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Dehydration-induced structural relaxation effects in poly(methyl methacrylate)

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SUMMARY: The Thermally Stimulated Depolarization (TSD) dielectric technique and Dielectric Relaxation Spectroscopy (DRS) have been used in order to investigate aging phenomena in poly(methyl methacrylate) (PMMA). Earlier TSD studies on amorphous PMMA report peculiar dielectric relaxation signals within the range of the glass transition (at ~378 K) and the secondary relaxation (~230 K). In the present study, an intense TSD current relaxation band maximizing around 310 K is tentatively attributed to the molecular mobility due to a residual free volume below the glass transition temperature, T_g, that allows structural recovery at the free volume released from the desorption of H_2O molecules during evacuation. Limited motions in the main backbone provoke dipole (re)orientation of the ester carbonyl pendant groups with an activation energy $E=0.85\pm0.05$ eV, being responsible for the latter dielectric relaxation effect. Alternative attributions based on the short-range jump relaxation of electric charges and boundary effects are also discussed.

1. Introduction

The presence of localized molecular motions in the glassy state of a polymer structure has been recognized as an inborn property of disordered materials, where frozen-in density fluctuations create islands of mobility. During this process, the glassy state approaches a state of thermodynamic equilibrium. This type of structural relaxation is frequently described as "physical aging" and involves changes in several properties of the material. For more than two decades structural recovery (below T_g) has been shown to affect thermodynamical properties like the specific volume [1] or enthalpy [2-4], as well as dynamic-mechanical [5-7] and dielectric relaxation [7,8] parameters of amorphous solids. In one casee, the enthalpic aging process(es) occurring in poly(methyl methacrylate) were interpreted in terms of the phenomenological multiparameter or the Cowie-Ferguson models [3]. It is widely accepted nowadays that aged samples manifest an increase in modulus [6,7], and a decrease in permittivity, dielectric loss [8] and specific volume [1] within a limited temperature range between the glass transition temperature, T_g, and the temperature at which local motions freeze in.

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An electrical stress (stimulus) can couple several modes of the mobility of molecules or molecular segments in polymers, provided that these are associated with the reorientation of a dipole vector. The above perturbation and the corresponding dielectric relaxation spectroscopy studies have shed much light in the field of sub-glassy relaxation phenomena in polar macromolecular systems. A typical polar thermoplastic polymer with high technological impact is poly(methyl methacrylate) (PMMA, Fig. 1).

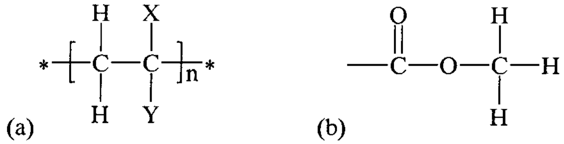

Fig. 1: (a) The structure of the PMMA macromolecule [repeat unit with X=CH_3 and Y=$COOCH_3$], and (b) the ester group responsible for the dipole moment of PMMA.

Earlier investigations [9,10] on amorphous PMMA have reported a peculiar dielectric relaxation signal around 300 K, within the range of T_g (~378 K) and the secondary β-relaxation (at ~230 K). In the present work this relaxation (denoted as β'-relaxation) has been recorded and thoroughly studied in several PMMA specimens (50% of the investigated samples), produced by typical free radical polymerization, in order to correlate its behavior with the relaxation mechanisms involved. The dielectric response of PMMA has been studied by means of the TSD current technique in the temperature range 10-320 K, with the sample under vacuum conditions. The discussion is further supported by results obtained by means of the ac counterpart of TSD, the Dielectric Relaxation Spectroscopy (DRS) method [11].

2. Experimental

2.1 Technique description

The application of the TSD current technique in polymers consists of monitoring the restoration of the non-polarized state of a polymeric thermoelectret as a function of the temperature of the polymer sample. The thermoelectret is generated by applying an electric field, E_p, for time t_p, at a suitable constant temperature, T_p, typically between the glass-transition temperature, T_g, and the melting point, T_m, of the corresponding polymer. The electric stimulus causes an alignment of permanent or induced dipoles as well as a drift of real charges (homo- or heterocharges). By rapidly cooling the sample, at T_0, the orientation of the dipoles may be frozen in and charges may be trapped. These mechanisms decay in a short time when heated up to higher temperatures with a constant heating rate, h, or upon aging. Thus, by observing the thermally stimulated discharge as a function of temperature, phase transitions and molecular motions in the polymer can be studied. The recovery of the system is monitored by measuring the depolarization current $I(T)$. For a single relaxation mechanism the asymmetric current density band, $J_D(T)$, is described by

