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THERMAL BEHAVIOUR AND SLOW MOLECULAR MOBILITY IN TWO ISOMERS OF BIPHENYLMETHANOL
DSC and TSDC study

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The thermal behaviour of 2- and 4-biphenylmethanol were studied by differential scanning calorimetry (DSC). It was found that the 2-isomer shows a relatively strong resistance to crystallisation, and that it easily vitrifies on cooling. Oppositely, 4-biphenylmethanol readily crystallizes on cooling. The slow molecular mobility of 2-biphenylmethanol in the amorphous solid state was studied by DSC and by thermally stimulated depolarisation currents (TSDC). Both techniques indicate that 2-biphenylmethanol is a relatively strong glass-former, with a fragility index of ~50 in the Angell's scale.

Keywords: *differential scanning calorimetry, fragility, glass transition,* β*-relaxation, thermally stimulated depolarisation currents*

Introduction

When a pure crystalline substance is heated up from very low temperatures, several phase transitions will occur. Crystal to crystal transitions reveal the presence of crystal polymorphism. The melting of the crystal followed, at higher temperature, by the vaporisation of the liquid, are some examples of equilibrium first order thermodynamic transitions, i.e. occurring at a well defined characteristic temperature, and being accompanied by sudden changes of energy and volume. However, most of the phase transitions that we observe in nature, or that occur in technological processes, take place in nonequilibrium conditions. For example, many liquids can be undercooled below their freezing point without crystallizing, giving rise to metastable states that can persist over long periods of time [1]. This is the case for 2-biphenylmethanol, that is reported to display excellent glass-forming ability, with a wide supercooled liquid temperature region, and high thermal stability against crystallization [2]. However, as will be shown in this work, the isomer 4-biphenylmethanol shows an opposite behaviour, with no tendency to undercool, readily crystallizing on cooling even for high cooling rates.

The study of the behaviour of low molecular mass substances against crystallization, and of the slow molecular mobility of glass-forming liquids in the amorphous state, is presently a very active field of research [1, 3]. In the present work we will compare the behaviour of the previously referred isomers of biphenylmethanol. We will use the technique of differential scanning calorimetry (DSC) to compare the thermal behaviour of the two isomers, and to characterise the glass transition in 2-biphenylmethanol. Moreover, we will report results obtained by using the dielectric technique of thermally stimulated depolarisation currents (TSDC) to get information concerning the slow molecular motions present in the glassy state of 2-biphenylmethanol.

Experimental

Materials

Two isomers of biphenylmethanol ($C_6H_5C_6H_4CH_2OH$) have been studied in the present work. The isomer 2-biphenylmethanol (CAS n° [2928-43-0]), was purchased from Aldrich (catalogue n° 18,882-4, 99% purity). The isomer 4-biphenylmethanol (CAS n° [3597-91-9]), was purchased from Aldrich (catalogue n° 12,383-8, 98% purity).

Before the experiments both isomers were purified by sublimation at $P\approx4\cdot10^{-2}$ Torr and T=30°C (isomer *ortho*) and T=55°C (isomer *para*).

Methods

XRD and elemental analysis

X-ray powder diffractometry (XRD), carried out using a Rigaku Geigerflex diffractometer employing CuK_α-radiation, over the range $5°<2\theta<35°$ for both molecules, do not shown any contamination of one

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isomer by the other. Elemental analysis, made with a Fisions Instruments EA1108 apparatus, led to the following results for the mass fractions of C and H in $C_{13}H_{12}O$: calculated C, 0.8475; H, 0.0656; found (isomer *ortho*) C, 0.8460; H 0.0681 and (isomer *para*) C, 0.8432; H 0.0664 (average of two independent runs). The Fourier-transform infrared spectrum of both samples in KBr determined with a Jasco 430 spectrophotometer calibrated with polystyrene film, are similar to one published in the literature [4].

