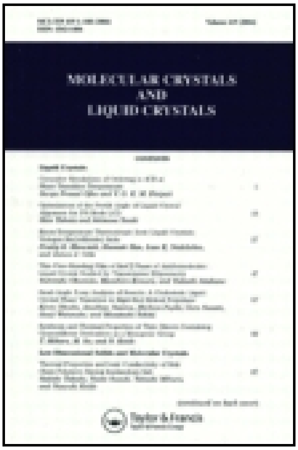

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Glass-Forming Terephthalic Esters with Lateral Phenylthio Groups and their Relaxation Behavior

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Version of record first published: 04 Oct 2006

To cite this article: M. Pötter, H. Dehne, H. Reinke, J. Dobbertin & C. Schick (1998): Glass-Forming Terephthalic Esters with Lateral Phenylthio Groups and their Relaxation Behavior, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 312:1, 55-68

To link to this article: http://dx.doi.org/10.1080/10587259808042431

Mol. Cryst. Liq. Cryst., 1998, Vol. 312, pp. 55–68
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Glass-Forming Terephthalic Esters with Lateral Phenylthio Groups and their Relaxation Behavior

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(Received 4 March 1997; In final form 4 August 1997)

The esters of 2,5-*bis*(2-carboxy-phenylthio)terephthalic acid **4a–f** were prepared by reaction of 2,5-*bis*(2-carboxy-phenylthio)terephthalic acid **2** *via* chloride **3** with alcohols or phenols. These novel glass-forming compounds are of the sulfur ligated "trilling" type. Two structures were established by X-ray analysis as well. The thermal behavior was characterized by DSC. In dependence of the different lateral substituents we found calorimetric glass transition temperatures (T_g) in the range of −50°C to 85°C. The molecular dynamics were investigated by use of dielectric spectroscopy (10^{-2}Hz – 10^9Hz). The temperature time dependence for the α-relaxation, which is associated with the glass transition, is discussed in the fragility concept of liquids.

Keywords: Esters of 2,5-*bis*(2-carboxy-phenylthio)terephthalic acid; sulfur ligated "trillings"; glass transition; DSC; dielectric relaxation; fragility

INTRODUCTION

As shown in numerous publications [1–6] compounds with a glass transition temperature, T_g, are of specific interest. This is due to the fact that a lot of technical important substances like polymers, pharmaceuticals, foods and inorganic glasses are applied in the glassy state. Nevertheless,

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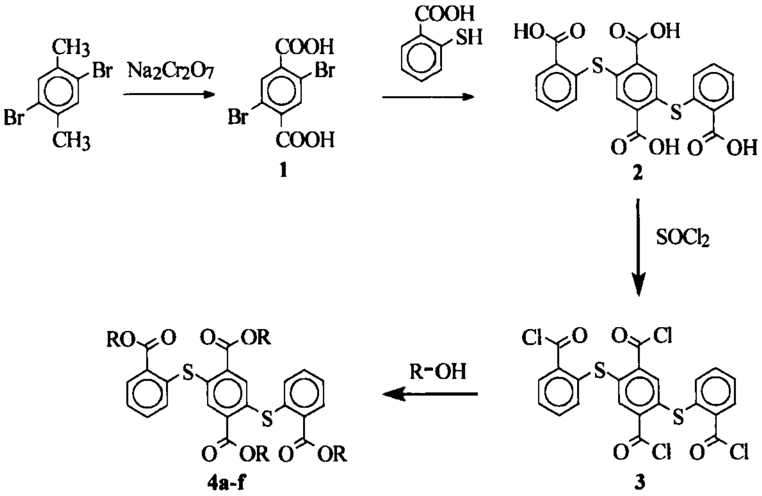
[*] Corresponding author.

there is no general accepted theory for the glass transition. To get further information about the glass transition we study low molecular mass organic compounds. Previously we described [7, 8] the glass transition of sulfur ligated siamese twin mesogens. The object of this paper is to examine the molecular dynamics of novel sulfur ligated "trillings". Dielectric spectroscopy is used as one of the most successful techniques for such investigations.

EXPERIMENTAL

Synthesis

The following scheme shows the pathway of preparation of compounds **4a – f**:



Elemental analyses were performed by a CHNS-932 LECO analyzer and mass spectra were taken with an AMD 402-3 spectrometer (Intectra GmbH). Melting points were determined by a polarizing microscope (LEITZ Laborlux 12 Pol with Mettler-heating stage FP 90) and by DSC measurement.