$$J_D(T) = \frac{P_0}{\tau_0} exp\left(-\frac{E}{k_\beta T}\right) exp\left[-\frac{1}{h\tau_0}\int_{T_0}^{T} exp\left(-\frac{E}{k_\beta T'}\right) dT'\right] \qquad (1)$$

where P_0 is the saturation polarization, E the activation energy, and τ_0 the pre-exponential factor of the Arrhenius equation that describes the temperature dependant relaxation time,

$$\tau(T) = \tau_0\, exp\left(E / k_\beta T\right). \qquad (2)$$

Equation (1) is similar to that characterizing thermoluminescence or thermally stimulated conductivity processes obeying first-order kinetics. Deviations of the theoretical TSD current peaks are frequently attributed to a distribution of $\tau(T)$.

2.2 Experimental details

The material used in this experiment was PMMA polymerized in our laboratory. Commercially supplied methyl methacrylate (MMA) was washed three times in 5 % NaOH and 20 % NaCl in water to free it from its inhibitor, hydroquinone monomethyl ether, followed by repeated washing with distilled water, and then dried with anhydrous sodium sulphate. Prior to the polymerization procedure, the chemically pure liquid monomer was stored at temperature $T<273$ K, in order to minimize the effect of spontaneous polymerization. Free radical polymerization was performed at 313 K for 3 days, initiated by 0.125 % by mass of benzoyl peroxide dissolved into the monomer MMA. From the resulting transparent PMMA block, ten samples, with typical dimensions (5×5×1) mm, were cut and subsequently polished in order to obtain smooth surfaces. After polymerization, the samples were kept for at least three months in the air at room temperature (RT). Prior to the dielectric measurements both surfaces of the samples were cleaned with CCl_4. High-resolution proton nuclear magnetic resonance (NMR) measurements indicate a random stereochemistry of the tertiary carbons in the macromolecules (amorphous), with ~ 55 % syndiotactic triads. No differences in syndiotacticity between samples with and without the β' relaxation have been detected.

The TSD scans were carried out in a ROC 10-300 refrigerator-cooled cryostat (Leybold-Heraus, LH), modified for electrical measurements. The R210 two stage refrigerator used to operate the cryostat is a cryogenerator utilizing the provided closed helium-gas cycle by a RW2 compressor. The experiments were performed in vacuum ($\cong 10^{-4}$ - 10^{-5} Torr), using a Drytel pump. The dc field was applied with the sample between stainless steal electrodes electrolytically covered by Cr. The computer controlled measurements were carried out in the range 10-320 K with the typical experimental conditions of T_P=320 K, E_P=(3-5)$\times 10^6$ V/m and t_P=5 min (at T=T_P). Apparatus safety limitations and the need to decrease the interference of the α-relaxation current signals imposed the selection of a polarizing temperature well below the glass transition temperature. At the same time, the values of T_P, E_P and t_P are sufficiently high enough to achieve the saturation polarization of the relaxation mechanisms in PMMA that are of interest in the present study. The temperature program employed a rate of h=0.083±0.003 degrees/sec (temperature controller: model LTC 60, LH). Current signals were monitored by a Keithley 617 electrometer. DRS measurements were performed at RT with use of an impedance analyzer (model SI 1260, Solatron), part of a sensitive dielectric spectrometer (model BDC S, Novocontrol).

3. Results and discussion

The sub-glassy dielectric peaks of different polymers have attracted great interest. Some of them, in terms of the Goldstein's theory of relaxation behavior in viscous liquids, are frequently connected with "islands of mobility" in the stiff glassy-polymer state and may be considered as precursors of the large conformational main chain motions in the glass-rubber transition region [12]. In PMMA, the principal sub-glassy mechanism (β-relaxation) involves the rotational mobility of the lateral groups. Among other studies, a theoretical molecular mechanics study of the side group motions in PMMA, by Heijboer *et al.* [13], has partially confirmed that the broad β-relaxation band originates from the local motion of the lateral carboxymethyl groups with a specific intramolecular barrier. Furthermore, its apparent activation energy E has a smooth energy distribution, which may be associated with intermolecular interactions that contribute to this relaxation. The relaxation time τ is thus an average time between changes in two stable orientations of the ester unit. As the temperature increases in the TSD run, the average time between these changes decreases and dipolar (re)orientation results to a significant current band.

