a nonisothermal technique as is, for example, the case for differential scanning calorimetry. As a consequence, measurement can, in some situations, interfere with aging processes. On the other hand, a drawback of TSDC is clearly its narrow frequency range. However, TSDC is a low-frequency technique,[21] which leads to a high sensitivity, with an enhanced resolution of the different relaxation processes. As a consequence of this feature, the $\beta$-relaxations appear most often in the TSDC spectra as a very broad peak, well separated from the main relaxation. The most important advantage of TSDC is however the possibility of using the experimental procedure of thermal sampling, or partial polarization (PP), which enables to resolve a global distributed peak into its individual relaxation modes and allows the calculation of the temperature-dependent relaxation time associated with a given single mode of motion (see Experimental section). Note that DRS is not able to determine the temperature-dependent relaxation time of a single (or narrowly distributed) relaxation mode, but rather the mean relaxation time of the whole distribution. Finally, since the secondary relaxations appear in the TSDC spectrum at temperatures much lower than the glass transition temperature, temperatures at which aging is substantially slowed down, the TSDC experimental technique appears as very useful to the study of such relaxations given that the measurement hardly interferes with the aging process.

Ethyl cellulose was our choice for this first study because it is a fully amorphous polymer and nonhygroscopic, and a relatively recent DRS study is available in the literature.[14]

## EXPERIMENTAL

Ethyl cellulose, CAS number 9004-57-36, ethoxy content 48%, was purchased from Acros. It was used as received. The glass transition temperature was found to be 122 °C from DSC (midpoint) and from conductivity measurements,[14] a value that we confirmed by DSC.

TSDC experiments were carried out with a TSC/RMA spectrometer (TherMold, Stamford, CT) covering the range from −170 °C (103 K) to +400 °C (673 K). For TSDC measurements the sample was placed between the electrodes of a parallel plane capacitor with effective area of ~38 $\mathrm{mm}^2$ (thickness of ~0.5 mm). The sample is immersed in an atmosphere of high-purity helium (1.1 bar). Some measurements were carried out on samples dried under vacuum at 185 °C for a period of time of at least 6 h, and similar results were obtained with dried and nondried samples.

The fact that the relaxation time of the motional processes is temperature dependent and becomes longer as temperature decreases, enables to immobilize them by cooling. This is the basis of the TSDC technique, which is particularly adequate to probe slow molecular motions. To analyze specific regions of the TSDC spectrum, different methods of polarizing the sample can be used, namely, the so-called TSDC global polarization experiment and the PP experiment (often called thermal sampling or windowing or cleaning). In the global polarization experiment the polarizing electric field scans a wide temperature interval so that the polarization of the sample is constituted by a wide distribution of relaxation modes. The result of a global polarization experiment is referred as a global peak. Oppositely, the PP method, where the polarizing field is applied in a narrow temperature interval, enables to resolve a global peak into its individual relaxation modes. A more complete explanation of the electric and thermal treatments most often used in the TSDC studies can be found in refs. 22 and 23. The PP procedure allows to retain (or to freeze) a polarization that arises from a narrow variety of dipolar motions. In the limit of a very narrow polarization window, the retained polarization (and, of course, the current peak that is the result of a PP experiment) would correspond to a single, individual dipolar motion.[22]

In this work, the analysis of the PP peaks is based on the Debye relaxation concept and corresponds to the so-called Bucci method.[24] In this context, the assumption is that, at each temperature of the linear heating ramp, the decay of the polarization with time is a first order rate process. For an elementary, single motional process, we can thus write as follows:

$$\frac{\mathrm{d}P(T)}{\mathrm{d}t} = -\frac{P(T)}{\tau(T)} \tag{1}$$

where $P(T) = P(t)$ is the remaining polarization at temperature $T$ (at time $t$) of the heating ramp, and $\tau(T)$ is a temperature-dependent relaxation time, characteristic of the elementary mode of motion under consideration. Since the depolarization current density [current intensity per unit area, $J(T)$], is the rate of decreasing of the polarization, it comes out that

$$J(T) = \frac{P(T)}{\tau(T)}. \tag{2}$$

As reported earlier, an important feature of the TSDC technique is that it allows the study of elementary or single relaxational processes using the so-called thermal sampling (PP) procedure. The importance of eq 2 is that it allows the calculation of the temperature-dependent relaxation time of a single relaxation process from the