Starting Materials

2,5-Dibromo-*p*-xylene [9] and 2,5-dibromo-terephthalic acid **1** were prepared by the procedures cited in literature [10] in yields of 74% and 42%, respectively.

Preparation of 2,5-Bis(2-carboxy-phenylthio) terephthalic Acid 2 [11]

2,5-Dibromo-terephthalic acid **1**(3.24 g, 10 mmol), thiosalicylic acid (3.08 g, 20 mmol) and copper(I)oxide (0.715 g, 5 mmol) were added to a solution of 1.5 ml pyridine in 15 ml quinoline. The mixture was heated under reflux with argon purge for 3 h. After cooling to room temperature, ice and concd hydrochloric acid (30 ml) were added, then, over a period of 4 h, the crystals were filtered off, washed with water and redissolved in 10% aq NaOH (50 ml). After heating with activated charcoal (0.3 g) for 10 min, the solution was filtered and acidified with 18% aq HCl at 0°C. The precipitate was filtered off and recrystallized from glacial acetic acid to give **2**; yield: 3.6 g (76.5 %), mp 318–320°C, ($C_{22}H_{14}O_8S_2$(470.47/470). Calculated: C 56.61; H 3.00; S 13.63, found: C 56.31; H 2.99; S 13.35).

Preparation of Esters of 2,5-Bis(2-carboxy-phenylthio) terephthalic Acid 4a–f

2 (0.94 g, 2 mmol) was heated in 5 ml thionyl chloride at 70°C for 4 h. The red solution was cooled to room temperature and 5 ml of dry benzene were added. Removal of the solvent under reduced pressure left a dark yellow oil. This oil was dissolved in 5 ml dry benzene, then the solvent was evaporated under reduced pressure and a yellow powder resulted. To a solution of this chloride **3** in 5 ml pyridine the corresponding hydroxy compound (8 mmol) in 5 ml pyridine was added dropwise while stirring at room temperature. After addition the mixture was refluxed for 2h and quenched with ice/hydrochloric acid. The precipitate was filtered off and purified by recrystallization from glacial acetic acid. Analytical data for the products **4a–f** are given in Table I.

X-ray Investigation

X-ray measurements were performed to prove the structures of the novel compounds. This is necessary to get information about the relation between chemical structure and physical behavior.

Crystals of **4a** and **4c** were measured on a Siemens P4 diffractometer with $\lambda = 0.71073$ Å (Mo-K$_a$), graphite monochromator in routine ω-scan. Both unit cells were found to be triclinic with $a = 7.989(1)$, $b = 8.995(1)$, $c = 9.214(1)$ Å, $\alpha = 85.15(1)$, $\beta = 78.91(1)$, $\gamma = 67.66(1)°$, space group $P\bar{1}$ (No. 2 I.T.), $Z = 1$, $V = 600.95(12)$ Å^3, $\rho_{\text{calcd.}} = 1.455$ gcm^{-3}, temp: 213 K for **4a** and $a = 8.226(2)$, $b = 11.959(2)$, $c = 12.025(1)$ Å, $\alpha = 79.68(1)$, $\beta = 89.69(1)$,

TABLE I Analytical data of Esters of 2,5-Bis(2-carboxy-phenylthio)terephthalic acid **4a–f**

Comp. 4	*R*	*Yield* %	T_m °*C*	ΔS *J/mol·K*	T_g °*C*	Δc_p *J/mol·K*	*Empirical formula molecular mass/ MS found*	*C/H/S-analysis calcd./found* *C*	*H*	*S*
a	CH_3	45	178.0	143	22.1	231	$C_{26}H_{22}O_8S_2$ 526.58/526	59.31 59.25	4.21 4.27	12.18 12.23
b	C_2H_5	42	124.8	160.4	−4.2	256	$C_{30}H_{30}O_8S_2$ 582.68/582	61.84 61.80	5.19 5.17	11.00 10.92
c	C_6H_{13}	54	52.3	256.7	~−50	*	$C_{46}H_{62}O_8S_2$ 807.11/806	68.45 66.29	7.75 7.75	7.94 7.82
d	$C_{12}H_{25}$	36	64.3	365.8	~−37	*	$C_{70}H_{110}O_8S_2$ 1143.76/1142.2	73.51 72.58	9.69 9.52	5.61 5.55
e	4-C_6H_5-C_6H_4	64	209.4	170.6	78.5	388	$C_{70}H_{46}O_8S_2$ 1079.25/1078	77.90 77.71	4.30 4.17	5.94 5.85
f	4-NO_2-C_6H_4	71	241.0	170.8	84.7	372	$C_{46}H_{26}N_4O_{16}S_2$ 954.85/954	57.86 57.43	2.74 2.69	6.72 6.57

*not assignable.