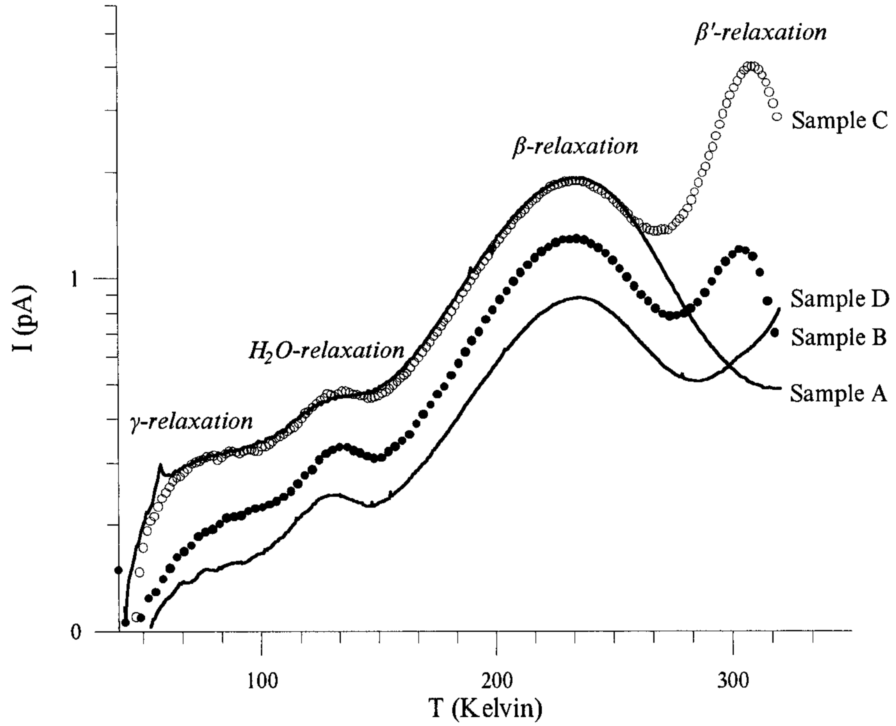

Fig. 2: TSD current spectra of four different PMMA samples cut from the same block.

In atactic PMMA with a high content of syndiotactic triads (55 %), the TSD dielectric β-relaxation peak has a maximum at about 230 K (Fig. 2), for a heating rate of 0.083 degrees/min. The corresponding dielectric loss peak occurs around 10 Hz, for isothermal experiments around RT (~298 K). Around 130 K and superimposed to the rising part of the secondary relaxation, appears a TSD band attributed to the rotational relaxation of the polar water molecules. Much lower, around 75 K, the weak band is associated with the rotation of α-methyl (γ-relaxation). The latter relaxations are expected to give loss peaks in the MHz–GHz frequency regions. Gourari *et al.* [9] report multiple current peaks in atactic PMMA specimens, maximizing in the vicinity of the prominent glass transition peak, which they relate to the presence of syndiotactic/isotactic minority phases and the so-called liquid-liquid or T_{LL} transitions.

The most intriguing element in Fig. 2 is the appearance of a strong high temperature (HT) peak (denoted β'-relaxation) in samples B and C, located at 310 K. At the same time the band is absent in the TSD spectrum of sample A. 50 % of the investigated samples (cut from the same PMMA block) exhibit the β'-relaxation peak, while 30 % of the samples simply show a current rise above 290 K (sample D). The remaining 20 % demonstrates a TSD spectrum similar to that of sample A. The absence of the β' peak in part of the sample collection may be connected to a shift of the band to higher temperature regions, above the measuring range (320 K). Nonetheless, the HT shift can not be explained in the present stage of our study. The β'-relaxation is probably hidden in the HT rising currents appearing in some of the samples (e.g. sample D). In a study of the dynamic-mechanical and dielectric behavior of bulk PMMA and several methyl methacrylate and methyl isopropenyl ketone (MIK) copolymers, Ribes-Creus *et al.* [10] found low peaks in the temperature range 280-295 K, irrespective of the MIK content. The signals were highly overlapped (on their HT side) by the strong α-relaxation band and the secondary relaxation at lower temperatures. The authors regarded this peak as a direct effect of physical aging produced by the heat treatment (quenching from $T>T_g$) prior to the experimental runs. All samples exhibited a high degree of syndiotactic character (60 % syndiotactic triad and 78 % syndiotactic dyad). Gourari *et al.* [9] report a similar signal, near 303 K, observed in atactic pure PMMA (54.5 % syndiotactic), but without giving any commentary on its origin.

In order to observe the time evolution of the depolarization current signal in the range above the maximum temperature of the secondary relaxation, we have kept the sample at constant temperature (320 K) and high vacuum for an extended period of time (thirty days). The dielectric response of the PMMA sample was recorded in the meantime by performing standard TSD runs. Figure 3 presents representative TSD spectra recorded at first and after several days of aging at 320 K. In time course, the spectrum presents a significant reduction in the current signals, in the range above the secondary relaxation. The H_2O-relaxation (Fig. 2) vanishes within the first 2-3 days of evacuation. The β- and γ-relaxation peaks decrease rapidly within the first short period of time and as we can see in Fig. 3 they only slightly decrease at longer aging times. Nevertheless, the reduction of the β'-relaxation band continues until the 26th day and only at that point the signal appeared stabilized (compare with the 27th day).

