

Molecular mobility and fragility in *n*-ethylene glycol dimethacrylate monomers

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Abstract

Di-, tri- and tetra-ethylene glycol dimethacrylate monomers were investigated by dielectric relaxation spectroscopy in the frequency range from 20 Hz to 1 MHz and in the temperature region comprised between -120 and $+25$ °C. A rather intense relaxation process associated with the glass transition is found for all the monomers in the temperature region between -80 and -50 °C. The mobility of the cooperative process decreases with the molecular weight increase. The temperature dependence of the relaxation times reveals some curvature, which increases with the size of the ethylene glycol moiety (di \cong tri $<$ tetra). In spite of this behavior the di- and tri-ethylene monomers could be treated as Arrhenius type, presenting similar activation energies. The fragility indexes estimated by both dielectric relaxation spectroscopy and differential scanning calorimetry techniques agree for the di- and tri-ethylene monomers only when Arrhenius behavior is assumed. Despite the different values estimated, the fragility is comparable to a quite strong glass former as glycerol.

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1. Introduction

If the crystallization of a liquid is avoided, it supercools entering in a state of metastable equilibrium. With continuous cooling, the viscosity, and consequently the relaxation time, of the supercooled liquid, increases dramatically until it forms a glass at a temperature below the glass transition temperature, T_g . It is common to characterize the entry in the glassy state by a relaxation time of 100 s and a shear viscosity of 10^{13} P [1]. In the glass, the structure of the supercooled liquid is retained in a non-equilibrium metastable state, and the material is no longer able to reach equilibrium within the experimental time scale.

It is known that the evolution of the relaxation time with the decreasing of temperature in supercooled liquids shows a departure from Arrhenius behavior. This departure is more pronounced in more fragile glass formers [2–5]. Fragility is a central parameter in glassy

state physics reflecting the stability of the structure to thermal degradation [6]. It arises from a highly temperature dependent structural configuration above T_g , i.e., a high structural weakness coming from a complex topology of the surface of the Gibbs energy landscape [7] being correlated with the non-exponentiality and non-linearity of the relaxation process [8]. The non-exponentiality is directly affected by intermolecular cooperativity increasing with the increase of the domain size [9]. The strength of intermolecular coupling is also one of the elements that determine fragility, where, for instance, liquids that form a hydrogen bonding structure are stronger than those of Van der Waals structure [9,10].

Dielectric relaxation spectroscopy is a suitable tool to monitor the relaxation time from the supercooled liquid state down to the glassy state, through the measurement of the complex dielectric constant when the material is under the influence of an alternating electrical field. Being a technique sensitive to the reorientation of the molecular dipoles, it is suitable to study the relaxation processes, and thus the molecular mobility, associated with the glass transition in materials containing permanent dipoles.

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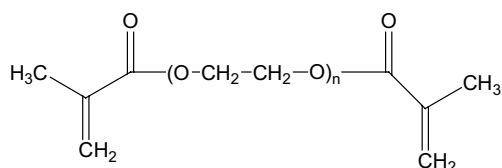
In the present work we measured the real $\varepsilon'(f)$ and imaginary $\varepsilon''(f)$ parts of the complex dielectric constant of three *n*-ethylene glycol dimethacrylate ($n = 2, 3,$ and 4) monomers, in the temperature region where the transition from supercooled liquid to a glassy state occurs. The fragility index of each glass former was determined by both dielectric relaxation spectroscopy and differential scanning calorimetry.

Multifunctional methacrylate monomers are the precursors of crosslinked polymers widely used in the production of coatings, information storage systems, spherical lenses and dental biomaterials [11–13]. Despite its great practical interest the dielectric studies involving these monomers are scarce in the literature [14]. To our knowledge no such studies are found in the literature for the three pure monomers.

2. Experimental

2.1. Materials

The studied monomers have the general formula



with n varying from 2 to 4. Polysciences, Inc., supplied diethylene glycol dimethacrylate ($n = 2$), $M_w = 242.30$, cat. nbr. 02214; Fluka supplied triethylene glycol dimethacrylate ($n = 3$), $M_w = 286.36$, cat. nbr. 90412 and tetraethylene glycol dimethacrylate ($n = 4$), $M_w = 330.42$, cat. nbr. 86680. All the products were used as received.

2.2. Measurements

2.2.1. Dielectric relaxation spectroscopy

The dielectric measurements were carried out using an impedance analyzer, covering a frequency range from 20 Hz to 1 MHz and in different increasing temperature steps from -100 up to $+25$ °C (in the temperature range between -80 and -50 °C the dielectric spectra were recorded every 1 °C and from -48 up to 0 °C the dielectric spectra were recorded every 2 °C; in the remaining temperature region the spectra were recorded every 5 °C). A drop of the liquid monomer with two silica spacers 50 μm thick was placed between two gold plated electrodes (diameter: 20 mm) of a parallel plate capacitor. The sample cell was mounted on a cryostat and exposed to a heated gas stream being evaporated from a liquid nitrogen dewar. The temperature control is performed within ± 0.05 °C.