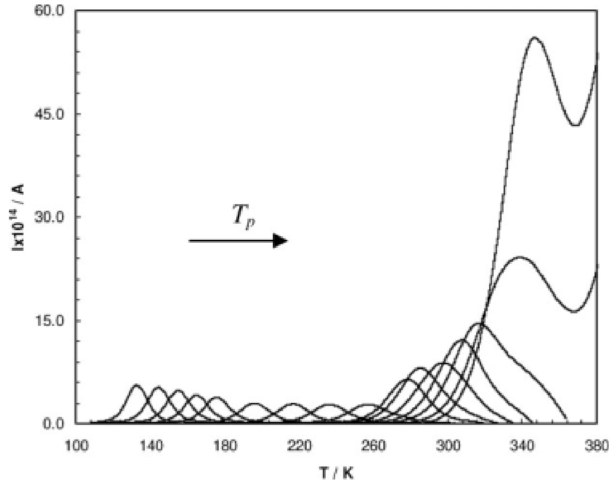

**Figure 1.** Partial polarization components of the sub-$T_g$ molecular mobility of amorphous ethyl cellulose in the lower temperature region. Polarization temperatures, $T_P$, were in the range from −140 to +65 °C from left to right. The other relevant experimental conditions were as follows: strength of the polarizing electric field, $E = 450$ V mm$^{-1}$; polarization time, $t_P = 5$ min; width of the polarization window, $\Delta T = 2$ °C; heating rate, $r = 4$ °C min$^{-1}$.

experimental result of the corresponding PP experiment. As the temperature rises linearly with time in the depolarization step, temperature and time are related by $T = T_0 + rt$, where $T_0$ (the so-called freezing temperature) is the temperature at the beginning of the heating ramp (at $t = 0$) and $r$ is the heating rate. In this context, the remaining polarization at temperature $T$, $P(T)$, is given as

$$P(T) = \frac{1}{r}\int_{T}^{\infty} J(T')\,\mathrm{d}T' = \frac{1}{r}\int_{T}^{T_\mathrm{f}} J(T')\,\mathrm{d}T' \qquad (3)$$

where $T_\mathrm{f}$ is a temperature well above the temperature of the maximum of the PP peak, where the sample is assumed completely depolarized. The temperature-dependent relaxation time associated with a given mode of motion can thus be calculated from

$$\tau(T) = \frac{\frac{1}{r}\int_{T}^{T_\mathrm{f}} J(T')\,\mathrm{d}T'}{J(T)} = \frac{\frac{1}{r}\int_{T}^{T_\mathrm{f}} I(T')\,\mathrm{d}T'}{I(T)} \qquad (4)$$

where $I(T)$ is the depolarization current intensity measured in the heating ramp of the PP experiment. The capability of directly calculating the relaxation time from the results of a single PP experiment constitutes an essential quantitative feature of the TSDC technique, and that is why TSDC is an experimental technique that provides important information on molecular mobility in solids, that is, on the kinetics of relaxational processes and the distribution of relaxation times. We note that eq 1 does not account for nonexponentiality, a feature of the main relaxation in complex systems. However, this study deals with secondary relaxations, so that the data treatment used seems to be adequate.

A recent review is available on TSDC applications.[25] The physical background of the TSDC technique and useful details on the analysis and interpretation of the results are presented elsewhere.[21,26–28]

## RESULTS AND DISCUSSION

### General Results

Figures 1 and 2 display the PP peaks that correspond to the motional modes of ethyl cellulose in the whole temperature interval of this study (from –165 up to 145 °C). Since $T_g = 122$ °C,[14] the peak appearing at 120–130 °C in Figure 2 probably corresponds to the glass transition mobility.