$\gamma = 73.79(1)°$, space group $P\bar{1}$ (No. 2 I.T.), $Z = 1$, $V = 1116.3(3)\,Å^3$, $\rho_{calcd.} = 1.201\ gcm^{-3}$, temp: 298 K for **4c**. The structures were solved by direct methods (XS program for crystal structure solution, version 4.2 for MS-DOS, Siemens Analytical X-ray Inst. Inc., 1990) and refined by the full matrix least squares method of SHELXL-93 [12]. The two structures were in agreement with the expectations of stereochemistry (see Fig. 1). However, the data set of **4c** was of poor quality with respect to the regression coefficients. Hence, attempts were made to collect data sets at 213 K. While the data collection for **4a** proceeded without problems, the attempts with **4c** failed. Unexpectedly the cooled crystal of **4c** showed very broad reflections and the unit cell determination yielded too bad results.

Details of the data collection and refinement for **4a** (Cambridge refcode: NAHJOV): Crystal size 0.4×0.3×0.24 mm, scan range $4.5° < 2\theta < 45°$, hkl range −2/8, −9/9, −9/9, measured refl. 1978, unique 1573, obs. 1315, obs. criterion $I > 2\sigma(I)$, ref. param. 168, $R1$ for obs. refl. 0.0480, $R1$ for all 0.0598, $wR2$ for all 0.1313, restrained goodness of fit $S = 1.067$, resid. electr. dens. 0.3567/−0.243 $e/Å^3$, the weighting scheme for the refinement was calculated according to $w = 1/[s^2(Fo^2) + (0.0548\,P)^2 + 0.2669\,P]$ with $P = (Fo^2 + 2Fc^2)/3$.

Details of the data collection and refinement for **4c** (Cambridge refcode: NAHMEO): Crystal size 0.52×0.26×0.18 mm, scan range $3.6° < 2\theta < 42°$, hkl range −1/8, −12/12, −13/13, measured refl. 3033, unique 2394, obs. 1803, obs. criterion $I > 2\sigma(I)$, ref. param. 254, $R1$ for obs. refl. 0.0865, $R1$ for all 0.1144, $wR2$ for all 0.3431, restrained goodness of fit $S = 1.36$, resid.

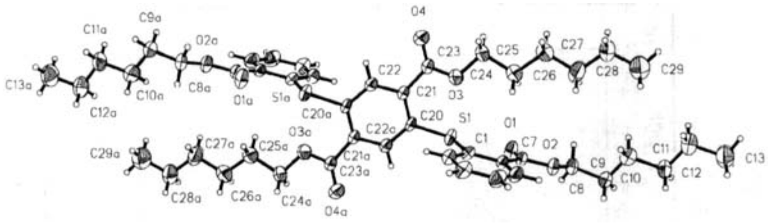


FIGURE 1 Molecular structure of **4c**, ORTEP, with 30% probability of the thermal ellipsoids.

electr. dens. 0.38/−0.242 e/Å^3, the weighting scheme for the refinement was calculated according to $w = 1/[s^2(Fo^2) + (0.1346P)^2 + 1.9971P]$ with $P = (Fo^2 + 2Fc^2)/3$.

The angles between the central and the peripherical aromatic ring planes are nearly 90° in compounds **4a** and **4c**. The projection of **4c** in Figure 1 is not perpendicular but 70° to the plane of the central ring.