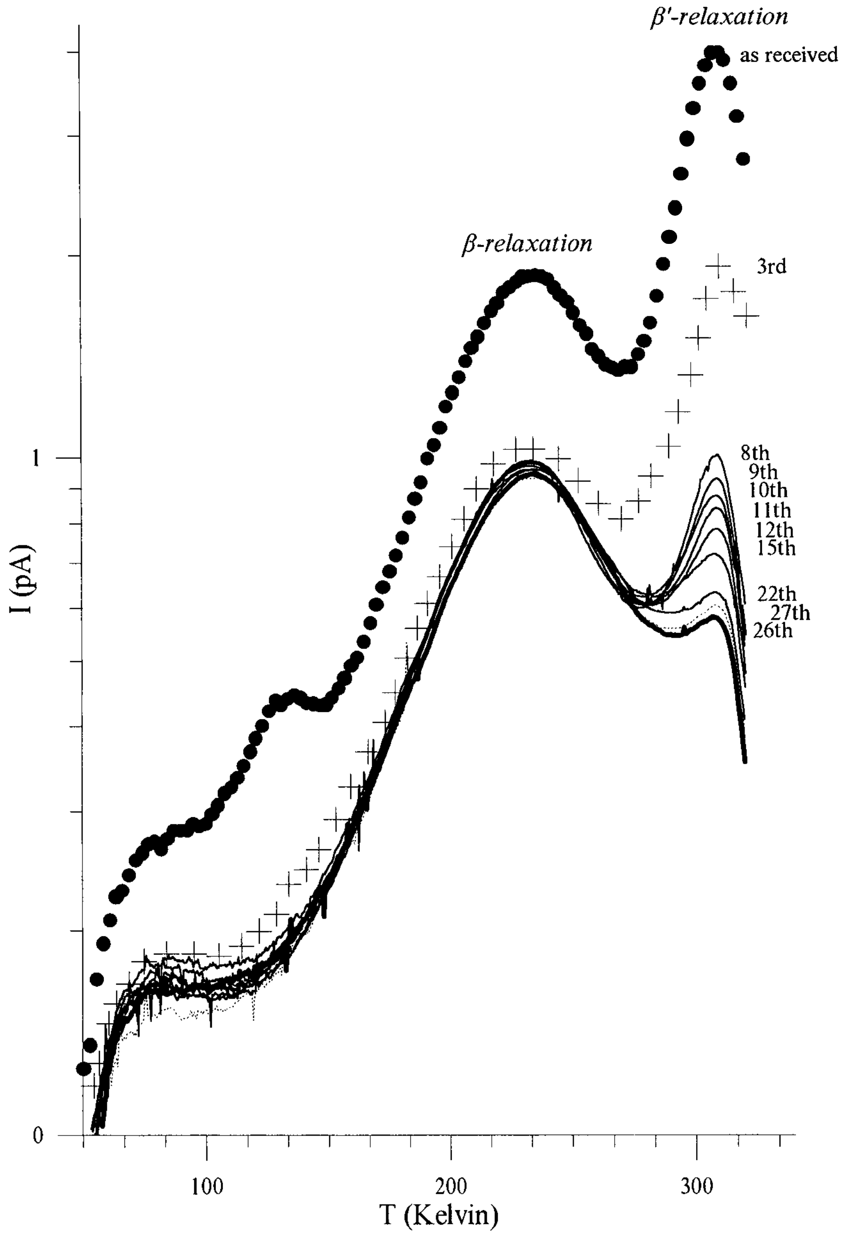

Fig. 3: Time evolution of the TSD current spectrum in the range 220-320 K of PMMA specimen (sample C). The information given beside each curve corresponds to the number of days with the sample at 320 K in high vacuum.

Figure 4 presents the dielectric loss spectrum, $\varepsilon''(f)$, of an as-received PMMA sample (curve I) as well as the spectra recorded for the same sample during the aging process (at RT), after heating in air at 403 K for one hour. The thermally untreated sample demonstrates a region of losses below 0.1 Hz, besides the β-relaxation loss peak at 10 Hz, Repetition of the measurement immediately after heating (time for the completion of the run approximately 3 hours) records intense rising losses below 0.1 Hz which gradually fall off with time. The structure appears to be completely relaxed only after 120 hours. By repeating the heating process we record poor low frequency losses (curve II).