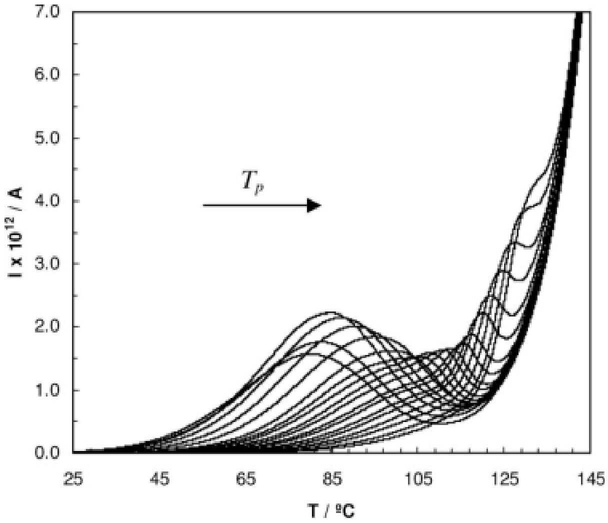

**Figure 2.** Partial polarization components of the sub-$T_g$ molecular mobility of amorphous ethyl cellulose up to the glass transformation region. Polarization temperatures, $T_P$, were in the range from +70 to +130 °C from left to right. Other relevant experimental conditions were as follows: strength of the polarizing electric field, $E = 450$ V mm$^{-1}$; polarization time, $t_P = 5$ min; width of the polarization window, $\Delta T = 2$ °C; heating rate, $r = 4$ °C min$^{-1}$.

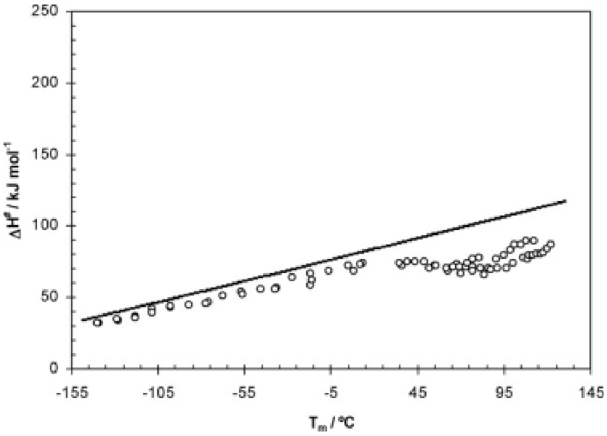

**Figure 3.** Activation enthalpy, $\Delta H^{\neq}$, of a series of motional modes of the of the amorphous solid ethyl cellulose as a function of the peak's location, $T_m$. The line is the zero entropy line.

However, since it strongly overlaps with another relaxation in the lower temperature side, and with a conductivity tail at higher temperatures, we were not able to analyze it to determine the corresponding kinetic parameters. In Figure 2, a relaxation peak is observed with maximum intensity at ≈80 °C, whose activation energy is ≈70 kJ $\text{mol}^{-1}$. These two relaxations shown in Figure 2 certainly correspond to those at 70 and 110 °C found in the TSDC study of ethyl cellulose previously reported.[16] On the other hand, Figure 1 displays a series of PP modes in the low-temperature region.

We note that the increase of the intensity of the peaks in the right-hand side of the figure indicates that we are going through modes with higher dielectric strength that correspond to the relaxation with maximum intensity at 80 °C shown in Figure 2.

