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Thermal Expansion Spectroscopy of Thin Polymer Films

introduction

Polymer films are of particular interest, e.g., for use in thin-film devices such as polymeric waveguides and field effect transistors. The control of the film thickness as a function of external parameters such as temperature is of major importance. Furthermore properties of polymer films are of scientific interest, e.g., when it comes to finding out what happens once the film becomes thinner than the diameter of gyration known from the bulk polymer. In any case thin polymeric films are studied by numerous experimental methods and among these broadband dielectric spectroscopy plays an important role [1]. Here we show how dielectric measurements can be used to study the thermal expansion of polymer films as a function of temperature, frequency, and cooling or heating rate. This novel technique relies on the temperature-induced variation of the capacitance of thin polymer films due to their thermal expansion or contraction [2-6]. The experiment allows for several modes of operation: either ramping of the temperature at a constant rate, or harmonic modulation of the temperature around a constant mean, or a combination of both. This family of thermal expansion spectroscopy (TES) methods is thus complementary to differential scanning calorimetry (DSC) and its modulated variant, except that in our case the dilatation of the sample rather than its heat capacity is detected.

It is quite simple to carry out the dilatometric experiments if a "thermostat" is available which allows to ramp the temperature at a constant rate or to modulate it in

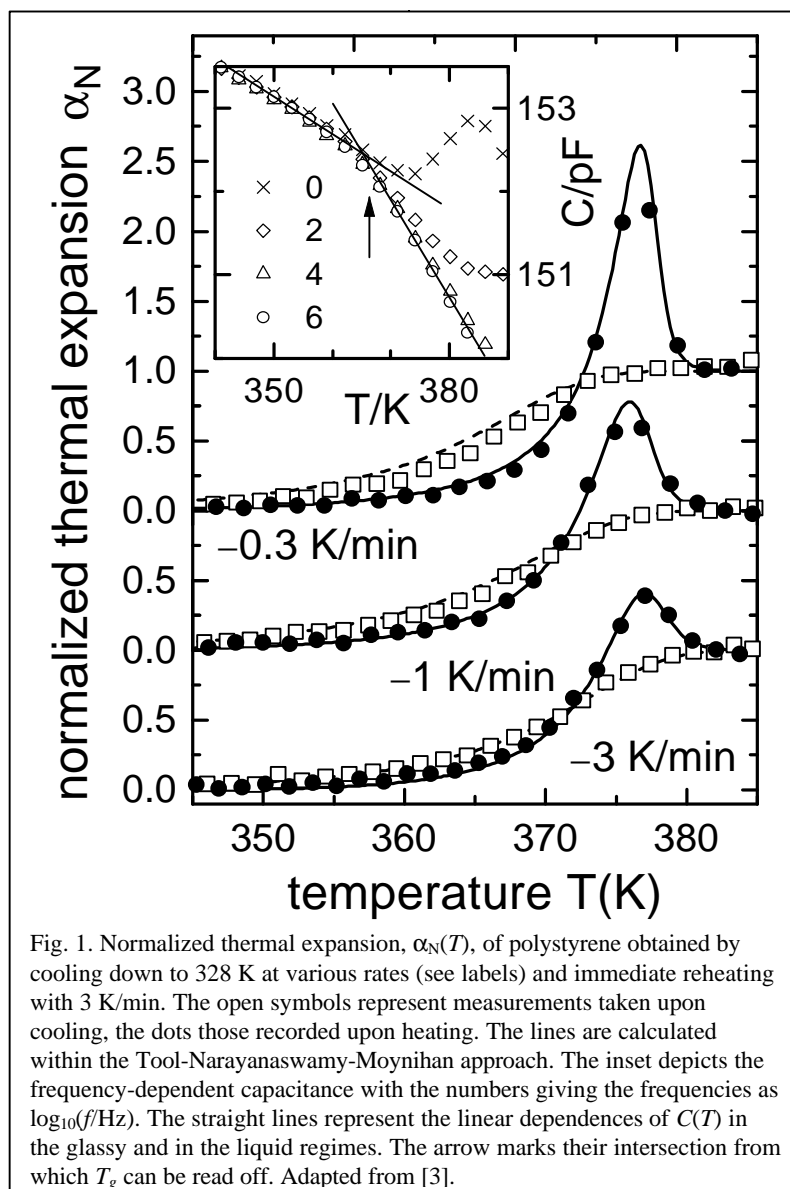


Fig. 1. Normalized thermal expansion, $\alpha_N(T)$, of polystyrene obtained by cooling down to 328 K at various rates (see labels) and immediate reheating with 3 K/min. The open symbols represent measurements taken upon cooling, the dots those recorded upon heating. The lines are calculated within the Tool-Narayananwamy-Moynihan approach. The inset depicts the frequency-dependent capacitance with the numbers giving the frequencies as $\log_{10}(f/\text{Hz})$. The straight lines represent the linear dependences of $C(T)$ in the glassy and in the liquid regimes. The arrow marks their intersection from which T_g can be read off. Adapted from [3].

