

**THERMALLY STIMULATED DEPOLARIZATION AND MECHANICAL
RELAXATION STUDY OF GLASS TRANSITION
IN POLYVINYLIDENE FLUORIDE**

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Measurements of the thermally stimulated depolarization currents (TSDC) have been employed to investigate molecular motion at glass transition in polyvinylidene fluoride (PVDF). Biaxially drawn film material was submitted to various conditions of sample polarization and isolated TSDC peaks were fitted by different equations for temperature dependence of relaxation time. For relaxation process at T_g were obtained: glass transition temperature T_g , apparent activation energy E_a and pre-exponential factor τ_0 (Arrhenius), average thermal expansion coefficient of free volume α_f , pre-exponential factor τ_∞ , temperature T_∞ (Vogel), dipolar strength $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, the relaxation frequency of the dominant realignment process at T_g . The results obtained by means of TSDC method are compared with the ones obtained by dynamic-mechanical measurements.

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1 Introduction

Polyvinylidene fluoride (PVDF) is semicrystalline polymer with exceptional mechanical and electrical properties. For technical applications this polymer is popular mainly for its strong piezo- and pyroelectricity [1–3]. Although the basic repeat unit is chemically simple ($-\text{CH}_2-\text{CF}_2-$), the physical properties are in a great extent variable. Besides the noncrystalline (amorphous) phase there are known three crystal forms designated as Form I, II and III, which are all stable at room temperature [4]. Forms I and II are designated also as β (orthorhombic, trans-trans conformations) and α type (monoclinic with trans-gauche conformations) [5], respectively. The amount of individual structural forms depends on thermal, mechanical and electrical treatment of PVDF material. Structural studies show that the polar Form I (or β) plays a significant role in the electrical responses.

Besides the structural factors the mobility of polymer chains plays a significant role in macroscopic responses of material. Experimental studies, based mainly on dynamic-mechanical analysis (DMA), dielectric measurements (DM) and nuclear magnetic resonance (NMR— ^1H and

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¹⁹F), indicate that there are three principal relaxations denoted as α , β and γ with decreasing temperature [6]. The fourth relaxation, β' , has been confirmed in DMA [7] and NMR [8] measurements.

The aim of our study was to obtain some new results about molecular motions mainly at glass transition of the above mentioned polymer. Thermally stimulated depolarization currents and dynamic-mechanical measurements have been employed in our study. The samples for study were selected biaxially stretched films—for missing in literature data obtained on such samples by TSDC method. Because of considerable current background presented in global TSDC of PVDF (unstretched α -form PVDF [9]), special accent in our measurements was given on selection of the conditions of polarization and measurement procedure (U_p, T_p, t_p) in order to separate “clean” current peaks reflected only the dipole reorientation of main chain segments of polymer.

2 Experimental

2.1 Principle of TSDC method

The thermally stimulated depolarization current method was proposed by Bucci and Fieschi [10] in 1964. This technique is useful in understanding the dielectric relaxation and in elucidating molecular parameters such as relaxation times, distribution function, activation energies, etc.

The sample to be investigated is polarized by an external electric field E_p at a temperature T_p , higher than the glass transition temperature T_g , for a period t_p —much longer than the relaxation time $\tau(T_p)$. After cooling the sample with linear sweep of temperature to temperature T_0 (lower than temperature region with relaxation process to be studied), the electric field is turned off. The sample is then short-circuited for time t_0 to remove the stray surface charges. Depolarization current $i(T)$ is recorded as a function of linearly increasing temperature and permits us to find the relaxation processes in the material. (For description of the thermal sampling (TS) method—see [11].)

If we assume Debye model of the dipolar relaxation with a single relaxation time $\tau(T)$, the equation for the decay of polarization $P(t)$ is

$$\frac{dP(t)}{dt} = -\frac{P(t)}{\tau(T)}. \quad (1)$$

Taking the temperature sweep defined by

$$T(t) = T_0 + qt, \quad (2)$$

where T_0 is temperature mentioned above and q is the heating rate, then after integration of equation (1) we obtain:

$$P(T) = P_0 \exp\left(-\frac{1}{q} \int_{T_0}^T \frac{dT'}{\tau(T')}\right), \quad (3)$$

and for depolarization current density $i(T)$:

$$i(T) = \frac{P_0}{\tau(T)} \exp\left(-\frac{1}{q} \int_{T_0}^T \frac{dT'}{\tau(T')}\right). \quad (4)$$