The activation enthalpies of the motional modes displayed in Figures 1 and 2 are plotted in Figure 3 as a function of temperature location, $T_m$ (temperature of maximum intensity), of the corresponding TSDC peaks. As pointed out earlier, the Debye approach was used for TSDC data treatment, because we are dealing here with secondary relaxations. For the alpha relaxation, nonexponentiality must be accounted for.[29] This representation in Figure 3 is often called the Starkweather plot[30–32] which is a useful way of presenting TSDC data to highlight the degree of co-operativity of the different motional processes. The line in Figure 3 is the so-called Starkweather line, or zero activation entropy line, that depicts the behavior of non–co-operative relaxations. Figure 3 does not show significant positive deviations from the Starkweather line, which indicates that the mobility modes whose dielectric signature is shown in Figures 1 and 2 are local and non–co-operative, have negligible activation entropy, or, stated differently, have pre-exponential factors of the order of the Debye time ($10^{-13}$ s).

It is worth to recall that the quantity $\tau_D = h/kT_0 = 1.76 \times 10^{-13}$ s (with $T_0 = 273.15$ K), often called Debye time,[2] represents the characteristic time, at room temperature, of a process with no activation Gibbs energy. It is the pre-exponential factor of the Eyring equation, so that the deviation of the Arrhenius prefactor, $\tau_0$, from $\tau_D$ correlates to the activation entropy associated with reorientation in the relaxation process. High values of the activation entropy, or smaller values of $\tau_0$ relative to $\tau_D$, can be interpreted to arise from co-operativity of the orientational motion.

The small negative deviation observed for the points in the right-hand side of Figure 3 (that refers to the relaxation at 80 °C in Fig. 2) should correspond to a negative activation entropy. In a chemical reaction, a negative activation entropy indicates that the activation complex is more ordered than the reactants. Viscoelastic relaxations tend to have positive activation entropies. The zero entropy line defines a lower limit for the activation energies of viscoelastic relaxations.[30] Since the experimental uncertainty in the activation energy is often of the order of 3–4 kJ $\text{mol}^{-1}$, it is not certain if the activation entropy is exactly zero or has a small positive or negative value. However, these are very small effects that do not explain the negative deviations from the zero entropy line shown in Figure 3. Despite the fact that we have no satisfactory explanation for the observed behavior, we are nevertheless able to conclude that the mobility we are analyzing by TSDC in amorphous ethyl cellulose is essentially non–co-operative. This topic of the degree of co-operativity of the secondary relaxations will be discussed later.

### Effect of Aging on the Secondary Relaxations of Ethyl Cellulose

The experimental technique of TSDC is adequate to this purpose of studying the aging effect on the secondary relaxations, because the $\beta$ and $\alpha$ processes are usually well resolved in TSDC. Oppositely, in DRS the proximity of the two relaxations often hides the weaker $\beta$-relaxation under the high-frequency flank of the $\alpha$-relaxation. Some glass formers show several secondary relaxations, and the molecular mechanisms underlying them can be different. This is often observed in amorphous polymers where high-frequency subsidiary peaks appear in the dielectric relaxation spectrum. They are usually labeled as $\beta$, $\gamma$, $\delta$, … in the order of increasing frequency (decreasing temperature) and are characteristically broad. DRS often shows a poor ability to resolve different secondary relaxations given that they correspond to local motions with activation energies of low and similar magnitude. On the contrary, TSDC generally displays secondary relaxations as relatively well-resolved broad peaks. Finally, and very important, the measurement hardly interferes with the aging process, since the secondary processes appear in TSDC at very low temperatures, at which aging is substantially slowed down. This is no longer true for the TSDC study of the aging effect on the $\alpha$-relaxation, since the thermal history needed to produce the depolarization current involves thermal treatments in the temperature region below but near $T_g$, so that the experiment will influence the aging process. The molecular mechanism of a secondary process can be intramolecular (internal rotation about a sigma covalent bond of a group of atoms of the entire molecule, conformational flip of a cyclic unit) or intermolecular (local motion of the whole molecule or, in the case of a polymer, of the whole monomer or of a short segment of the main chain). The intermolecular secondary relaxation is often called Johari–Goldstein (JG) relaxation.