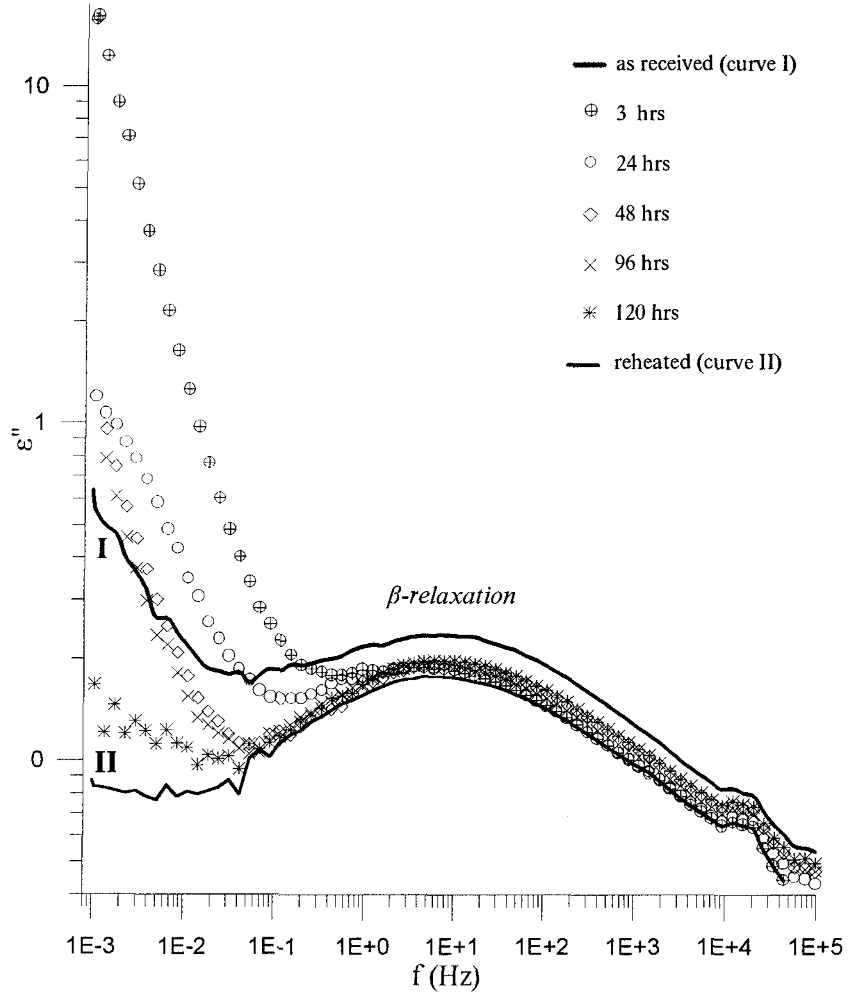

Fig. 4: Time evolution of the DRS spectrum in the range 1 mHz - 100 kHz of PMMA.

Differential scanning calorimetry (DSC) and dynamic-mechanical studies of PMMA by Muzeau *et al.* [5] indicate that the isothermal aging at temperatures between T_g-100 K and T_g-30 K lead to DSC pre-peaks and a diminution of the mechanical loss tangent. In this study, the β-relaxation was not affected by aging. The proposed model for the interpretation of the results in reference [5] was based upon the concept of annihilation of *quasi-point* defects through diffusion. Diffusion was considered to occur by means of hierarchically correlated structural movements, characterized by a special correlation factor. In the present study, the presence and aging time behavior of the TSDC β'-relaxation peak can be associated with the mobility due to a residual free volume, below T_g, that allows structural recovery at defect regions. The latter are created from the desorption of water molecules during vacuum treatment (in TSD) or high temperature heating (in DRS measurements). The most probable microscopic relaxation mechanism being responsible for the latter dielectric effect can be related with the rotational mobility of the polar groups in PMMA. In the above frame, the limited motions in the main backbone provoke a dipole (re)orientation of the ester carbonyl pendant groups with an activation energy of E=0.85±0.05 eV. Clearly, the HT relaxation peak can not be regarded as the manifestation of the glass transition of a stereoregular microphase since the glass transition temperatures corresponding to atactic (~370-390 K, T_g=383 K in the present case), syndiotactic (~407 K) and the minority isotactic phases (~325 K) are well above 300 K [9]. In addition, the HT relaxation can not be directly related to the enhanced presence of syndiotactic stereoregularity, e.g. as a special dielectric relaxation mechanism within the syndiotactic microphases. The latter is supported by the absence of the HT band in several other structurally "partially" relaxed PMMA samples of similar syndiotacticity (e.g. sample A in Fig. 2). This is to be expected from the fact that the phenomenon of physical aging is mostly independent of the material's stereoregularity and relates, principally, to the free volume (re)distribution in polymers, at temperatures far below the glass transition temperature. The association of the high temperature TSD relaxation peak with the low frequency signals in the DRS spectrum can be justified as follows. Taking under consideration the β' peak maximum temperature in the TSD thermogram (T_M=310 K) and using equation