the sub-Hz regime. In our experiments this task was performed utilizing a Novocontrol temperature control unit. Then both the capacitance of the polymer film and its temperature need to be read out continuously. In order to ensure that the dielectric properties do not interfere with the dilatometric ones high-frequency capacitance monitoring (in the $f > 0.1$ MHz range) is advisable. TES works best for non-polar and low-polar polymers. So far TES was applied to polystyrene, polybutadiene, and

polyvinylacetate. One of the advantages of TES is that it allows the simultaneous detection of dielectric and dilatometric properties. Furthermore it can be applied to thin and ultra-thin films with no loss of sensitivity (which is often a problem in DSC studies of such films).

Some theoretical background for TES can be found in [5]. Let us mention here that so far two capacitor geometries were used. These involved either (approximate) constant-area (CA)

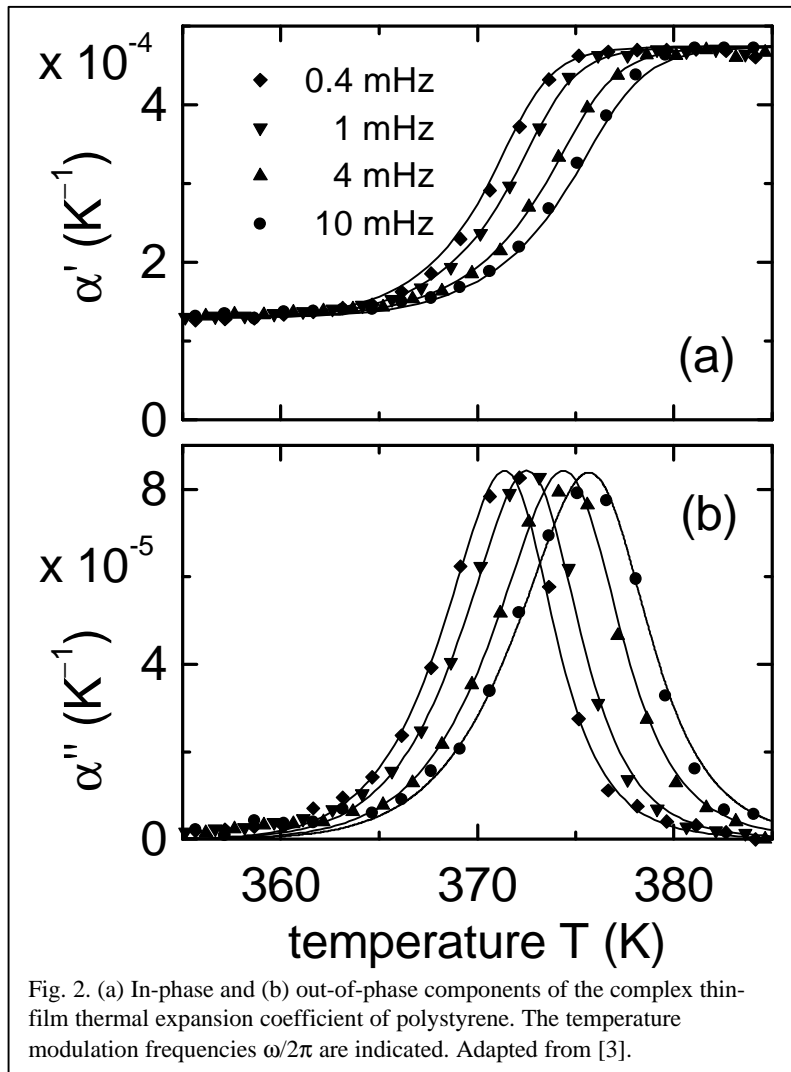


Fig. 2. (a) In-phase and (b) out-of-phase components of the complex thin-film thermal expansion coefficient of polystyrene. The temperature modulation frequencies $\omega/2\pi$ are indicated. Adapted from [3].

or constant-gap (CG) conditions. Under these circumstances the expansion of the polymer film is restricted to one or two dimensions, respectively, and the clamped (or thin-film) thermal expansion coefficients α_{CA} and α_{CG} , rather than the bulk (or constant-pressure) coefficient, α_p , are measured. The determination of absolute values of α_p which was accomplished already previously using capacitive methods, requires knowledge of the elastic properties (Poisson's ratio ν) and relies on relations such as $\alpha_{CA} = \alpha_p (1 + \nu)/(1 - \nu)$ [5, 7]. However, since in our applications only the temperature and/or frequency dependences of the dilatometric properties are a concern, no external input is needed.