The low-temperature TSDC thermogram showing the secondary relaxations of amorphous unaged and aged ethyl cellulose is presented in Figure 4(a,b). In Figure 4(a) the sample was aged at the same temperature ($T_{ag} = 115$ °C) for different times. Figure 4(b), on the other hand, where the sample was aged during the same aging interval ($t_{ag} = 2$ h) at different aging temperatures, shows the increase of the aging rate with increasing aging temperature, $T_{ag} < T_g$. It can be seen in both Figure 4(a,b) that the secondary relaxation peak is broad and presents some kind of structure, with two local peaks separated by a saddle (as is also visible in Fig. 1). Furthermore, the results displayed in Figure 4(a,b) show that the lower temperature modes of the secondary relaxation (PP peaks in the left-hand side of Fig. 1) are not influenced by aging, but that the higher temperature components (PP peaks in the right-hand side of Fig. 1 and of the relaxation with higher intensity at ~80 °C in Fig. 2) are strongly affected by aging. Furthermore, those manifestations of the physical aging on the secondary relaxations are reversible as the aging effects can be erased by heating above $T_g$ to the metastable liquid or plastic state. The work by Struik was a pioneer for the understanding of physical ageing.[33] He showed that aging is a general feature of the glassy state, that the different aspects of aging can be qualitatively explained from the free volume concept, that aging is thermoreversible, that the isothermal aging rate (at $T_a$) decreases almost exponentially as ($T_g$ – $T_a$) increases, and that it

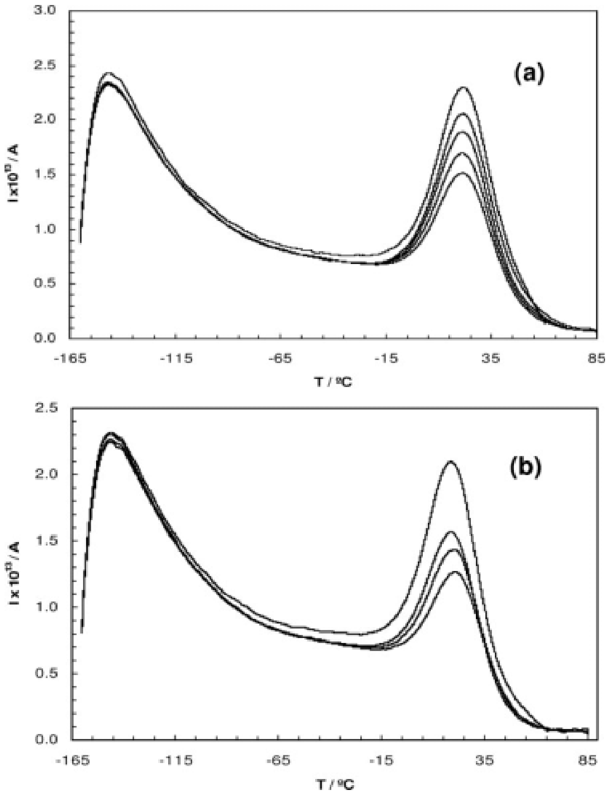

**Figure 4.** TSDC thermogram showing the secondary relaxations of amorphous unaged and aged ethyl cellulose: (a) at different aging times; (b) at different aging temperatures. In (a), the aged sample was annealed prior to the experiment at the aging temperature of $T_{ag} = 115$ °C during periods of time of $t_{ag} =$ 20, 80, 200, and 380 min. In (b), the aged sample was annealed prior to the experiment for an aging time of $t_{ag} = 120$ min at the aging temperatures of $T_{ag} = 105$, 110, and 115 °C. The other relevant experimental parameters were as follows: strength of the polarizing electric field, $E = 450$ V mm$^{-1}$; polarization time, $t_P = 5$ min; polarization temperature, $T_P = 15$ °C; freezing temperature, $T_0 = -165$ °C; heating rate, $r = 8$ °C min$^{-1}$.