$$\tau_0 = \frac{k_\beta T_M^2}{hE} exp\left(- \frac{E}{k_\beta T_M} \right), \tag{3}$$

we estimate a mean pre-exponential factor τ_0 in the range 0.01−1 psec. In the $\varepsilon''(f)$ dielectric loss spectrum at RT (where $T \cong T_M$), the corresponding mechanism is expected to appear as a loss peak with maximum at a characteristic frequency, f, obeying the relation

$$2\pi f \cdot \tau(T_M)=1, \tag{4}$$

from which we obtain frequencies between 0.001 and 0.01 Hz. The latter are in good agreement with the frequency range of the losses presented in Fig. 4.

The α-methyl group hinders the partial rotation of the lateral carboxymethyl group. In addition to the above intramolecular barrier, an intermolecular energy contribution may arise from constraints on the motion provoked by torsion angles in the chain backbone. This signifies the role played by the macromolecular chains in the shape of the β-relaxation band, through the densification via aging. Diaz-Calleja *et al.* [7], state that aging is not expected to decrease the intermolecular distances throughout the bulk of the testing material but only in loosely packed "defective" zones, with a simultaneous lowering of the population of relaxing molecular species.

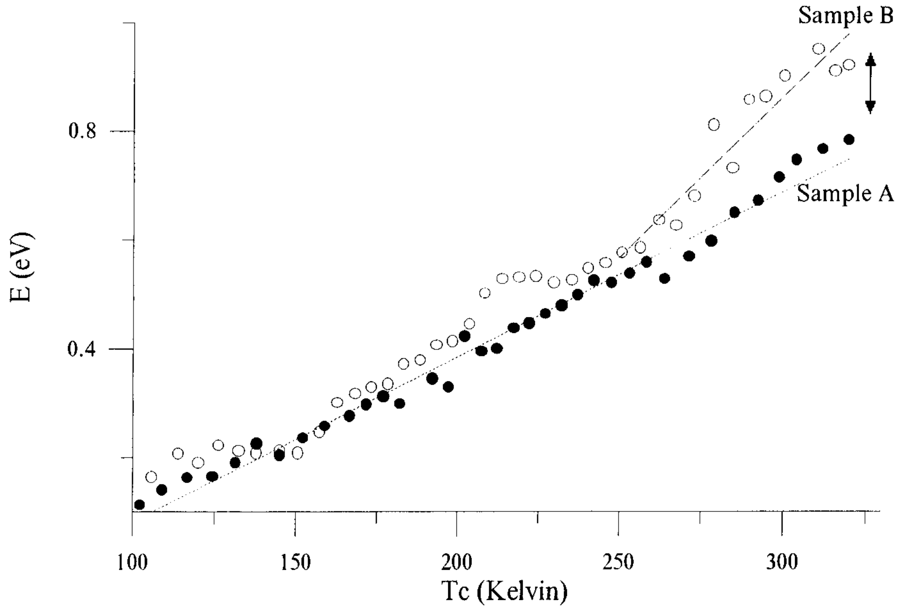

Fig. 5: Energy spectrum recorded via the partial heating method for PMMA samples, A (without the β' relaxation signal in the range 275-320K) and B (demonstrating the β'-relaxation).

In agreement with the data reported by Diaz-Calleja *et al.* [7] and the TSD spectra presented here, aging decreases the height of the dielectric β-relaxation but not the relative position of peak's maximum (i.e. constant energy barrier [14] opposing the rotation of the ester group). The phenomenon is effectively illustrated in Fig. 5, which compares the activation energy distributions in PMMA samples with and without the HT signal. In both cases the energy spectrum in the range of the β-relaxation is similar, within the limits of experimental error, while in the temperature of the HT peak there appear significant deviations. Thus, it seems rational to apply similar reasoning for the explanation of the aging behavior of the β'-relaxation band. The descending trend in peak's intensity can be related to the annihilation of defective "empty space" zones, at which the carboxymethyl rotational relaxation in PMMA is produced. In agreement to the above hypothesis are ^{13}C-NMR studies of atactic PMMA that distinguish a collection of motions involving $-CH_2-$, CH_3-, CH_3O- groups and a combined motion of the side chain and backbone around room temperature. The CH_3- and CH_3O- mobilities are measurable even at cryogenic temperatures and present high frequencies around RT [14].