2.2.2. Differential scanning calorimetry

A calorimeter fitted with a liquid nitrogen cooling accessory was used for the differential scanning calorimetry (DSC) experiments. Dry high purity He gas with a flow rate of 30 cm^3/min was purged through the sample. 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 (see *Experimental* of Ref. [15]). The transition from glass to supercooled liquid was recorded in the heating mode for all monomers, from -130 up to 0 °C. In the assays with different cooling rates, the thermograms for the TeEGDMA monomer were only collected up to -30 °C in order to avoid crystallization.

3. Results

3.1. Dielectric relaxation spectroscopy

The dielectric loss spectra, $\varepsilon''(f)$, for the TeEGDMA monomer, are shown in Fig. 1(a), in logarithmic scale, for temperatures between -74 and -46 °C, in temperature steps of 2 °C. In Fig. 1(b) the loss curves of TeEGDMA (squares) are compared with the loss curves of TrEGDMA (triangles) and DEGDMA (circles) at two different temperatures, -72 °C (open symbols) and -57 °C (full symbols).

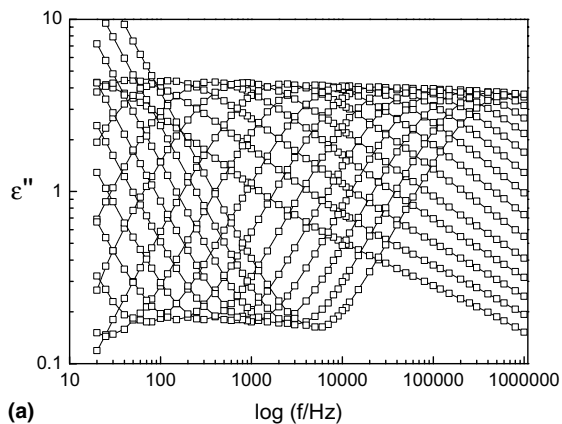
Fig. 2 presents the plots of ε'' at 1 kHz (taken from the isothermal measurements) for the three monomers is a function of temperature; the inset will be discussed later on. The di-ethyleneglycoldimethacrylate monomer exhibits a maximum around -75 °C. The tri-ethylene and tetra-ethylene monomers exhibit maximums at slightly higher temperatures, the temperature of the maximum increasing with n ; this behavior follows the same order of the glass transition temperatures observed in DSC measurements (shown in the next section); moreover the temperature values are closely related.

Therefore, the relaxation process observed in this temperature region is related with the glass transition of the monomers, being an α -type process.

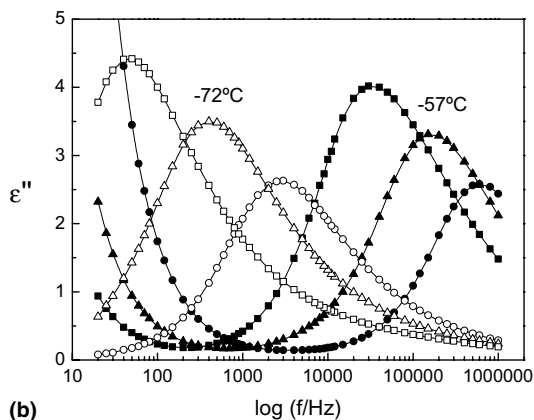
This rather intense process, observed for all the materials, can be fitted by the well-known empirical Havriliak–Negami [16] (HN) function:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (i\omega\tau)^{\alpha_{\text{HN}}}]^{\beta_{\text{HN}}}}, \quad (1)$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric strength, i.e., the difference between the real permittivity values at, respectively, the low and high frequency limits, $\tau \approx (2\pi f_{\text{max}})^{-1}$ is the characteristic relaxation time, and α_{HN} and β_{HN} , the shape parameters ($0 < \alpha_{\text{HN}} < 1$, $0 < \alpha_{\text{HN}} \cdot \beta_{\text{HN}} < 1$); the α_{HN} value is related with the broadness of the relaxation while β_{HN} describes its asymmetry (Debye



(a)



(b)

Fig. 1. (a) Dielectric loss spectra in logarithmic scale for the TeEGDMA monomer between -74 and -46 °C in temperature steps of 2 °C; (b) Loss curves for the three monomers at -72 °C (open symbols) and -57 °C (full symbols); DEGDMA (circles), TrEGDMA (triangles) and TeEGDMA (squares).