Calorimetric Measurements

In order to obtain an overview about transition temperatures and thermal stability we checked the compounds with simultaneous Thermogravimetry-DSC (Labsys, Setaram). For further thermal investigations a Perkin-Elmer DSC-2 differential scanning calorimeter was used. The temperature scale of the calorimeter was calibrated with indium and lead for the scanning rate used and for the heat flow by sapphire. The purge gas was nitrogen. The temperature of the calorimeter block as well as the room temperature were kept well stabilized at temperatures of (−75 + /−0.1)°C and (27 + /−0.5)°C, respectively, in order to realize reproducible scans. Sample mass was of about 10 mg and the scanning rate 10 K/min for heating. First the compounds (crystals obtained from recrystallization) were heated to a temperature above the melting point (see curve 1 in Fig. 2). The first heating of compound **4e** shows two small exothermic peaks around 150°C and 180°C and one large endothermic melting peak at 209.4°C. For other compounds we did not found such exothermic effects at first heating indicating a more stable crystalline structure. The reason for the differences is still not understood. Then the samples were cooled with a rate of 10 K/min. During this scan some compounds crystallize and other form glasses due to a wide super-cooling of crystallization. After that a second heating scan with the same rate was started (see curve 2 in Fig. 2). In most compounds a glass transition can be observed (step in the specific heat capacity). Only such compounds are discussed in this paper. Sometimes a cold crystallization above the glass transition occurs

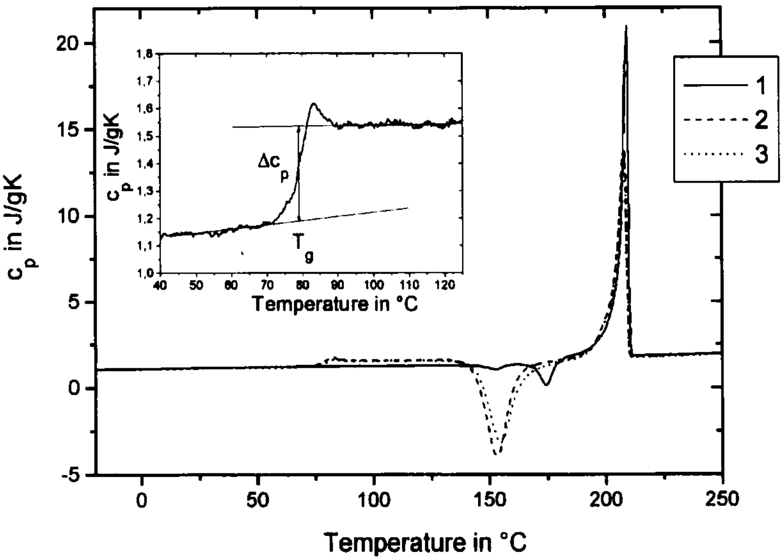


FIGURE 2 DSC thermograms (heating scans with 10 K/min) for compound **4e**: 1, crystals from synthesis, 2, after cooling with 10 K/min; 3, after cooling with 80 K/min. Inset shows the DSC thermogram in the glass transition region with the determination of the thermal glass transition parameters.

(exothermic peak at about 150°C). Then also a melting peak at about 210°C can be seen. Some of the compounds show pre-melting and recrystallization peaks, indicating polymorphism. The third heating scan was performed after a cooling with a rate of 80 K/min (see curve 3 in Fig. 2). All compounds form 100% amorphous structures (glasses) at this high cooling rate. The difference between curves 2 and 3 gives some information about the tendency to crystallize and the crystallization rate. From these scans the glass transition temperatures were determined. The melting points (Tab. I) as well as the entropy of fusion were determined from the first heating scan. The glass transition temperatures T_g (Tab. I) of the compounds were taken as the midpoint temperature determined in the third heating scan. The midpoint temperature is defined in the usual way as the temperature of the half step-height Δc_p at the glass transition (see inset in Fig. 2).

Dielectric Measurements

Temperature scans at constant frequency (Fig. 3 and Fig. 4) and frequency scans at constant temperature (Fig. 5) were performed to detect the