In the following we will first demonstrate the dilatometric temperature ramping technique, called capacitive scanning dilatometry (CSD). Then we show

how the frequency dependence of the thermal expansion can be mapped out using modulated capacitive dilatometry (MCD). Finally, a recent TES application to the study of ultra-thin polymer films is discussed [6].

capacitive scanning dilatometry

Atactic polystyrene films with a thickness d of up to several μm were produced by spin coating or drop casting. As an example in the inset of Fig. 1 we show the capacitance of such a film as recorded under constant-area conditions upon cooling with a rate of $q = -0.08 \text{ K/min}$. It is seen that for measuring frequencies larger than about 10 kHz the dilatation behavior can be mapped out faithfully in the considered temperature range. A break in the slope of the capacitance $C(T)$ of the polymer film marks the rate-dependent glass transition temperature $T_g(q)$ at which the

thermal expansion coefficient of the polymer film changes its magnitude. From these data the thermal expansion can simply be obtained by $\alpha_{CA} = N^{-1}(dC/dT)_{CA}$. Here $N = C_0[\epsilon_\infty + (\epsilon_\infty - 1)(\epsilon_\infty + 2)/3]$ is a constant which is determined by the reference capacitance C_0 and the high-frequency permittivity ϵ_∞ . In Fig. 1 the normalized derivative signals $\alpha_N(T) = [\alpha(T) - \alpha_{\text{glass}}] / (\alpha_{\text{liquid}} - \alpha_{\text{glass}})$ are presented for several scanning rates. Typical q dependences and in particular the "overshoot" upon reheating, well-known from DSC near the vitrification transition of amorphous materials, are observed [8]. These results establish CSD as a useful method for the characterization of polymer films which is most simple to implement, particularly if dielectric equipment is already available.

modulated capacitive dilatometry

Now let us turn to MCD, i.e., to the measurement of the complex, frequency-dependent thermal expansion or dilatational susceptibility. Here one varies the temperature of the specimen harmonically and simultaneously records the thickness-modulated capacitance $C(t)$ as well as the temperature $T(t)$. This procedure is analogous to varying the external electrical field and monitoring the dielectric displacement. From $T(t) = \langle T \rangle + \Delta T \exp(-i\omega t)$ and from $C(t) = \langle C \rangle + \Delta C \exp[-(i\omega t + \theta)]$ the amplitudes ΔT and ΔC as well as the phase lag, θ (analogous to the loss angle), can be determined using a harmonic analysis (digital lock-in technique). From this information the real and imaginary parts of the thermal expansion coefficient can be mapped out.

In Fig. 2 we present $\alpha_{CA}(\omega) = \alpha'_{CA}(\omega) + i \alpha''_{CA}(\omega)$ of polystyrene for several modulation frequencies ω . Dispersion effects are clearly revealed in the in-phase as well as in the out-of-phase components. The relatively narrow range of temperature modulation frequencies $\omega/2\pi$ (of about two decades from 0.4 mHz [3] to ~ 20 mHz [6]) is limited on the low-frequency end by the necessity to avoid physical aging effects (i.e., by the patience of the