If relaxation time obeys Arrhenius equation (frequent case at $T < T_g$)

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right), \quad (5)$$

where τ_0 is pre-exponential factor, E_a is activation energy (needed to disorient molecular dipoles), then depolarization current density can be written as

$$i(T) = \frac{P_0}{\tau_0} \exp\left[-\frac{E_a}{RT} - \frac{1}{q\tau_0} \int_{T_0}^T \exp\left(-\frac{E_a}{RT'}\right) dT'\right]. \quad (6)$$

If relaxation peak cannot be described by a single Debye relaxation, the distribution of relaxation times is needed (distribution in τ_0 or/and in E_a) in relation (4).

2.2 Principle of dynamic-mechanical method

Applying a sinusoidal tensile strain on one end of sample, and evaluating the phase angle δ of the strain against the stress generated at the other end of the sample, the storage modulus E' and the loss modulus E'' may be calculated from measured amplitudes of stress and strain. The dynamic moduli E' and E'' for the single-time relaxation process may be expressed in a simple form [12,13]:

$$E' = \frac{A}{1 + \omega^2 \tau^2}, \quad \text{and} \quad E'' = A \frac{\omega \tau}{1 + \omega^2 \tau^2}, \quad (7)$$

where A is called 'relaxation strength' determining the maximum value of E'' , ω is the angular frequency of the applied oscillating tensile strain and τ is the 'relaxation time'.

As we can see from (7) the loss modulus E'' reaches maximum value for $\omega \tau = 1$. The real part E' of the complex dynamic modulus shows a steep decrease in the range of the loss maximum.

In our case we analyse the temperature dependence of E'' for PVDF films.

2.3 Samples and experimental equipments

In our study the commercial films (Solef X10N, Solvay Belgium) have been used. The material with 25 μm thickness was biaxially stretched (3:2). The other material parameters: $\rho = 1.79 \text{ g/cm}^3$, $M_n = 171.000 \text{ g/mole}$, $M_w/M_n = 2.05$, crystallinity 55–60% (^1H NMR, X-ray), content of polar β phase in crystal regions app. 65%. The same material was studied by solid state ^{19}F NMR in [14,15]. In that papers many of references concerning the phase structure investigation of PVDF are cited.

For TSDC measurements 25 μm films were supplied with aluminium electrodes evaporated onto both sides in a vacuum. These samples with $S = 7.1 \text{ cm}^2$ electrode area were then thermally prepared at 383 K during 1 hour and submitted to TSDC measurements in temperature chamber with dry nitrogen atmosphere. Temperature sweep ($q = 1.71 \text{ K/min}$) was controlled by temperature variator, temperature of the sample was measured by the J type thermocouple with direct contact to the sample surface.

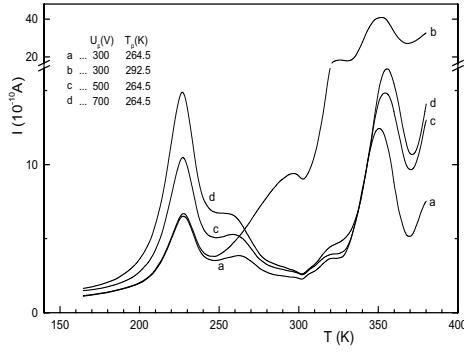


Fig. 1. Global TSDC spectra of PVDF with different conditions of sample polarization.

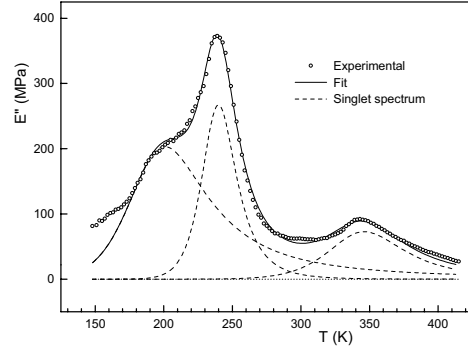


Fig. 2. Temperature dependence of loss modulus E'' of PVDF with decomposition into three Debye singlets.