Differential scanning calorimetry

DSC measurements were performed with a 2920 MDSC system from TA Instruments Inc. The measuring cell was continually purged with high purity helium gas at 30 mL min^{-1}. An empty aluminium pan, identical to that used for the sample, was used as the reference. The baseline was calibrated scanning the temperature domain of the experiments with an empty pan. The temperature calibration was performed taking the onset of the endothermic melting peak of several calibration standards [5]. The temperature calibration for the different heating rates was performed considering the heating rate dependence of the onset temperature of the melting peak of indium and benzoic acid, as explained elsewhere [6]. The enthalpy scale was also calibrated using indium (enthalpy of fusion: $\Delta_{\text{fus}}H$=28.71 J g^{-1}). Samples of both sublimed products in the range ~6–10 mg were independently introduced in aluminium pans, hermetically sealed using a sample encapsulating press. The DSC study was carried out in the temperature range between –80 to 60°C. The amorphous solid phase of 2-biphenylmethanol was produced by cooling the isotropic melt inside the aluminium pan. The evidence that the samples prepared by this procedure is fully amorphous is two-fold: (1) no exothermic crystallization signal was detected on cooling from the isotropic liquid; (2) the value of ΔC_p across the glass transformation region is found to be very reproducible and similar on cooling and subsequent heating mode.

Thermally stimulated depolarisation currents

TSDC experiments were carried out with a TSC/RMA spectrometer (TherMold, Stamford, CT, USA) covering the range from –170 to 400°C. For TSDC measurements the sample was placed between the electrodes of a parallel plane capacitor with effective area of ~38 mm^2 (thickness of ~0.5 mm). The sample is immersed in an atmosphere of high purity helium (1.1 bar). The amorphous samples of 2-biphenylmethanol submitted to TSDC measurements were prepared by cooling the isotropic melt inside the electrode assembly.

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. In order to analyse specific regions of the TSDC spectrum, different methods of polarising the sample can be used, namely the so-called TSDC global polarisation experiment and the partial polarisation (*PP*) experiment (often called thermal sampling or windowing or cleaning). The *PP* method, where the polarising field is applied in a narrow temperature interval, enables to resolve a global peak into its individual relaxation modes. The thermal sampling procedure allows to retain (or to freeze) a polarisation that arises from a narrow variety of dipolar motions. In the limit of a very narrow polarisation window, the retained polarisation (and, of course, the current peak that is the result of a partial polarisation (*PP*) experiment) would correspond to a single, individual dipolar motion [7].

The capability of directly calculating the relaxation time from the results of a single partial polarisation experiment constitutes an essential quantitative feature of TSDC, and that is why TSDC is an experimental technique that provides important information on molecular mobility in solids, i.e. on the kinetics of relaxational processes and the distribution of relaxation times.

The physical background of the TSDC technique is presented elsewhere [8, 9]. The basic description of the TSDC experiment, and the discussion of the nature of the information it provides, is presented in detail in previous publications [7, 10, 11].

Results and discussion

Thermal behaviour of 2- and 4-biphenylmethanol

As underlined before, 2-biphenylmethanol is reported to display excellent glass-forming ability, with a wide supercooled liquid temperature region, and high thermal stability against crystallization. The isomer 4-biphenylmethanol shows an opposite behaviour, with no tendency to undercool, readily crystallizing on cooling even at high cooling rates. It is interesting to note that, contrarily to biphenylmethanol, the isomers 2- and 4- of hydroxybiphenyl show a similar behaviour against crystallization: both isomers readily crystallize on cooling, and thus show a poor glass-forming ability.

The melting temperature of the isomer 2-biphenylmethanol is reported to be T_m=327 K=54°C and the glass transition temperature T_g=244 K= –30°C (without indication of the value of the heating rate) [2].