occurs in a wide temperature range between $T_g$ and the first (highest) secondary transition $T_\beta$.[33,34]

More recent investigations[35] show that an effective aging rate is observed at low annealing temperatures, close to $T_\beta$. On the other hand, about secondary relaxations, Struik believed that well-separated secondary peaks are insensitive to aging, that is, their temperature location, height, and activation energy are hardly influenced by the thermal history.[34,36] However, he observed an aging effect on the higher temperature side of the secondary relaxation peak, which he attributed to the tail of the glass transition,[36] but this could well correspond to an aging effect on what we presently call the JG relaxation. Aging effects on the secondary relaxations of different amorphous polymers have been observed from dynamical mechanical analysis.[37–40] In particular, the work by Cerrada and McKenna[40] looks at the physical aging response under isothermal and isostructural conditions. TSDC studies of aging effects on the secondary relaxations are scarce; as an example we refer the study on polycarbonate.[41] It is now believed[42] that the isothermal aging of the secondary relaxation can occur at low temperatures, deep in the glassy state, several tens of degrees below $T_g$. Furthermore, several authors argue that the dynamics of aging of the secondary relaxation is determined by the structural relaxation process.[43]

Coming back to our TSDC results shown in Figure 4, their usefulness is that they give a particularly clear picture of the differentiation of two types of secondary relaxations, and of their evolution as a function of the aging time. Given that density increases, and the free volume decreases, on structural relaxation, we suggest that the faster motional modes (detected at lower temperatures), which are not affected by aging, must have an intramolecular origin.[44–46] These are local motions that consist of internal rotations of one part of a molecule relative to the other part, or conformational modifications of a cyclic unit, which occur without significant interference of the neighboring molecules. In the case of ethyl cellulose, these local motions could be associated to the pendant ethoxymethyl group. On the other hand, the slower motional modes, at higher temperatures, that correspond to mobility components of the secondary relaxation and are affected by aging have probably an intermolecular origin. We thus suggest that the modes that are independent of aging constitute the fast $\beta$- or $\gamma$-relaxation, while the aging-dependent mobility modes constitute the so-called slow $\beta$ or JG relaxation.[47] There are given in literature, with several reports showing the aging effect on the JG relaxation.[48–50]

## Co-operativity of the *β*-Relaxation

As underlined earlier, the molecular nature of the motions that originate the secondary relaxations is still a matter of debate despite the numerous experimental studies carried out on this topic. The molecular motions in the glassy state fall into two broad categories: (i) local modes, and (ii) long-range collective or co-operative modes. The secondary and, particularly, the $\beta$-relaxations were, for many years, considered as originating from local, non–co-operative motional processes. However, some authors who observed an aging effect on the secondary relaxations interpreted this observation as a consequence of a given degree of co-operativity attributable to these relaxations.[51] Furthermore, the co-operative character of the $\beta$-relaxation in cellulosic polymers and other glass-forming systems is claimed by several authors[5,12,14,52–55] on the basis of the small value of the experimental Arrhenius prefactor obtained from DRS data in comparison with the so-called Debye time, $\tau_D = h/kT$. In a paper published several years ago[56] we tried to show that the results obtained by TSDCs on the $\beta$-relaxation of several glass-forming systems seem to contradict this claim, that is, the TSDC results clearly reveal the non–co-operative nature of the $\beta$-process. In this work we will show the same type of data for the presently studied molecule and will use the same arguments to strengthen this idea that the slow $\beta$-relaxation is non–co-operative. Figure 5 shows a comparison between the DRS and TSDC results for the $\beta$-relaxation of ethyl cellulose in the form of a relaxation map.