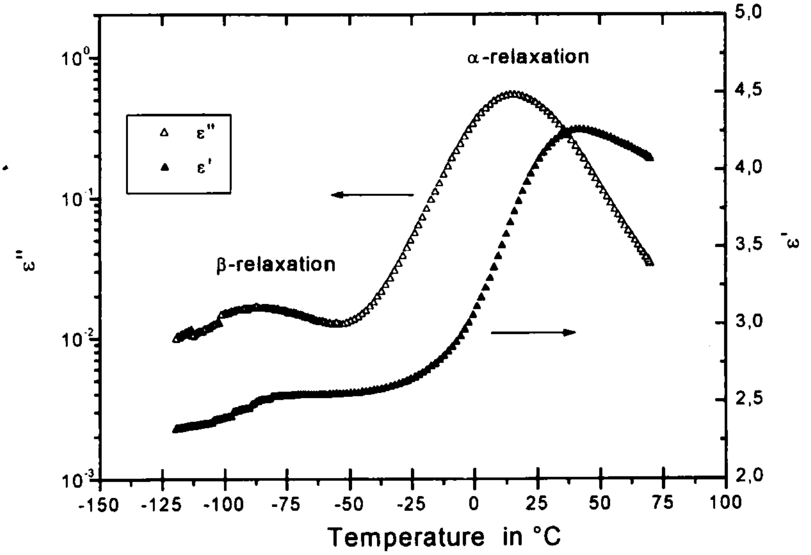


FIGURE 3 Dielectric spectra of compound **4c** at constant frequency. $\nu = 1$ MHz; heating rate 5 K/min.

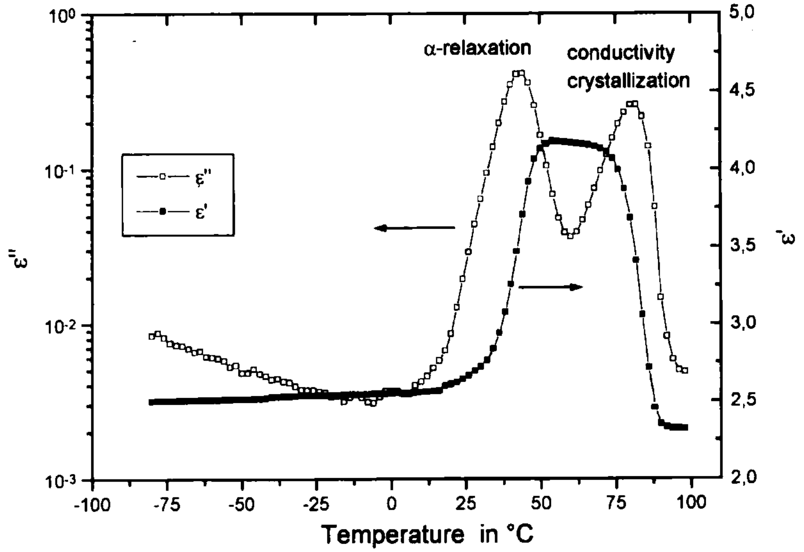


FIGURE 4 Dielectric spectra of compound **4a** at constant frequency. $\nu = 1$ kHz; heating rate 5 K/min.

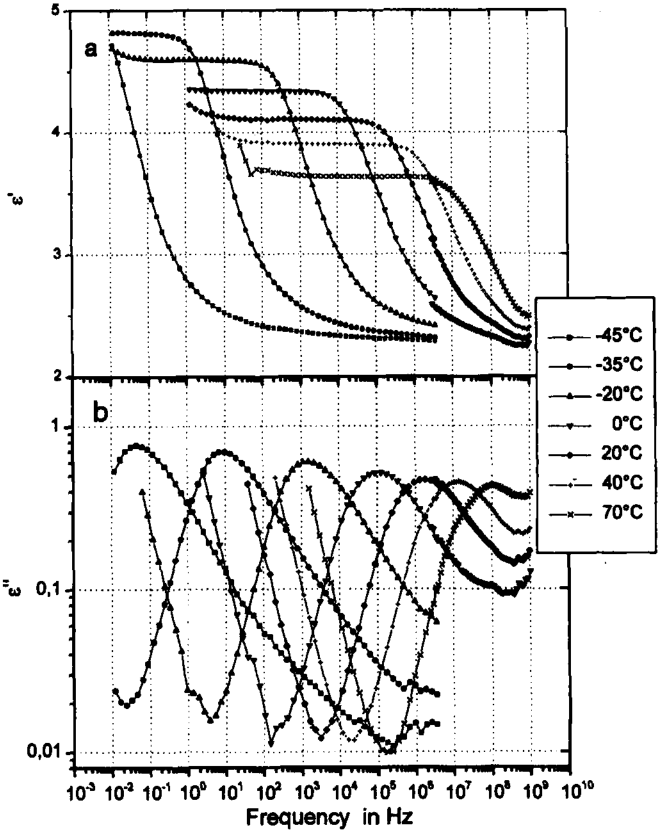


FIGURE 5 Real part (a) and imaginary part (b) of the complex dielectric function in the glass transition region of compound **4c** at different temperatures.