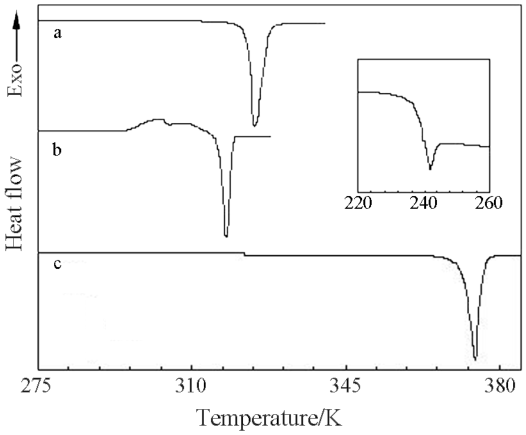

Fig. 1 Results of DSC experiments performed on biphenylmethanol. Curves a – first ramp on the crystalline sample at 4 K min^{-1} and b – ramp beginning from the glassy sample at 5 K min^{-1} are relative to the 2-isomer. The insert shows the glass transition signal observed in ramp b, after cooling from the melt. Curve c was obtained with the 4-isomer at 5 K min^{-1}

Our crystalline sublimed samples showed an endothermic melting peak with onset at T_on=(49±0.3)°C and maximum intensity at T_m=(51±0.3)°C at 10 K min^{-1} (curve a in Fig. 1). No crystallization was detected by DSC on cooling from the isotropic liquid. However, cold crystallization was sometimes observed when the amorphous solid sample was heated up. It was found that cold crystallization originated a polymorph with melting temperature at T_m=44°C (curve b in Fig. 1). We are not able to further quantify this point. In fact, the behaviour of the substances upon crystallization often lacks reproducibility due to the fact that nucleation and crystal growth are somewhat probabilistic events [12].

The melting enthalpy of the most stable polymorph 2-biphenylmethanol (T_m=51°C) was found to be $\Delta_\mathrm{m}H$=(19.7±0.1) kJ mol^{-1} (average of 6 determinations).

The endothermic melting peak of the isomer 4-biphenylmethanol showed an onset at T_on=(100.5±0.3)°C and a maximum at T_m=(102±0.3)°C=375 K (at 10 K min^{-1}, curve c in Fig. 1), and the enthalpy of melting was $\Delta_\mathrm{m}H$=(27.0±0.1)kJ mol^{-1} (average of 21 determinations). Other polymorphs have been detected with melting temperatures of 98 and 101°C, but the respective formation conditions could not be unequivocally determined.

Molecular mobility in amorphous 2-biphenylmethanol

Conventional differential scannning calorimetry

Since no crystallisation is observed on cooling from the melt, 2-biphenylmethanol becomes a metastable liquid below the melting temperature, and vitrifies on further cooling. The DSC signature of the glass transition is a sigmoidal change in the heat flux, that arises from a difference in the heat capacity, ΔC_p, between the glassy state and the metastable supercooled liquid (insert in Fig. 1). The glass transition temperature (identified with the onset of the DSC glass transition signal) was found to be T_g=–34°C=239 K (at 10°C min^{-1}, on heating). On the other hand, the heat capacity jump at the glass transition was found to be ΔC_p=(116±1) J K^{-1} mol^{-1} (average of 44 determinations on heating and on cooling).

It is well known that the temperature of the onset of the DSC fingerprint of the glass transition tends to higher temperatures as the heating (or cooling) rate increases. One of the methods of thermal analysis allowing the determination of glass-former fragility is based on the scanning rate dependency of T_g [13]. We thus used the DSC technique in order to estimate the activation energy of structural relaxation at T_g, E_a and the fragility index, *m*, of 2-biphenylmethanol. It was shown [14, 15] that the dependence of the glass transition temperature, T_g, on the heating or cooling rate, $|q|$, of a conventional DSC experiment is given by

$$\frac{\mathrm{d}\ln|q|}{\mathrm{d}1/T_\mathrm{g}}=-\frac{E_\mathrm{a}}{R} \tag{1}$$

where E_a is the activation energy for the relaxation times controlling the structural relaxation. The results of our experiments on the influence of the heating rate on the onset temperature, $T_\mathrm{g,on}$, of the glass transition signal are shown in Fig. 2.