The thicker line in Figure 5 is the log $\tau_\beta{}^*$ versus $1/T$ line of the $\beta$-relaxation obtained by DRS ($E_{app} = 55$ kJ mol$^{-1}$; $\tau_0{}^* = 10^{-17}$ s).[14] The thinner and shorter lines, on the other hand, are the log $\tau_\beta$ versus $1/T$ lines, obtained by TSDC for the PP components of the same $\beta$-relaxation (some of them shown in Figs. 1 and 2). We note that all the information included in Figure 3 is exported to Figure 5 which is nothing but a different graphical way of displaying the TSDC data. From the TSDC results presented in Figure 5 we can make the following comments:

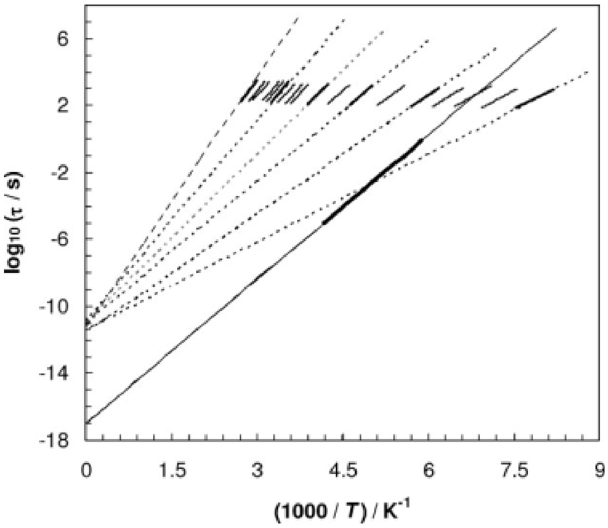

**Figure 5.** Relaxation map for the secondary relaxations of ethyl cellulose. The thicker line was obtained from DRS data (see text). The smaller and thinner lines are the log $\tau$ versus $1/T$ lines of the partial polarization components of the secondary relaxations of ethyl cellulose, obtained by TSDC. The dashed and dotted lines are only extrapolations of the fits to the experimental data. The experimental conditions used in the TSDC experiments are those indicated in Figures 1 and 2. The two extreme lines, on the left- and right-hand sides, correspond to TSDC experiments performed with polarization temperatures, +70 and −140 °C, respectively.

1. The log $\tau_\beta$ versus $1/T$ lines of the different TSDC fractions or segments of the $\beta$-relaxation of ethyl cellulose are strictly linear, indicating an Arrhenius behavior.
2. All these lines converge, as $1/T$ approaches zero, to points close to the Debye time (the logarithm of the extrapolated infinite temperature relaxation time is $\log_{10} \tau_0 = -11 \pm 1$). This is equivalent to saying that the different components of the $\beta$-relaxation, as studied by TSDC, are non–co-operative, that is, they do not present any entropy of activation (they obey the zero entropy approximation as shown in Fig. 3). The molecular motions that originate this relaxation thus appear as simple, local motional processes. Note that the TS lines of the components of the $\alpha$-relaxation show, on the contrary, prefactors to be much smaller than Debye time, indicating a high degree of co-operativity.[57,58]
3. The log $\tau_\beta$ versus $1/T$ lines of the different components of the $\beta$-relaxation of ethyl cellulose show a slope which increases as the temperature increases (the lines in the right-hand side of Fig. 5 have a lower slope than those in the left-hand side). Since the slope of these lines is proportional to the activation energy (or enthalpy) of the PP components, it appears that we are in the presence of a relaxation distributed in energy but not in prefactor (or entropy): the activation energy varies roughly from 30 kJ mol$^{-1}$ (right-hand side) to 60 kJ mol$^{-1}$ (left-hand side).
4. The value of the apparent activation energy obtained from DRS data ($E_a = 55$ kJ mol$^{-1}$) is within the energy interval of the energy distribution obtained by TSDC.