Experimental set-up for TSDC and TS measurements was constructed in our laboratory with Keithley 485 picoammeter. This set-up enables the application of polarized voltage up to 8 kV and current measurement down to 0.1 pA in temperature region $\approx 110 - 420$ K.

Dynamic-mechanical measurements were performed using Rheovibron model DDV-II (Toyo Measuring Instrument Co., Ltd., Tokyo) at the frequency of 110 Hz in the temperature range from 150 K up to 420 K. A slow heating rate, approximately 0.5 K/min, was applied. The loss modulus E'' of the sample with dimensions of 8 mm, 50 mm and 25 μm , respectively, have been calculated at each temperature by means of equation:

$$E'' = \frac{F L}{S \Delta L} \frac{\tan \delta}{\sqrt{1 + \tan^2 \delta}}, \quad (8)$$

where F and ΔL are amplitudes of oscillating force and sample extension, L and S are length and cross-sectional area of the measured sample, respectively. The loss-factor $\tan \delta$ was measured directly by means of Rheovibron DDV-II.

3 Results and discussion

Some of the measured global TSDC spectra are presented in Fig. 1 and DMA spectrum in Fig. 2. As we can see from these figures, both spectra consist of several overlapping peaks. The most pronounced peak observed in both spectra situated at 227 K (TSDC) and at 239 K (DMA) corresponds to glass transition as it was determined by other authors [6–8]. This assumption will be confirmed by detailed analysis in the following. Similarly, the peak situated at about 350 K (in both spectra) corresponds to α -relaxation process. Additional 'peaks' may be identified as shoulders of these principal peaks. The shoulder on lower temperature side of β -peak in DMA (situated at $T \approx 200$ K), not resolved in TSDC, probably corresponds to γ -relaxation [8]. The peaks in TSDC (seen as shoulders of α -peaks) situated around temperature 320 K would be ascribed to β' -relaxation process. This process is less pronounced in DMA spectrum. Finally,

measur. num.	U_p [V]	T_p [K]	t_p [min]	T_{max} [K]	I_{max} [10^{-10} A]	Q_{tot} [10^{-10} C]	Q_{lt} [10^{-10} C]
1	100	348	30	227.8	1.19	729	412
2	100	320	30	227.6	1.23	754	434
3	100	292.5	30	227.2	1.24	836	458
4	100	264.5	5	227.4	1.26	840	454
5	300	320	30	227.4	3.87	2632	1485
6	300	292.5	5	227.1	3.98	2765	1540
7	300	264.5	30	227.2	3.98	2774	1547
8	300	264.5	5	227.1	3.75	2539	1438
9	500	320	30	227.0	6.73	4540	2542
10	500	292.5	5	226.8	6.64	4481	2460
11	500	264.5	5	226.6	6.60	4429	2448
12	700	320	5	226.9	9.89	6927	3914
13	700	292.5	5	226.5	9.81	6750	3692
14	700	264.5	5	226.6	9.85	6862	3874

Tab. 1. Conditions of samples polarization and results computed from isolated TSDC peaks (extracted from global TSDC spectra).

peaks (as shoulders) near polarization temperature T_p are observed only in TSDC spectra. The origin of these peaks can not be connected with relaxation process in PVDF [16].

At TSDC measurements, the strong dependence of spectra on the conditions of sample polarization was observed (see Fig. 1). After any polarized conditions (summarized in Tab. 1), a distinct peak in each TSDC spectra with maximum at $T = T_{max} = 227$ K can be seen. Amplitude of that peak depends only on polarized field intensity E_p (or voltage applied on the sample U_p). Positions and amplitudes of the others current peaks are strongly dependent on all polarized parameters— U_p , T_p , t_p . From these reasons we decided to analyse only peak at 227 K.

To study of glass transition the polarized conditions were selected in that way to enable separation of glass transition peak from peaks reflected another relaxations or current background. As the most advantage polarization of the sample was observed the polarization at low temperatures ($T_p = 264.5$ K). At such polarization the separation $T_p - T_g$ is still sufficient to fill the condition $t_p \gg \tau(T_p)$. In Fig. 3 are presented isolated TSDC peaks obtained at different U_p ($E_p = U_p/d$, where d is sample thickness) and at constant T_p and t_p . By arrow is indicated position of T_p on temperature scale. Analogous peaks were separated from another TSDC spectra. Their characteristics: T_{max} —position of peak maximum and I_{max} —amplitude of peak are listed in Tab. 1.