Experiments were also carried out on cooling (not shown in Fig. 2), and the rough experimental results are presented in the Table 1. It is to be enhanced that a necessary constrain for correctly applying Eq. (1) on heating is that, prior to reheating, the glass must be cooled from above to well below the glass transition region at a rate equal or proportional to the reheating rate [15]. Our procedure was such that the

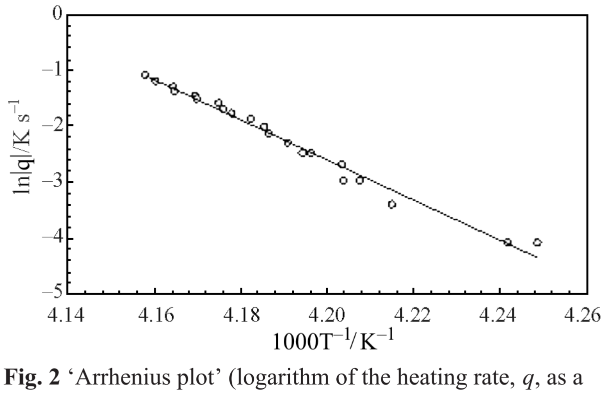

Fig. 2 'Arrhenius plot' (logarithm of the heating rate, *q*, as a function of $1/T_\mathrm{g,on}$) for the glass transition of 2-biphenylmethanol studied by DSC

heating of the glass was performed with a rate equal to the vitrification rate. From the linear regression analysis of the data on heating (points in Fig. 2), the slope is found to be –35.9 (with a confidence interval of ±1.0). From this slope, the value of 298.2 kJ mol^{-1} (standard deviation of ±8.4 kJ mol^{-1}) was obtained (using Eq. (1)) for the activation energy.

The fragility index, *m*, of a substance was defined as the slope of the log$\tau(T)$ *vs.* T_g/T line at the glass transition temperature, i.e. at $T=T_g$ [16, 17],

$$m=\left[\frac{\mathrm{d}\log\tau(T)}{\mathrm{d}(T_\mathrm{g}/\mathrm{T})}\right]_{T=T_\mathrm{g}} \tag{2}$$

where τ is the structural relaxation time which slows down to ~100 s at T_g. Equation (2) can be expressed in terms of the apparent activation energy, E_a, as

$$m=\frac{1}{2.303}\left[\frac{E_\mathrm{a}}{RT_\mathrm{g}}\right] \tag{3}$$

Introducing the value of 298.2 kJ mol^{-1} previously reported in Eq. (2), and considering T_g= –34°C=239 K (onset temperature of the glass transition signal measured on heating at 10 K min^{-1}), leads to the value of m = 65 for the fragility index of 2-biphenylmethanol. From data obtained on cooling (Table 1), that was found to be more scattered compared with data obtained on heating [6], we found E_a=(298.3±13.7) kJ mol^{-1} and *m*=64±3.

Table 1 Temperature of the onset, T_{on}, of the DSC glass transition signal as a function of the rate of the linear ramp, *q*, in the heating and cooling modes

Heating		Cooling	
q/K s^{-1}	T_{on}/K	q/K s^{-1}	T_{on}/K
0.0167	235.4	0.0167	239.0
0.0167	235.7	0.0333	240.0
0.0333	237.2	0.0333	240.3
0.0500	237.9	0.0500	240.7
0.0500	237.7	0.0500	241.3
0.0667	237.9	0.0667	241.4
0.0833	238.4	0.0833	241.6
0.0833	238.3	0.0833	241.9
0.1000	238.6	0.1000	241.7
0.1167	238.9	0.1167	242.1
0.1333	238.9	0.1333	242.2
0.1500	239.1	0.1500	242.4
0.1667	239.3	0.1667	242.1
0.1667	239.3	0.1667	242.8
0.1833	239.5	0.1833	242.3
0.2000	239.5	0.2000	243.2
0.2167	239.8	0.2167	243.2
0.2333	239.9	0.2333	242.8
0.2500	240.1	0.2500	243.7
0.2667	240.1	0.2667	243.5
0.3000	240.4	0.3000	243.9
0.3333	240.5		