molecular dynamics of the compounds. The dielectric measurements were carried out in the frequency range of 0.01 Hz to 1 MHz with a BDS 4000 broadband dielectric Spectrometer (Novocontrol GmbH). A frequency response analyzer SI 1260 (Solatron-Schlumberger), which was supplemented by a high-impedance preamplifier of variable gain [13], was used to extract the complex dielectric function

$$\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu) \tag{1}$$

(ν: frequency, ε': real part, ε'': imaginary part). In the frequency range from 1 MHz to 1 GHz a coaxial line reflectometer HP 4191A was used. The dielectric measurements were performed after melting the substances between two condenser plates (diameter 16 mm and 5 mm, respectively) and quenching below glass temperature. The samples with a thickness of approximately 50 μm were kept in a cryostat where the sample temperature was controlled by using a nitrogen gas stream of controlled temperature. Frequency scans were performed at constant temperature, with a temperature stability better than 0.1 K [14].

Figure 5 shows typical frequency scans for the compound **4c**. The measured dielectric function can be described quantitatively by generalized relaxation functions. The most general one is the Havriliak-Negami (HN) equation [15]

$$\varepsilon^*(\nu) = \varepsilon_\infty + \frac{\varepsilon_{\mathrm{st}} - \varepsilon_\infty}{(1 + (i\nu/\nu_c)^\beta)^\gamma} \quad (0 < \beta,\ \beta \cdot \gamma \leq 1) \tag{2}$$

β and γ are shape parameters; ν is the frequency of the applied field; ν_c the characteristic frequency; and, $\Delta\varepsilon = \varepsilon_{\mathrm{st}} - \varepsilon_\infty$ the relaxation strength ($\varepsilon_{\mathrm{st}} = \varepsilon'(\nu)$ for $\nu \ll \nu_c$; $\varepsilon_\infty = \varepsilon'(\nu)$ for $\nu \gg \nu_c$). The characteristic frequency ν_c resulting from the fitting procedure depends to some extent on the chosen shape parameters β and γ. The frequency of the dielectric loss maximum ν_{max} is not influenced by the shape parameters and has been used in the following as the relaxation frequency. If the relaxation process is influenced by neighboring processes, e.g., conductivity on the low frequency tail, then these processes must be included in the fitting procedure [16].

RESULTS AND DISCUSSION

After thermal characterization by DSC dielectric temperature scans at constant frequency of mostly 1 kHz were performed to get an overview of the dielectrically detectable relaxation phenomena (Figs. 3 and 4). In all compounds we found a strong high temperature relaxation which is related to the thermal vitrification process and called segmental- or α-relaxation. Below the thermal glass transition temperature a weak low temperature relaxation occurs, called β-relaxation (secondary or sub-T_g process). The crystallization behavior of the compounds is quite different. During the measurements for some samples no detectable crystallization occurs (compounds **4b** and **4c**). These can also be measured in the high temperature (high frequency) range with the HP 4191A. Other compounds such as **4a**, **4e** and **4f** crystallize rapidly (discernible in the strong decrease in ε', see Fig. 4) reaching crystallization temperature and can only be measured up to this temperature. For the compound **4d** we found an unusual behavior. The thermal glass transition is superimposed with a melting and the beginning of crystallization. That's why it is not possible to determine a step height in c_p and the temperature dependence of the α-relaxation. The observed phase transition in the glass transition range may be related to the crystallization of the alkyl chains [29].

To investigate the temperature time dependence of the α-relaxation we performed isothermally frequency scans (Fig. 5). The results are shown in Figure 6 in an activation or Arrhenius plot. To include the vitrification temperatures T_g in this plot it is necessary to transform cooling rates q of DSC experiments into frequency. We used the transformation formula developed by Donth [17] which we experimentally verified in a previous publication [18]. For a cooling rate of 10 K/min the calculation yields in a corresponding frequency of about 10^{-3}Hz. From Figure 6 it can be seen that the points for vitrification are in good agreement with the high temperature dielectric α-relaxation process. This indicates that the α-relaxation process is related to vitrification.