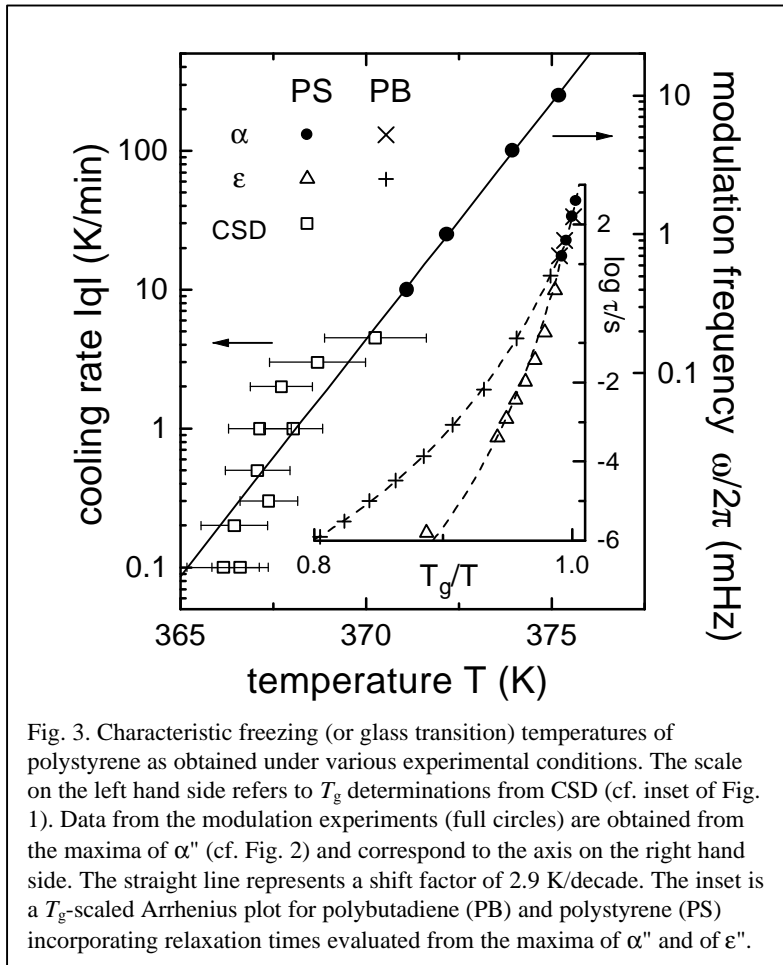


Fig. 3. Characteristic freezing (or glass transition) temperatures of polystyrene as obtained under various experimental conditions. The scale on the left hand side refers to T_g determinations from CSD (cf. inset of Fig. 1). Data from the modulation experiments (full circles) are obtained from the maxima of α'' (cf. Fig. 2) and correspond to the axis on the right hand side. The straight line represents a shift factor of 2.9 K/decade. The inset is a T_g -scaled Arrhenius plot for polybutadiene (PB) and polystyrene (PS) incorporating relaxation times evaluated from the maxima of α'' and of ϵ'' .

experimenter). Towards higher frequencies it is restricted by the requirement to achieve a uniform thermal modulation of the entire capacitance cell.

Via the familiar relation $\omega\tau \approx 1$ the peak maxima in Fig. 2 allow one to evaluate the time scale, τ , on which the expansivity response takes place at a certain temperature. In Fig. 3 the time scales from MCD are compared with results from CSD in order to determine the shift factor. Furthermore, in the inset of Fig. 3 complementary dilatometric and dielectric data for polystyrene and polybutadiene are summarized in a T_g -scaled Arrhenius plot. From such a representation the steepness of $\log_{10}(\tau/s)$ on the T_g/T scale is evident. This steepness, frequently called the fragility parameter m [9], is a key parameter of glass-forming materials.

In a recent application of TES this ability to map out not only dilatometric time scales but also the fragility parameter was demonstrated for ultra-thin polystyrene films down to a

thickness of 13 nm [6]. In Fig. 4 we reproduce the thickness dependence of the fragility parameter of polystyrene films with various molecular weights, M_w , as obtained by Fukao and Miyamoto. The data in Fig. 4 show clearly that