Thermally stimulated depolarisation currents

The study by TSDC of 2-biphenylmethanol in the amorphous solid state revealed a very sharp relaxation peak at –38°C (at a heating rate of 4 K min^{-1}), which surely corresponds to the relaxation associated with the glass transition (α-relaxation) given the proximity of this peak relative to the calorimetric glass transition temperature T_g= –34°C at 10 K min^{-1} on heating. The technique of partial polarisation (*PP*) was used to analyse the detail of this relaxation. Figure 3 shows the results of some of the *PP* experiments we carried out in this temperature region. Figure 3a shows some mobility components of the lower temperature side of the glass transition, while Fig. 3b displays a number of higher temperature components.

A secondary relaxation was detected at low temperatures. The analysis of the experimental results in this temperature region (not shown due to the very low intensity of the corresponding discharge peaks) showed that the observed peaks corresponded to local motions (points in the lower temperature side of Fig. 4).

The analysis of the partial polarization peaks obtained in the glass transition region indicated that the corresponding kinetic parameters display a clear departure from the zero entropy behaviour (Fig. 4). The so-called zero-entropy behaviour is an important reference to discuss the mobility features in the TSDC context. In fact, the zero entropy line depicts the behaviour expected for non-cooperative relaxations [18]. It gives the activation enthalpy of the *PP* peaks as a function of the peak's location, T_m, for a given heating rate, for local, non-cooperative relaxations, i.e. for relaxations involving the motion of small groups of atoms with weak interactions with other portions of the molecule or neighbouring molecules. For a local, non-cooperative motional process, with zero activation entropy, the equation of the so-called 'zero entropy line' is given by [19]:

$$\frac{RT_\mathrm{m}^2}{r(\Delta H^{\neq}+RT_\mathrm{m})}=\frac{h}{kT_\mathrm{m}}\exp\left(\frac{\Delta H^{\neq}}{RT_\mathrm{m}}\right) \tag{4}$$

where *r* is the heating rate, T_m is the temperature of maximum intensity of the *PP* peak, and $\Delta H^{\neq}$ is the activation enthalpy of the corresponding motional process. Equation (4) defines a simple reference behaviour, which is the lower limit for the activation