For TSDC spectra analysis is important the calculation of charge released at depolarization. In Tab. 1 is listed the total charge Q_{tot} released in all temperature interval of isolated peak

$$Q_{tot} = \frac{S}{q} \int_{T_0}^{T_r} i(T) dT, \quad (9)$$

where S is electrode area, q is heating rate, T_r is temperature, at which $i(T)$ falls to zero.

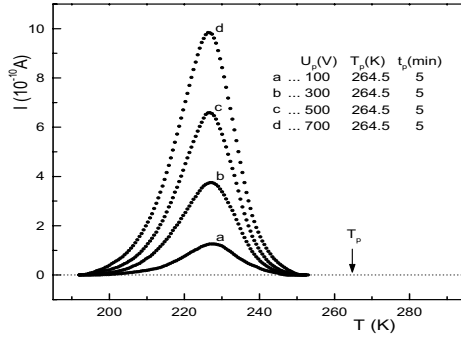


Fig. 3. Isolated TSDC peaks of PVDF at glass transition temperature T_g at different conditions of sample polarization.

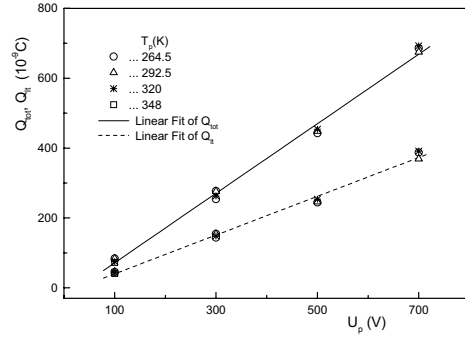


Fig. 4. Total (Q_{tot}) and low temperature (Q_{lt}) released charge at TSDC of PVDF as function of polarized voltage U_p .

As Q_{lt} is labelled charge released at low temperature part of isolated spectrum (in equation (9) T_{max} stands instead of T_r). Results for released charges as a function of polarized voltage U_p are illustrated in Fig. 4. From this graph it results that the both dependencies can be considered as linear. It is necessary condition for interpretation that investigated relaxation peaks are owing to dipole depolarization unlike space charge depolarization. Independence of T_{max} on parameters U_p , T_p and t_p and independence of Q_{tot} on T_p and t_p —all that confirm that the depolarization is connected with reorientation of segments of the main chains. Because of low heating rate ($q = 1.71$ K/min) used in all measurements, the temperature T_{max} can be identified with temperature of glass transition T_g . Moreover, from the equation which is valid for Debye dipole depolarization:

$$Q_{\text{tot}} = \varepsilon_0(\varepsilon_s - \varepsilon_\infty) \frac{S}{d} U_p, \quad (10)$$

where ε_s and ε_∞ are the static (relaxed) and optical (unrelaxed) dielectric constant, it is possible to determine the dielectric strength $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ at temperature T_p . From parameters of linear regression in Fig. 4 was obtained for PVDF and temperature $T = T_p = 264.5$ K value of $\Delta\varepsilon \approx 3.9$.

In Debye model with single relaxation time from equations (1) and (2) can be derived expression for temperature dependence of relaxation time

$$\tau(T) = \frac{1}{q} \left(\int_T^{T_r} i(T') dT' \right) / i(T). \quad (11)$$

According to that expression, by means of experimental data, $\tau(T)$ for each spectrum were calculated. In Fig. 5 there are represented three of calculated dependencies—all with $T_p = 264.5$ K—in Arrhenius plot. From that figure it is evident that the fitting of whole spectrum according to (6) can not be successful because of non linearity at peak temperature region. However, good linearity of dependence $\ln \tau = f(1/T)$ in temperature region below T_g ($= T_{\text{max}}$) allows to fit experimental $i(T)$ at this region according to equation (6).

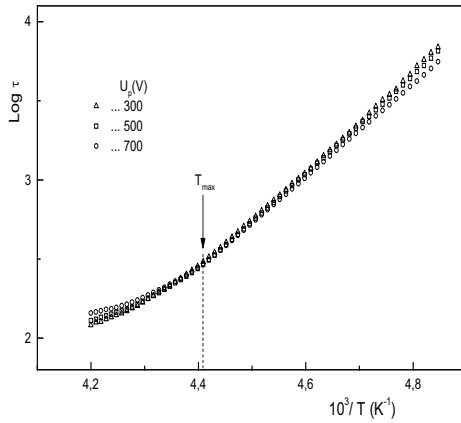


Fig. 5. Arrhenius plot of relaxation time for PVDF sample.