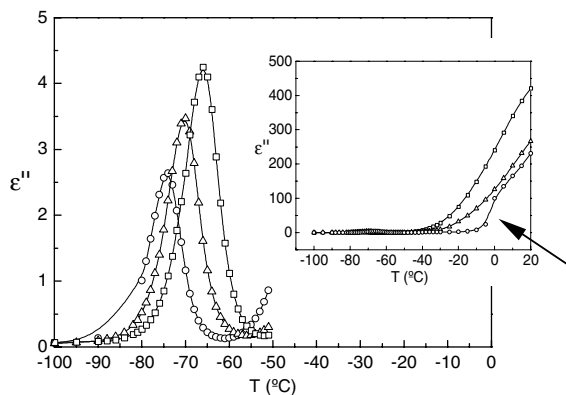


Fig. 2. ϵ'' values at 1 kHz, taken from isothermal measurements, for the three monomers; the inset shows at temperatures higher than -10 °C (indicated by the arrow) the effect in the loss values of cold crystallization of TeEGDMA (see text further on). The previous symbols were used.

behavior is given by $\alpha_{\text{HN}} = \alpha_{\text{HN}} \cdot \beta_{\text{HN}} = 1$). A term $-i\sigma/\omega^c \epsilon_0$ was added to take into account the dc conductivity contribution in the low frequency side for

temperatures higher than around -60 °C, where ϵ_0 is the vacuum permittivity, σ and c are fitting parameters: σ is related to the dc conductivity of the sample and c describes the broadening of the relaxation time distribution for the dc conductivity.

The value of the α_{HN} shape parameter for the three monomers remains almost constant in the temperature region where the loss peaks were detected: $\alpha_{\text{HN}} = 0.92 \pm 0.06$. The β_{HN} parameter does not vary up to -70 °C ($\beta_{\text{HN}} = 0.47 \pm 0.05$), but for higher temperatures β_{HN} increases with increasing temperature and decreasing size of the ethylene moiety (for example, at -60 °C, $\beta_{\text{HN}} = 0.70 \pm 0.05$ for $n = 2$ and $\beta_{\text{HN}} = 0.57 \pm 0.05$ for $n = 3$); for $n = 4$ the β_{HN} value stays close to 0.44 ± 0.04 in all temperature range. Nevertheless the shape differences are not very significant as illustrated in the normalized plot of the loss factor curves presented in Fig. 3, for -72 , -65 and -58 °C, which nearly give rise to a master curve.

As already noticed in the loss spectra of the higher monomer (Fig. 1(a)), the loss curves at the lowest temperatures exhibit a high-frequency flank.

The dielectric strength, which is presented in Fig. 4, remains almost constant for each monomer, increasing with n : $\Delta\epsilon = 8 \pm 1$ for $n = 2$, $\Delta\epsilon = 11 \pm 1$ for $n = 3$ and $\Delta\epsilon = 14 \pm 1$ for $n = 4$.

The difference in the dielectric strength values between consecutive monomers is around 3. This value can be taken as the increase in the dielectric strength due to each additional ethylene glycol moiety.

The relaxation times, τ , in a logarithmic scale, are presented as a function of the inverse of the temperature in Fig. 5 for all three systems (the usual symbols are used).

In DEGDMA and TrEGDMA the temperature dependence of the α process shows relatively little curvature, whereas TeEGDMA, presents an enhanced

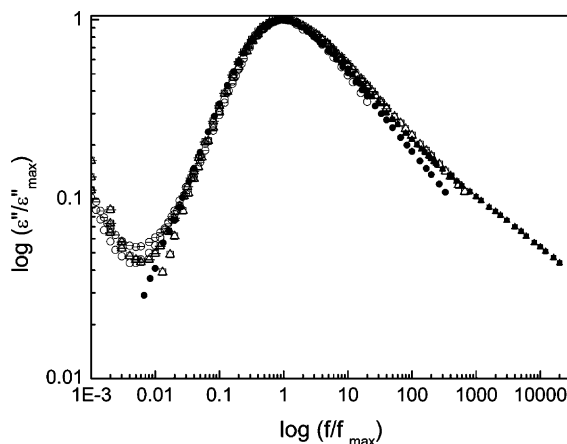


Fig. 3. Normalized loss curves for the temperatures of -72 °C (open symbols), -65 °C (full symbols) and -58 °C (crossed symbols); DEGDMA (circles), TrEGDMA (triangles) and TeEGDMA (squares).

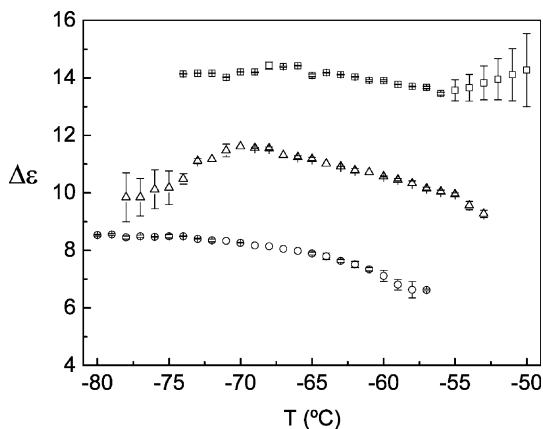


Fig. 4. Dielectric strength values in function of the temperature DEGDMA (circles), TrEGDMA (triangles) and TeEGDMA (squares).