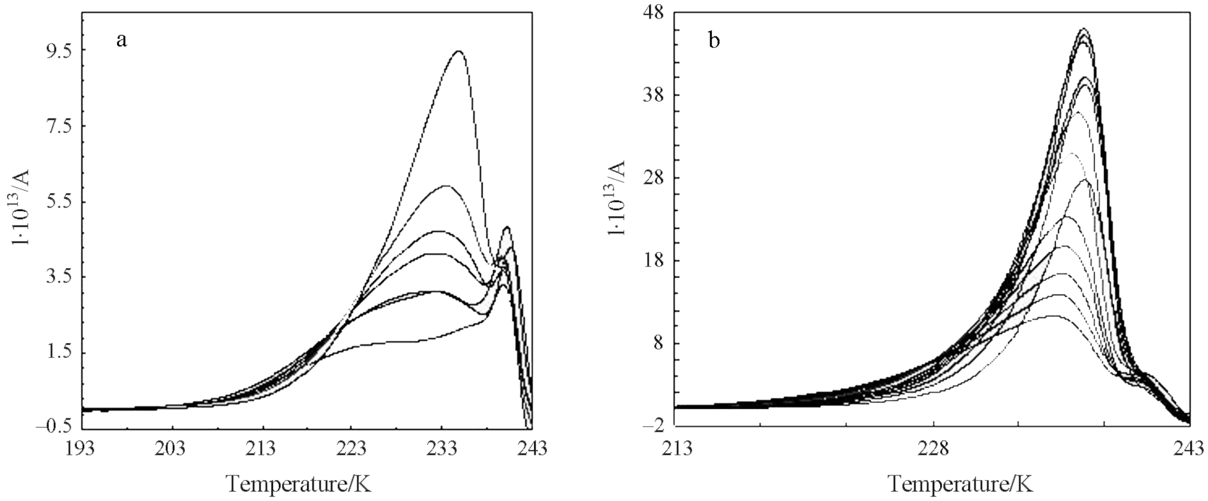

Fig. 3 Partial polarisation components of the slow mobility of amorphous 2-biphenylmethanol obtained at a heating rate of 4 K min^{-1}, with a polarising electric field of E=450 V mm^{-1}, and with a polarisation window of ΔT=2°C. The property in the ordinate axis is the current intensity expressed in Ampere, I(A). a – Low temperature components of the relaxation at ~ – 40°C obtained with polarisation temperatures from T_p= –60°C up to T_p= –53°C. b – Components of the relaxation at ~ – 40°C obtained with polarisation temperatures from T_p= –52°C up to T_p= – 40°C

enthalpy of viscoelastic relaxations and is shown in Fig. 4 as a dashed line.

It is clear from this figure that the points corresponding to partial polarization mobility components in the glass transition region show, as underlined before, a clear deviation from the zero entropy line. On the other hand, the individual molecular motions that appear well below the glass transition temperature, show negligible activation entropy (the points are in the proximity of the zero entropy line [7]), which indicates that these motions have a localised, non-cooperative, nature.

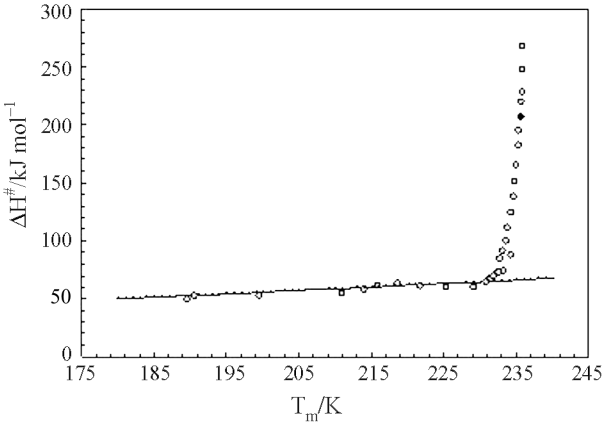

Fig. 4 Activation enthalpy of the partial polarisation peaks of the slow mobility of amorphous 2-biphenylmethanol, as a function of the peak's location, T_m. The uncertainty in the enthalpy values is less than 2%. The continuous line corresponds to the zero entropy prediction. The point represented by a full symbol, corresponds to the *PP* peak with maximum intensity in the glass transition region (higher intensity peak in Fig. 3b)

The point in Fig. 4, represented by a full symbol, corresponds to the *PP* peak with maximum intensity in the glass transition region (higher intensity peak in Fig. 3b). The temperature location of this peak is at T_m=–37.5°C=235.7 K. As shown elsewhere [20, 21], this peak is the manifestation of a mobility component that is characteristic of the glass transition, and the analysis of this partial polarization mode allows the determination of the activation energy for the structural relaxation, and of the fragility index of the glass forming system. We found $E_a(T_g)$=210 kJ mol^{-1} for the activation energy at the glass transition temperature and, using Eq. (3) with T_g=235.7 K, the value m=47±2 was obtained for the fragility index. The TSDC and DSC values of the fragility, 47 and 64, respectively, show a significant mutual deviation. Note, however, that in the Angell's fragility scale, 2-biphenylmethanol thus appears as a strong glass former, with a fragility of the order of that of glycerol.