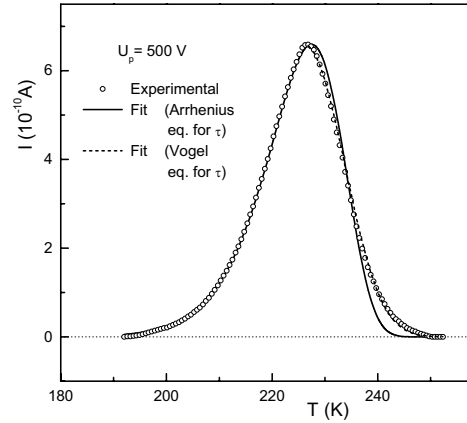


Fig. 6. Experimental TSDC spectrum of PVDF and outputs of fitting procedures. (Solid line – fit for T up to T_g , Arrhenius equation for τ , illustrated in whole peak region; dash line – fit for $T > T_g$, Vogel equation for τ , illustrated only for $T > T_g$.)

The results of such fitting is presented in Fig. 6 (fit for T ranging from T_0 to T_{max} , theoretical $i(T)$ with optimized parameters is illustrated in whole peak region). Important parameters of the molecular motion—activation energy and pre-exponential factor in Arrhenius equation—obtained from fitting procedure are presented in first two columns of Tab. 2. With regard to spectra intensity (against to current background) as more correct can be considered the results obtained at $U_p \geq 300$ V. The values of E_a in Tab. 2 are in good agreement with value of $E_a = 54.5$ kJ/mole for β -process in relaxation map of PVDF in [17]. From mean values of τ_0 and E_a have been calculated the relaxation frequency of dominant realignment process as $f = 1/\tau(T_g) = 3.2 \times 10^{-3} \text{ s}^{-1}$.

The failure in fitting $i(T)$ for $T > T_g$ by means of Arrhenius equation for relaxation time indicates that above T_g barrier effect is not dominant. If the relaxation is determined by 'free volume' effect [18] the relaxation time follows the Vogel equation

$$\tau(T) = \tau_{\infty} \exp[\alpha_f(T - T_{\infty})]^{-1}, \quad (12)$$

where τ_{∞} is pre-exponential factor, α_f is average thermal expansion coefficient of free volume, T_{∞} is critical temperature at which the relaxation time becomes infinite.

This equation is equivalent, after parameters transformation to WLF (Williams-Landel-Ferry) equation [19].

For fitting process the equation (12) has been substituted for (4) and as fit parameters were chosen α_f , T_{∞} and τ_{∞} . Results of those fitting are listed in Tab. 2 and illustrated for one experimental spectrum in Fig. 6. Values of α_f , T_{∞} and τ_{∞} obtained from our measurements are similar to those for polycarbonate in [20].

measur. num.	E_a [kJ/mole]	τ_0 [s]	α_f [10^{-3}K^{-1}]	T_∞ [K]	τ_∞ [10^{-2}s]
1	63.3	8.0×10^{-13}	1.35	145.6	2.8
2	64.1	5.0×10^{-13}	1.37	141.2	5.5
3	58.8	8.6×10^{-12}	1.41	143.9	6.3
4	61.5	2.2×10^{-12}	1.36	139.1	7.3
5	58.6	9.9×10^{-12}	1.42	144.5	5.8
6	57.2	2.1×10^{-11}	1.45	144.0	6.5
7	57.4	1.9×10^{-11}	1.39	139.4	8.4
8	57.3	1.9×10^{-11}	1.43	143.5	6.7
9	56.9	2.3×10^{-11}	1.43	140.7	8.6
10	56.3	3.2×10^{-11}	1.40	139.8	7.9
11	58.1	1.2×10^{-11}	1.42	142.4	6.9
12	56.7	2.6×10^{-11}	1.44	143.3	7.2
13	55.8	4.2×10^{-11}	1.38	141.2	6.3
14	56.0	3.7×10^{-11}	1.39	140.0	7.5

Tab. 2. The values of parameters E_a , τ_0 and α_f , T_∞ , τ_∞ in Arrhenius and Vogel equations, respectively, obtained from fitting of isolated TSDC peaks.