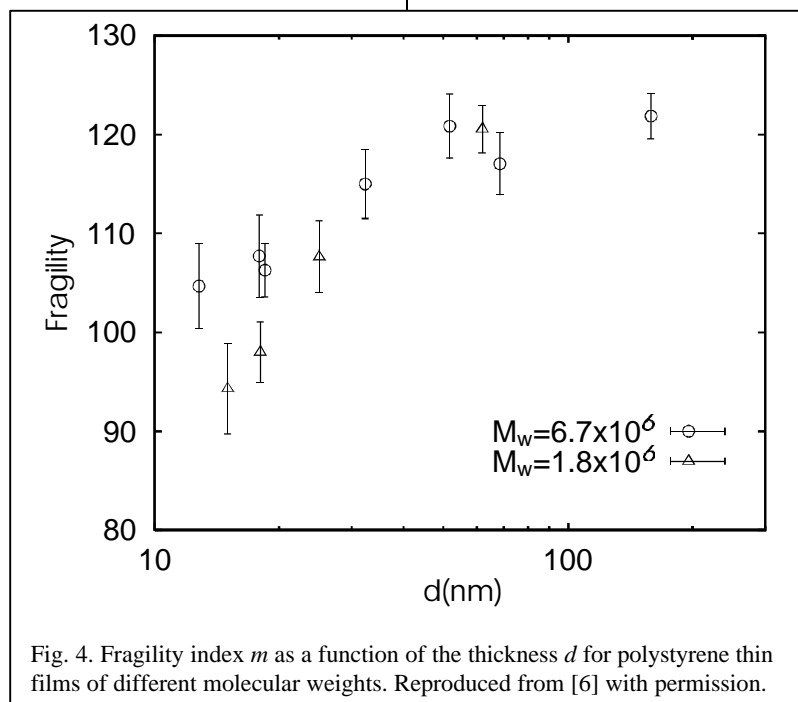


Fig. 4. Fragility index m as a function of the thickness d for polystyrene thin films of different molecular weights. Reproduced from [6] with permission.

in the thin-film regime the fragility decreases with decreasing thickness. This observation has led the authors to the conjecture that this change might be understood as one from cooperative dynamics (in the thicker films) towards single-particle dynamics as the films become thinner and thinner [6].

conclusions

In this note it was pointed out that the high sensitivity of dielectric spectroscopy can be exploited to measure the linear (rather than the volume) thermal expansion coefficient of thin films under various experimental conditions. This provides a direct measure of the glass transition temperature T_g of these films.

To perform the experiment one only needs a suitable temperature control unit in addition to an ordinary impedance measuring system, i.e., standard equipment which should be available in every dielectric laboratory. The preparation of films with a thickness in the μm range can be achieved using well established techniques such as spin coating and drop casting. Thinner films may require special precautions and procedures [10].

Several of the modes of operation that can be conceived for thermal expansion spectroscopy were already put into practice: In capacitive scanning dilatometry the sample thickness can be monitored

using various temperature ramping conditions and then yields information analogous to that usually available via differential scanning calorimetry. Temperature modulation techniques were also employed in connection with TES in order to measure the real and imaginary parts of the complex thermal expansion coefficient.

acknowledgment

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F. Kremer, L. Hartmann

Broadband Dielectric Spectroscopy and the Molecular Dynamics in Thin Polymer Layers

The structural and dynamic properties of thin (some 10 nm) free-standing polymer films or deposited polymer layers are in the scope of an intensive scientific discussion [1-4]. Usually studies are based on experimental methods like ellipsometry [5,6], x-ray reflectometry [7], positron annihilation lifetime spectroscopy [8], thermal expansion spectroscopy (s. the article by C. Bauer and R. Böhmer in this DNL and [9,10]) thermal probe measurements [11] or studies on the dewetting behaviour [12]. Not too many dielectric studies [13-16] were carried out up till now. They form the only measurements in which the molecular dynamics is directly detected. Additionally, they benefit from the advantage that the capacitance and hence the experimental sensitivity increase with decreasing thickness. On the other hand it is of course a challenge to apply electrically conducting metal electrodes to nm-thick molecular layers.

What makes thin polymer layers so interesting? This has several reasons: (i) It was an important discovery – first observed in ellipsometric studies [5,6] – that the glass transition temperature depends strongly on the thickness of a polymer layer or a self supporting film. Nowadays refined measurements were carried

out but the results are not well understood [2-4]. (ii) The interaction with solid surfaces [16-18] has a strong impact on the glass transition temperature of the deposited polymer layer. This is theoretically expected [19,20] but many details are open. (iii) If the thickness of the polymer layer becomes comparable to the radius of gyration of the polymer – according to de Gennes [21] – a special type of so-called "sliding modes" should exist. This conjecture is not yet proven experimentally. It could be possible done by analysing the normal mode spectrum of a type-A polymer in a correspondingly thin layer. (iv) nm-thick polymer films play an important role in coatings, free-standing membranes and layered structures. For all these applications knowledge of the molecular dynamics of the polymer is highly desirable.

Dielectric measurements can be really performed for polymer layers down to thicknesses of about 10 nm. The electrodes are provided either by evaporation of metal (typically aluminium or gold) or by the mica technique [15], which was described in the "Dielectric Newsletter" of November 2000. It is advantageous to use an arrangement with crossed electrodes as schematically shown in Fig. 1. As an example measurements on isotactic poly(methylmethacrylate) in i-PMMA are shown in Fig. 2. It is remarkable how well these spectra of the 20 nm layer resemble those on bulk samples. The data are fitted using the Havriliak-Negami function.