The exceptional stability of the β' peak as a function of the aging time or variations of T_p [15] implies a monoenergetic character, which is rare in the solid state and practically absent in amorphous materials as PMMA. A possible explanation can be envisaged as follows. A single energy, of intramolecular origin, may account for dipole (re)orientation in defective structural regions. As the structure approaches to a thermodynamically more stable arrangement, the loosely packed zones should decrease in number and size. Thus, the increasing contribution of the intermolecular interactions to the apparent energy barrier induces a smooth transition from a single E to an energy distribution. The most probable reason for the initiation of the structural aging process recorded in the TSD experiments is the presence of water in PMMA, and its gradual decrease through vacuum treatment. Water adsorption has a significant effect on several physico-chemical properties of PMMA (e.g. local conformational changes of the ester backbone as an effect of spreading polar solvents on the monolayers of poly(methyl methacrylate) [16]). The overall dimensional swelling of the PMMA with water uptake has been demonstrated in several cases [17]. Moisture adsorption has also a direct effect on the glass transition temperature, decreasing T_g by approximately 1 ^{0}C per 0.1 % of weight increase due to hydration [17]. Around room temperature the saturation concentration has been calculated to be 1.92 % (1.92 gr H_2O per 100 gr PMMA), while the limiting Henry's law gradient is 0.0115 % (w/w) per % RH (up to 35 % RH) [18]. The conventional dual mode kinetic sorption process, which explains the variation of density with water content, is supportive of a two stage sorption model: in the early stages of sorption, water molecules accommodate into the available free volume (around 30 % of the maximum water content), and at higher activities into simple solution [18]. In cases where the polymerization procedure takes place at low temperatures (around RT), an appreciable amount of water molecules is trapped in the polymeric network occupying structural openings. In agreement with earlier observations, after several days of vacuum drying the highest weight loss of a PMMA specimen was less than 0.6 % of the starting weight [17]. The above water content acts as an effective structural stabilizer, since it helps in hydrogen-bonded crosslinking of the polymer chains by the H_2O molecules through the lateral ester carbonyl groups of the untreated polymeric component. An intensified structural relaxation process is thus anticipated after water desorption, through high temperature heating (at $T \geq T_g$, in the DRS experiment) or alternatively prolonged vacuum drying (in the TSD runs).

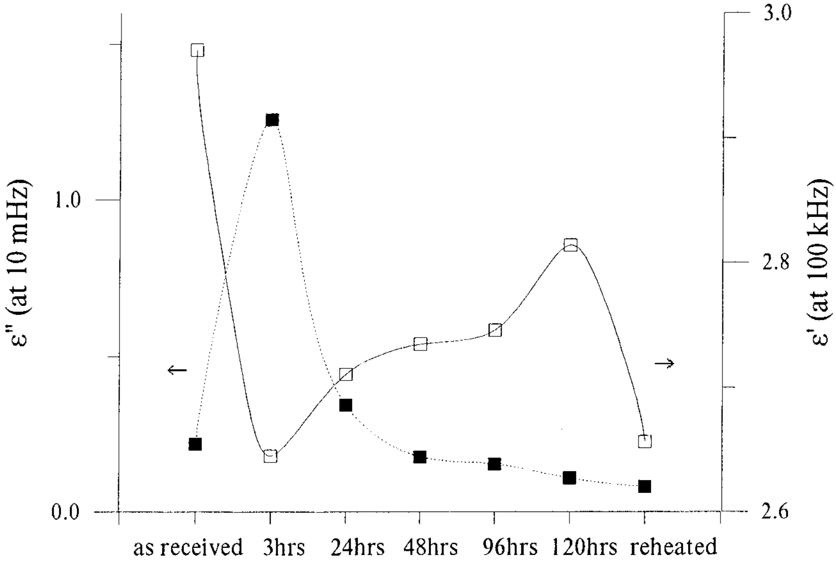

Fig. 6: Time evolution of the dielectric loss and permitivity values, at f=10 mHz and 100 kHz respectively, of the PMMA sample. The complete relaxation response is presented in Fig. 4.

Figure 6 presents in detail the variation of dielectric loss (ε'') and permittivity (ε') values at 10 mHz and 100 kHz respectively, with aging time (complete relaxation response presented in Fig. 4). The frequency of 10 mHz may be regarded as a critical frequency for the description of the variations in the strength of the structural relaxation losses with aging, while the permitivity values at 100 kHz partially reflect the strength of the high frequency H_2O relaxation modes in polymeric systems [19]. As expected, ε'(100 kHz) is maximum in the as received sample (with the highest water content) and reaches a minimum immediately after the heating procedures. The dielectric loss ε''(10 mHz) attains the maximum value after the first heating process. At that time, the structural free volume formerly occupied by water molecules become empty and hydrogen-bonded crosslinking of polymer chains reduces in number. Thus, the structural relaxation mechanism is facilitated, increasing the overall dielectric relaxation activity. Five days later, the partially relaxed structure shows a far less efficient structural relaxation mechanism, as we can see from the amplitude of the corresponding losses after the second heating cycle.