Conclusions

The structural isomerism in biphenylmethanol was found to have a strong influence in the glass forming ability. While 4-biphenylmethanol shows the so-called normal behaviour against crystallization, 2-biphenylmethanol can be cooled from the melt below the melting temperature, giving rise to a very stable metastable supercooled liquid. The metastable liquid vitrifies on further cooling.

The glass transition relaxation of 2-biphenylmethanol was studied by DSC and by

TSDC, and it was found that it is a relatively strong glass forming liquid. A β-relaxation was detected and characterised in the amorphous solid-state.

Crystal polymorphism was detected for both isomers, but the conditions for the formation of the different polymorphs could not be clearly established.

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References

1 P. G. Debenedetti, Metastable Liquids: concepts and principles, Princeton University Press, Princeton, New Jersey 1996.
2 N. A. Davydova, V. I. Lukashenko, J. Baran and M. Drozd, J. Mol. Struct., 704 (2004) 125.
3 R. Richert and A. Blumen (Eds), Disorder Effects on Relaxational Processes, Springer-Verlag, Berlin, Heidelberg 1994.
4 L. M. Babkov, J. Baran, N. A. Davydova, J. I. Kukielski and S. V. Trukhachev, J. Mol. Struct., 661–662 (2003) 41.
5 H. P. Diogo, S. S. Pinto and J. J. Moura Ramos, J. Therm. Anal. Cal., 77 (2004) 893.
6 J. J. Moura Ramos, R. Taveira-Marques and H. P. Diogo, J. Pharm. Sci., 93 (2004) 1503.
7 N. T. Correia, C. Alvarez, J. J. Moura Ramos and M. Descamps, J. Phys. Chem. B, 105 (2001) 5663.
8 J. van Turnhout, Thermally Stimulated Discharge of Polymer Electrets, Elsevier Sci. Pub. Co., Amsterdam 1975.
9 R. Chen and Y. Kirsch, Analysis of Thermally Stimulated Processes, Pergamon Press, Oxford 1981.
10 G. Teyssèdre and C. Lacabanne, J. Phys. D: Appl. Phys., 28 (1995) 1478.
11 B. B. Sauer in: S. Z. D. Cheng (Ed.), Thermally Stimulated Currents: recent developments in characterization and analysis of polymers, in Handbook of Thermal Analysis and Calorimetry: applications to polymers and plastics, Vol. 3: Elsevier, Amsterdam 2002, Chap. 15.
12 J. J. Moura Ramos, N. T. Correia and H. P. Diogo, Phys. Chem. Chem. Phys., 6 (2004) 793.
13 K. J. Crowley and G. Zografi, Thermochim. Acta, 380 (2001) 79.
14 C. T. Moynihan, A. J. Esteal, J. Wilder and J. Tucker, J. Phys. Chem., 76 (1974) 2673.
15 C. T. Moynihan, S.-K. Lee, M. Tatsumisago and T. Minami, Thermochim. Acta, 280–281 (1996) 153.
16 R. Bohmer, K. L. Ngai, C. A. Angell and D. J. Plazek, J. Chem. Phys., 99 (1993) 4201.
17 R. Bohmer and C. A. Angell, in: R. Richert and A. Blumen (Eds) Local and global relaxations in glass-forming materials, in Disorder Effects on Relaxational Processes, Springer-Verlag, Berlin, Heidelberg 1994.
18 B. B. Sauer, P. Avakian, H. W. Starkweather and B. S. Hsiao, Macromolecules, 23 (1990) 5119.
19 N. T. Correia, J. M. Campos and J. J. Moura Ramos, J. Chem. Soc., Faraday Trans., 93 (1997) 157.
20 C. Alvarez, N. T. Correia, J. J. Moura Ramos and A. C. Fernandes, Polymer, 41 (2000) 2907.
21 N. T. Correia, C. Alvarez, J. J. Moura Ramos and M. Descamps, Chem. Phys., 252 (2000) 151.

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