In the activation plot (Fig. 3) one observes that the (local) β -relaxation does not depend on the

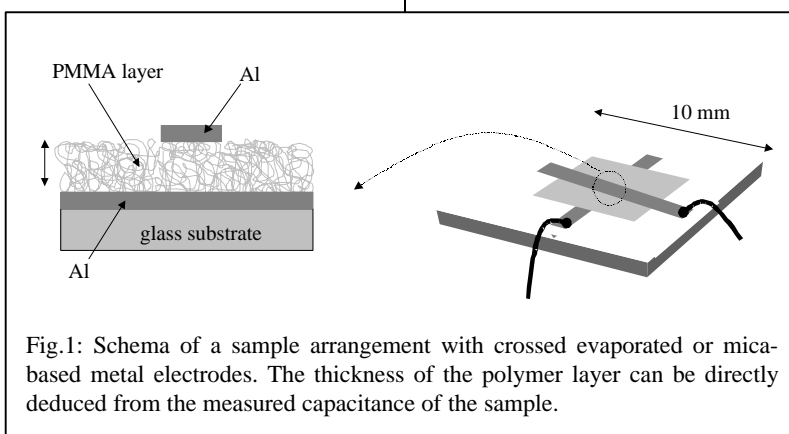


Fig.1: Schema of a sample arrangement with crossed evaporated or mica-based metal electrodes. The thickness of the polymer layer can be directly deduced from the measured capacitance of the sample.

thickness of the polymer layer while the α relaxation (dynamic glass transition) increases in its relaxation rate with decreasing thickness. Following the rule that at the calorimetric glass transition temperature the relaxation rate of the dynamic glass transition has a value of 10^{-2} Hz enables to determine its dependence on the thickness of the polymer layer. It decreases with decreasing sample thickness (Fig. 4). In contrast, ellipsometric studies on the identical sample but on a SiO_x surface and without a top layer of aluminium deliver an increase of the glass transition temperature. This discrepancy is presumably caused by the different surface interactions with the polymer. Additionally the dielectric studies allows to determine the dielectric strength of the α and β -relaxation. As shown in detail in [16] the local β -relaxation remains unaffected while for the α -relaxation the dielectric strength decreases strongly with decreasing sample thickness. From that directly within a layer model the thickness of immobilized polymer segments can be estimated. Furthermore the relaxation time distribution functions are available from the dielectric measurements [16].

In summary broadband dielectric spectroscopy enables to analyse in detail the molecular dynamics in thin polymer layers. This is the necessary condition for the understanding of the underlying molecular mechanisms of a manifold of macroscopic findings in thin polymer layers.

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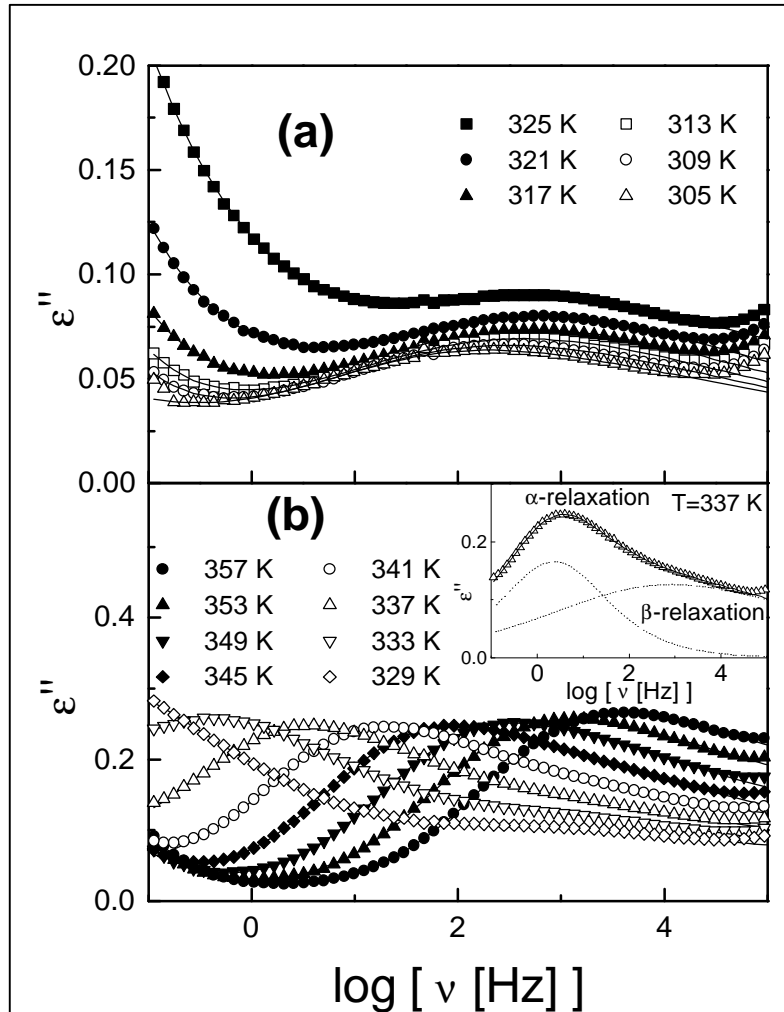