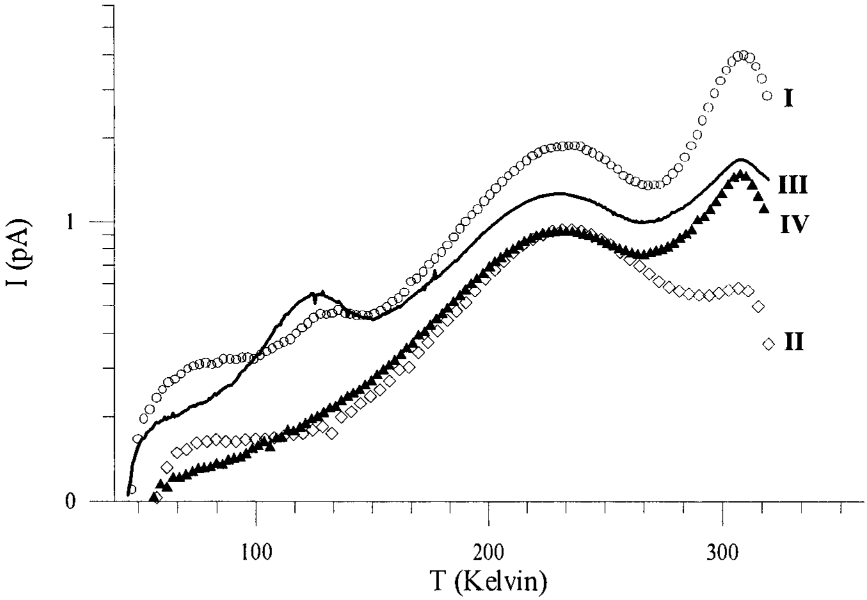

Fig. 7: Representative plot presenting the variations in the TSD spectrum of PMMA with dehydration/hydration and aging time: curve I (as received), II (after 26 days in vacuum at 320K), III (after immersion in boiling water) and IV (one day after measurement III).

In Figure 7, curves I and II correspond to the thermostimulated current spectra of the as received PMMA sample C, and of the same sample aged for 26 days at 320 K in vacuum.

Curve III records the dielectric response measured after the sample immersion in boiling deionized water for a few hours. Although the overall strength of the relaxation mechanisms in the range 40-320 K is partially restored after immersion, one day after vacuum treatment the relaxation spectrum below 250 K returns to its previous state (compare curves II and IV). The signals in the HT side of the spectrum exhibit again a slow decrease with aging time, as we observe in the as received sample (see Fig. 3).

In electrical measurements, one way for the discrimination between bulk molecular relaxation phenomenon and boundary effects at the electrode-sample interface is the implementation of different electrode configurations. A drastic change in the shape and the spectral positioning of a specific band, observed in TSD experiments employing, i.e., the usual ohmic contact between the sample and the metal electrode or a blocking electrode configuration, is characteristic of interface controlled relaxation mechanisms (electrode polarization, conduction currents, etc.) [20,21]. In the present case, samples B and D were deliberately blocked by insertion of a thin, highly insulating, Teflon layer between the sample and the metal, which prevented any injection and neutralization of charges at the interface. The TSD thermograms recorded with this setup were almost identical to those recorded in the ohmic electrode configuration, favoring the association of the β'-relaxation region to a bulk relaxation mode. The stability of the β'-relaxation peak's maximum temperature of 310 K, with variations of T_p in the range 260-320 K [15] is also in accordance with a dipolar interpretation. Another possible alternative attribution based on a space-charge relaxation mechanism, involving *short-range* jumps of electric charges, has also to be considered. The monoenergetic character of the TSD current peak and its gradual drop with evacuation complies with such an attribution, if we consider protons as the potential electric charge carriers. Nevertheless, the above mechanism is unable to interpret the low frequency dielectric relaxation response recorded in the ac experiments after heating. In the latter case, the water molecules desorption process (depicted by the drop of ε' at 100 kHz) should drastically decrease the corresponding signals. In addition, the space-charge relaxation does not explain the complete absence of the HT relaxation band in the TSD spectra of several other PMMA samples, and that despite the presence of H_2O relaxation signals around 130 K in the above materials.

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