To analyse the temperature dependence of E'' we tried to decompose it into three Debye singlets (see Fig. 2). The singlet situated at the lowest temperature with maximum at $T \approx 200$ K corresponding to γ -relaxation was analysed by means of Arrhenius equation for τ . The best fit of experimental data was obtained for following values of parameters: $A = 406$ MPa, $\tau_0 = 6 \times 10^{-7}$ s and $E_a = 13$ kJ/mole. Similarly, the singlet at highest temperature (α -peak) situated at temperatures about $T \approx 350$ K is characterized by parameters $A = 145$ MPa, $\tau_0 = 1.3 \times 10^{-9}$ s and $E_a = 40.1$ kJ/mole.

The β -peak, corresponding to glass transition was analysed similarly as that in TSDC measurements. The glass transition temperature T_g is 239 K. The region $T < T_g$ has been analysed by means of Arrhenius equation with parameters: $A = 534$ MPa, $\tau_0 = 7.3 \times 10^{-13}$ s and $E_a = 42.7$ kJ/mole and for $T > T_g$ by applying the Vogel equation we have obtained: $A = 545$ MPa, $\tau_\infty = 3.8 \times 10^{-7}$ s, $\alpha_f = 1.37 \times 10^{-3} \text{ K}^{-1}$ and $T_\infty = 152.2$ K.

The activation energies for γ - and α -processes, obtained by our DMA analysis, are both approximately two times lower than those obtained from transition maps for PVDF presented in paper [8]. These differences may be caused by distribution of correlation times τ , which was not taken into account in our analysis.

The values of T_g and T_∞ obtained from DMA analysis, are shifted according to the ones obtained from TSDC to higher temperatures on about 10 K, which is caused by different time-scales of these experiments. The time scale of TSDC experiment is defined by temperature sweep rate and may be thought as quasi-static in contrary to DMA, where the frequency of oscillating tensile strength (110 Hz) cannot be neglected and this method may be treated as dynamical, shifting the transition regions to higher temperatures.

The values of T_g obtained in our case are in accordance with the ones stated for PVDF materials in literature [21], where the interval of T_g is approximately from 220 K up to 240 K.

As an example we can state also the values obtained by [22] for PVDF film (Solef 6010) 235 K (DSC, $q = 10$ K/min), 238.6 K (DMA, $\tan \delta$, 10 Hz) and 243.6 K (DMA, $\tan \delta$, 30 Hz).

4 Conclusions

The glass transition in biaxially stretched polyvinylidene fluoride have been investigated. For study, the thermally stimulated depolarization current method and dynamic-mechanical method were used.

Glass transition temperature $T_g = (227.0 \pm 0.5)$ K was estimated from TSDC isolated peaks. From the measurement analysis resulted that the relaxation of main chain segments below T_g can be described by barrier theory with single relaxation time. From fitting process the apparent activation energy $E_a = (57 \pm 2)$ kJ/mole and pre-exponential factor $\tau_0 = (1 - 4) \times 10^{-11}$ s in Arrhenius equation were obtained. Above T_g the free volume theory is convenient to describe experimental results. Free volume average thermal expansion coefficient $\alpha_f = (1.42 \pm 0.03) \times 10^{-3} \text{ K}^{-1}$, pre-exponential factor $\tau_\infty \approx 7 \times 10^{-2}$ s and $T_\infty \approx 142$ K in Vogel equation were obtained. Relaxation frequency of dominant realignment process f and dipolar strength $\Delta\epsilon$ were calculated as $f = (3.4 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ and $\Delta\epsilon = (3.9 \pm 0.2)$ respectively.

The same procedure was used to analyse the isolated β -peak in DMA spectrum. The characteristic temperatures are: $T_g = 239$ K and $T_\infty = 152$ K, $\alpha_f = 1.37 \times 10^{-3} \text{ K}^{-1}$.

According to our results we may conclude, that both experimental methods (TSDC and DMA) provide consistent results for glass transition phenomena, namely at temperatures $T > T_g$, where free-volume concept (Vogel eq.) is taken into account.

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