Fig.2: Dielectric loss ϵ'' versus frequency for i-PMMA (sample thickness $d=21$ nm, $M_w=44900$ g mol $^{-1}$) at temperatures as indicated. (a) Only the β -relaxation is present. For $T=325$ K the high frequency wing of the α -relaxation appears. (b) Spectra at temperatures within and above the merging region. Solid lines represent fits according to the Havriliak-Negami equation. The inset illustrates the superposition of the α - and the β -relaxation for $T=337$ K in the merging region: dotted lines represent the α - and the β -relaxation, a solid line is used for the sum of all contributions. Note the different scales for ϵ'' in Fig. 1 (a) and (b) [16].

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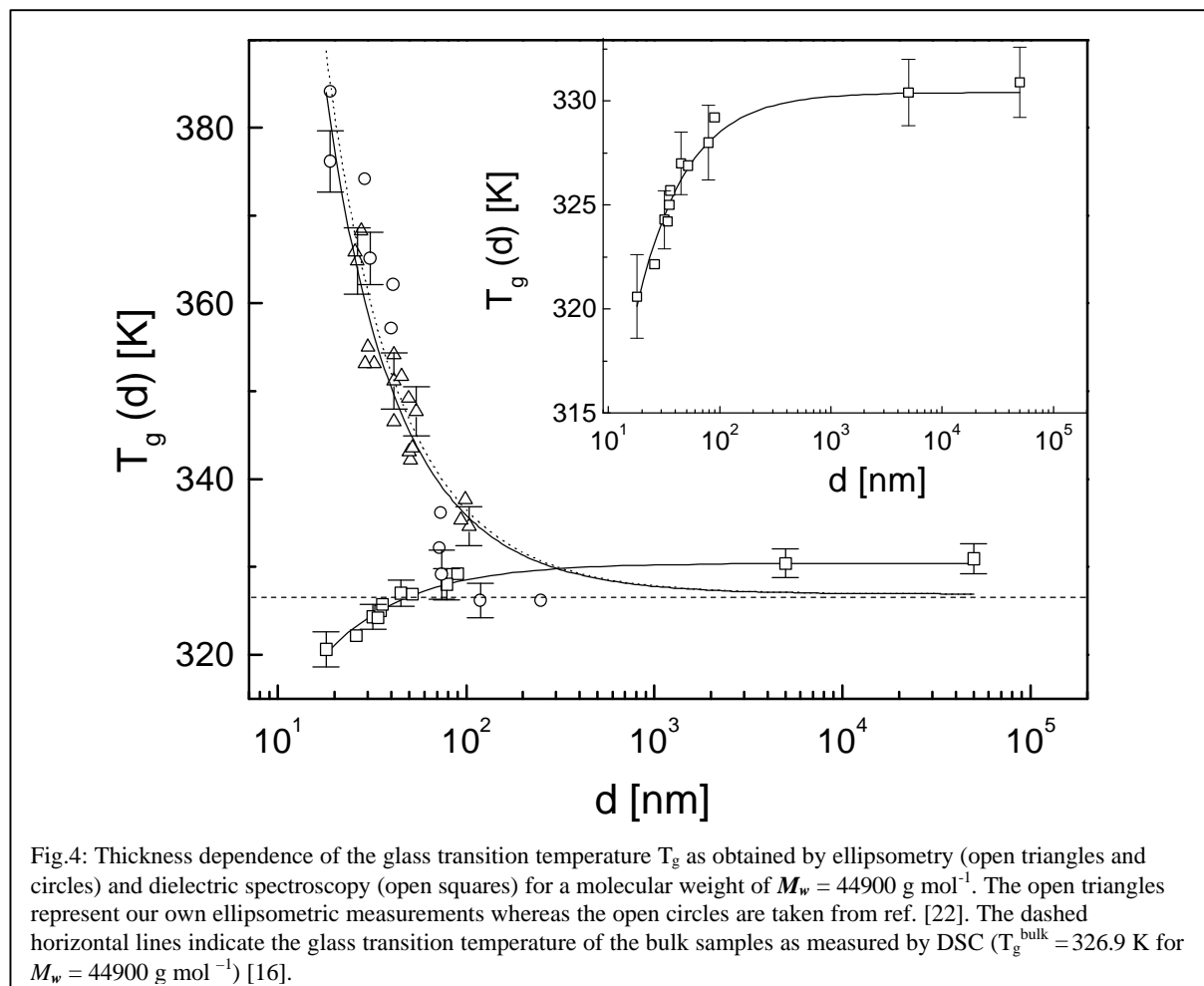
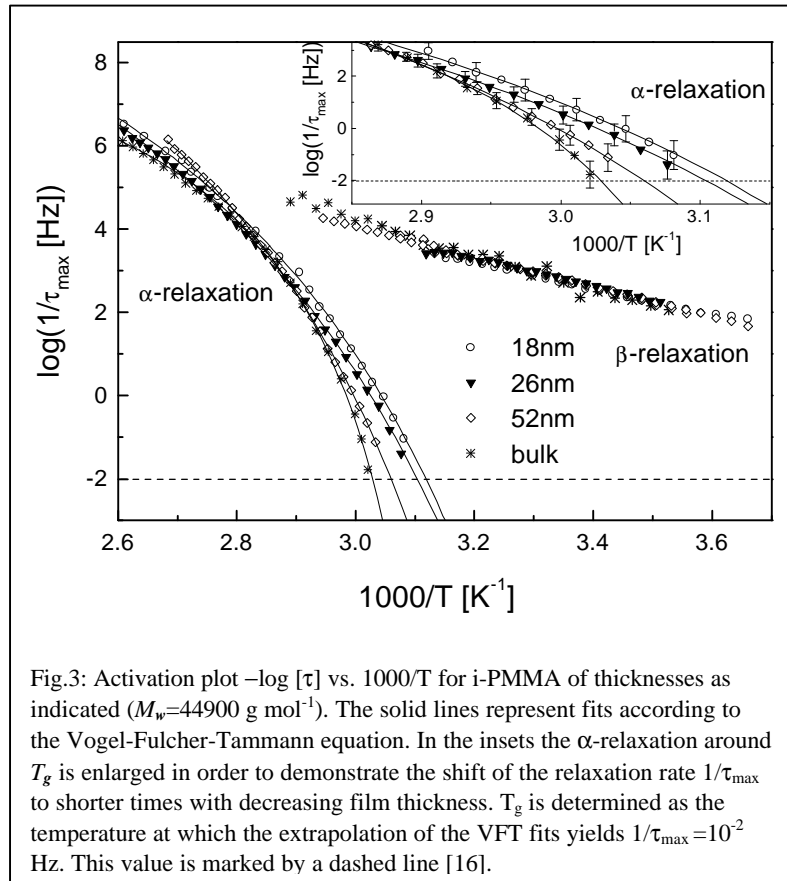
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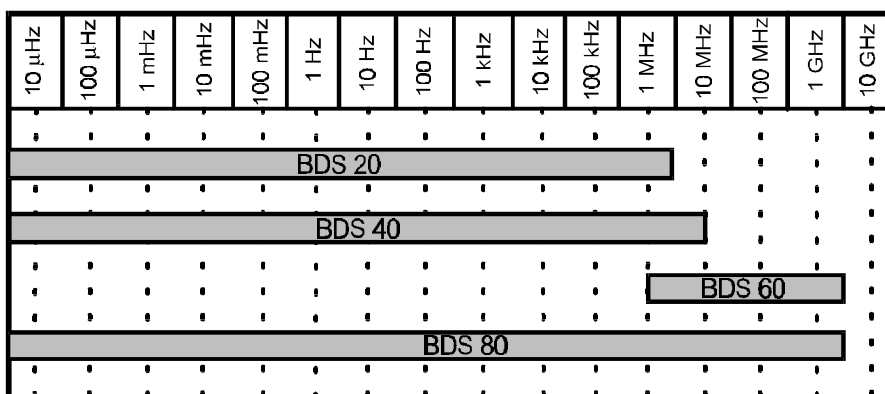
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