The temperature dependence of the relaxation rate of the α-relaxation can be described by the empirical Vogel-Fulcher-Tammann (VFT) equation [19, 20]

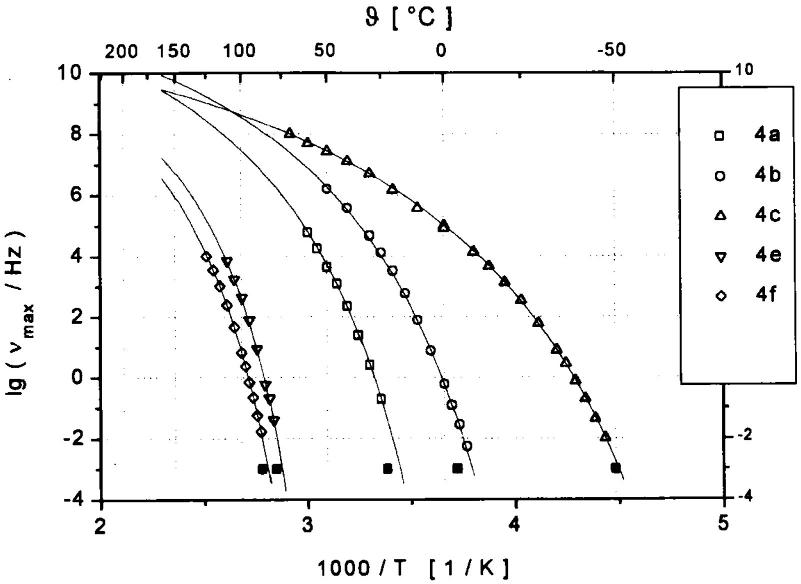


FIGURE 6 Arrhenius diagram of the dielectric α-relaxation for all compounds. Lines correspond to a VFT-equation (Tab. II).

$$\lg \nu_{\max} = A - \frac{B}{T - T_0} \tag{3}$$

which is characteristic of glass-forming systems. $A = \lg \nu_\infty$ and B are constants, and T_0 is the so called ideal glass transition or Vogel temperature. The VFT parameters from nonlinear least square fits are listed in Table II.

Due to the quite different thermal glass transition temperatures it is not possible to compare the temperature frequency dependence of the different compounds in the Arrhenius diagram (Fig. 6) directly. For such an analysis it is necessary to reduce the temperature with respect to the (dynamic) glass transition temperature [21–23] in a so called Angell plot. Often the temperature, where the maximum position of the imaginary part reached a relaxation time of 100 s, will be used as the dynamic glass transition temperature. Because this is outside our measurement window and to avoid large errors, we chose $\nu = 1$ Hz ($\tau = 1/2\pi\nu = 0.16$ s) to be the frequency for definition of the dynamic glass transition temperature $T_{g1\mathrm{Hz}}$, i.e., at temperature $T_{g1\mathrm{Hz}}$ the maximum position of the dielectric loss peak is at 1 Hz (Fig. 7). To distinguish calorimetric glass transition temperature, T_g, from cooling scans with q = 10 K/min and dielectrically determined dynamic glass transition temperatures, $T_{g1\mathrm{Hz}}$, we use the additionally index 1 Hz.

In such a T_g-scaled Angell or "cooperativity"-plot each substance has its own signature characterized by its slope or curvature (Fig. 7). To quanitfy this slope, Böhmer and Angell [24] introduced the fragility index m which is defined as

$$m = \left. \frac{d \lg \tau}{d(T_{g100\mathrm{s}}/T)} \right|_{T = T_{g100\mathrm{s}}} \tag{4}$$

Donth [25, 26] introduced another calculation for a fragility parameter. In his description the fragility parameter F is defined as

$$F = \frac{T_g}{T_g - T_0} \tag{5}$$

TABLE II VFT-parameters and fragility parameter F

Compound	A	B K	T_0 K	F
4a	13.6	800.2	242.2	5.5
4b	13.4	747.5	218.3	5.3
4c	12.1	675.9	177.6	4.9
4e	12.4	674.6	304.2	7.4
4f	13.0	846.6	303.5	6.6