It can be argued that the frequency range of the TSDC technique is narrow, which originates the segments in Figure 5 to be rather short. It can also be argued that the extrapolation of the short segments to the infinite temperature is long. However, in Figure 5 we have a set of many straight segments which coherently give the clear visual perception that the segments extrapolate to a region of the ordinate axis that corresponds to the viscoelastic relaxations. We believe that this large ensemble of data has a self-consistence that strengthens the conclusion that these motional modes are non–co-operative. Figure 5 thus indicates that the $\beta$-relaxation in ethyl cellulose arises from local and non–co-operative molecular motions and is characterized by a distribution in energy, which is not compatible with the claim statement by some authors[12,14] that the $\beta$-relaxation presents some degree of co-operativity or, otherwise stated, that the corresponding molecular motions have a significant activation entropy.

The adequacy of the TSDC technique for the study of the present problem was underlined in the previous section. Let us also recall that it is a low equivalent frequency technique,[21] a fact that leads to an enhanced resolution of the different relaxation processes. As a consequence of this feature, the slow $\beta$-relaxation appears most often in the TSDC spectra as a very broad peak, well separated from the main relaxation. Another important advantage of TSDC is the possibility of using the experimental procedure of PP which enables to resolve a global distributed peak into its individual relaxation modes. This is indeed an important feature of the TSDC technique, since it permits the experimental decomposition of a broad heterogeneous distribution into its narrowly distributed components. Furthermore, the temperature-dependent relaxation time of each mode of motion can be calculated from TSDC data, and this possibility constitutes a basic quantitative advantage of the technique. Note that DRS is not able to determine the temperature-dependent relaxation time of a single (or narrowly distributed) relaxation mode. Instead, the result of the analysis of the data provided by this technique is a mean relaxation time, $\tau_\beta$*, of the whole distribution.

Summarizing, we strengthen our previous suggestion[56] that the fact that DRS prefactor of the $\beta$-relaxation is often found to be lower than the Debye time, cannot be considered as an indication of a co-operative character of this relaxation. The apparent contradiction between the results from DRS and TSDC lies in the fact that the relaxation time determined by DRS is not the relaxation time of a single relaxation mode but rather a mean relaxation time, $\tau_\beta$*, of the whole distribution. The temperature dependence of this mean relaxation time can thus be affected if the nature of the distribution changes with temperature (if the most probable energy is temperature dependent). In this context, it is also possible that the present TSDC experiments highlight only one of the various components of a whole complex secondary relaxation. We note however that the secondary relaxation shown in Figure 4 is rather complex, with one component being aging independent and other being aging dependent, and that both appear in Figure 5 as a non–co-operative mobility. This is an interesting finding afforded by the TSDC results. The hypothesis of the existence of other components not shown in the TSDC spectra is nevertheless not excluded. Finally, we noted that the same kind of difference between the DRS and TSDC results is observed in many other glass-forming systems; it is not specific of ethyl cellulose, and thus it does not correspond to a fortuitous observation. It was reported earlier for sorbitol, maltitol, and different side-chain liquid crystalline polymers[56]; it is also observed for poly(vinyl acetate) and other amorphous polymers.[59]

## CONCLUSIONS

The mobility in the amorphous solid ethyl cellulose showed a broad and complex secondary relaxation revealing a clear structuration with two kinds of molecular motions, and with activation energies distributed between 30 and 60 kJ mol$^{-1}$. It was found that the lower temperature components of this complex secondary mobility are aging independent and correspond to the $\gamma$ or fast $\beta$-relaxation, while the higher temperature components are affected by aging and correspond to the slow $\beta$ or JG relaxation. The signature of the main relaxation in the TSDC spectrum of ethyl cellulose is hidden by the presence of a conductivity tale in a temperature region in the vicinity of the glass transformation.

Furthermore, we showed that the components of the distributed secondary relaxation of ethyl cellulose studied by TSDC, including the JG relaxation, present pre-exponential factors which are close to the Debye time, suggesting the presence of non–co-operative, local motional processes. This interpretation contradicts the perspective of several authors who claim a co-operative character for the JG relaxation.

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