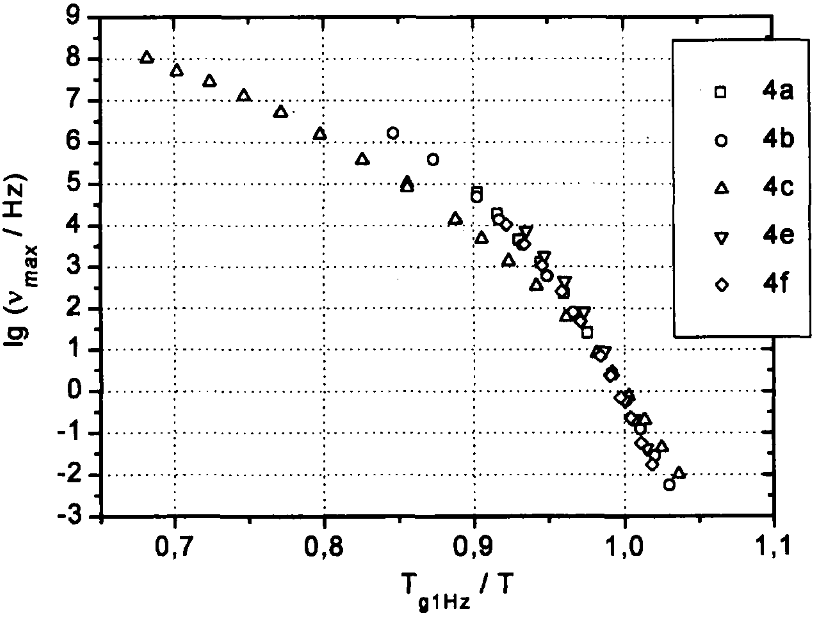


FIGURE 7 T_{g1Hz}-scaled temperature dependence of the relaxation frequency, ν_{max}, for all compounds. T_{g1Hz} is defined as the temperature at which $\nu_{max} = 1$ Hz.

with T_g as the thermal glass transition temperature and, T_0, the Vogel temperature, ascertained in a VFT analysis (Tab. II). Both determinations of a fragility give the same results. Using a relaxation time of $\tau_{max} = 100$ s for the Angell analysis results in $F = m/m_{min}$ with $m_{min} = 16$ [23]. We use the formulation of Donth because we have not measured the dynamic T_g at such low frequencies ($\nu \approx 10^{-3}$ Hz).

In our case there are some differences in the fragility. We found a strong fragility ($F \approx 7$) for compounds **4e**, **f** and for **4a–c** with alkyl chains a medium fragility ($F \approx 5$). With increasing length of alkyl chains (CH_3, C_2H_5, C_6H_{13}; **4a–c**) we obtained a decreasing fragility, cf. Table II. The same result was found and discussed for side-chain liquid-crystalline polymers by Ngai *et al.* [27].

Beside the temperature frequency dependence we also analyzed the shape of the relaxation spectrum. The values in Table III are taken at T_{g1Hz}. We found only little differences in this analysis (Tab. III). In accordance with other results from low molecular mass molecules [28] there is a near Debye like behavior at the low frequency side (characterized by HN-parameter $\beta \approx 1$) but a widening on the high frequency side (characterized by HN-

TABLE III HN-parameters at $\nu_{max} \approx 1$ Hz

Compound	*Temperature* °*C*	β	$\beta \cdot \gamma$	$\Delta\varepsilon$
4a	30	0.81	0.44	1.2
4b	0	0.82	0.44	3.8
4c	−40	0.91	0.38	2.6
4e	85	0.94	0.38	1.3
4f	95	0.95	0.49	7.4

parameter $\beta \cdot \gamma < 0.5$). That means the relaxation spectra are only slightly influenced by the different ester groups. The relaxation strength is more dependent on these ester groups. This is not suprising because for instance the dipole moment of NO_2 is much greater than that of the other carbon rests.

CONCLUSIONS

The investigated sulfur ligated "trillings" have a strong glass-forming tendency. Different ester groups shift the calorimetric glass transition temperature from −50°C to 85°C. The α-relaxation which is connected with the thermal vitrification process shows different temperature time (frequency) behavior in dependence on the different carbon rests.

The β-relaxation which is assumed to be connected with local movements was not investigated systematically. Due to the broad β-peak with a low intensity ($\varepsilon''_{max} \approx 0.01$ at $\nu = 1$ MHz) we are not able to make a satisfactory analysis.

Acknowledgment

This work has been supported by the DFG. J. D. would like to thank Mrs. G. Marlow and Mr. A. Hensel for careful thermal measurements.

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