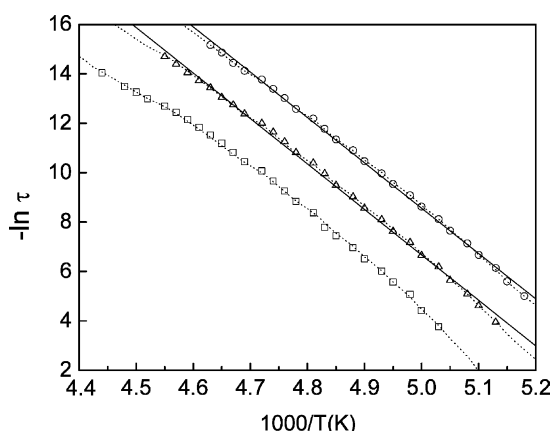


Fig. 5. Temperature dependence of the relaxation times for all three monomers (usual symbols); dashed lines – fitting by VFT equation, solid lines – fitting by Arrhenius equation.

departure from Arrhenius behavior by showing the usual curvature of fragile glass formers. All the curves were fitted by Vogel–Fulcher–Tamman [17–19] equation (dashed lines in Fig. 5):

$$\tau = \tau_0 e^{\frac{B}{T-T_0}} \quad (2)$$

with the following parameters: DEGDMA: $\tau_0 = (3.0 \pm 2.7) \times 10^{-23}$ s, $T_0 = 110 \pm 5$ K, $B = 3891 \pm 429$ K; TrEGDMA: $\tau_0 = (2.4 \pm 2.0) \times 10^{-21}$ s, $T_0 = 119 \pm 4$ K, $B = 3304 \pm 303$ K; TeEGDMA: $\tau_0 = (2.1 \pm 1.6) \times 10^{-15}$ s, $T_0 = 149 \pm 3$ K, $B = 1503 \pm 168$ K.

By replacing the VFT Eq. (2) in the activation energy equation

$$E_a = R \frac{\partial \ln \tau}{\partial (1/T)}. \quad (3)$$

It is possible to calculate the temperature dependent activation energy:

$$E_a(T) = \frac{R \cdot B}{(1 - T_0/T)^2}. \quad (4)$$

Therefore, the fragility index, defined as [4]

$$m = \frac{\partial \log \tau}{\partial (T_g/T)_{T=T_g}} \quad (5)$$

can be calculated, taking in account Eq. (3), as

$$m = \frac{E_a(T_g)}{\ln 10 R T_g} \quad (6)$$

T_g is estimated by replacing τ in Eq. (2) by 100 s (see Introduction).

The (T_g) values thus obtained, together with $E_a(T_g)$ and m values calculated respectively, by Eqs. (4) and (6), are included in Table 1.

Since the temperature dependence of the relaxation times, of both DEGDMA and TrEGDMA, shows relatively little curvature, it can be fitted by the Arrhenius equation (solid lines in Fig. 5 for $n=2$ and $n=3$; $R^2 = 0.99$ for both straight lines). Both pre-exponential and activation energy values, are very similar: $\tau_0 = (2.7 \pm 1.4) \times 10^{-44}$ s, $E_a = 151 \pm 1$ kJ mol $^{-1}$ and $\tau_0 = (1.4 \pm 0.8) \times 10^{-44}$ s, $E_a = 153 \pm 1$ kJ mol $^{-1}$ for, respectively, DEGDMA and TrEGDMA.

The fragility indexes for the Arrhenius fit of the data were obtained by using Eq. (6) with $E_a(T_g) = E_a$ and T_g

Table 1

Glass transition temperatures, fragility indexes and activation energy values for the three materials determined by differential scanning calorimetry, DSC and dielectric relaxation spectroscopy, DRS (see text for explanation of the different estimation methods)

			DEGDMA	TrEGDMA	TeEGDMA
DSC		(T_g) (K)	181	187	190
		m	43	44	48
		E_a (kJ/mol)	148	157	175
DRS	Arrhenius	(T_g) (K)	175	178	–
		m	46	45	–
		E_a (kJ/mol)	153	153	–
	VFT	(T_g) (K)	178	182	188
		m	64	65	80
		Q_{app} (kJ/mol)	218	228	288

obtained by replacing τ in the Arrhenius equation by 100 s. All the activation data and T_g values are summarized in Table 1.

3.2. Differential scanning calorimetry

The glass transition temperature for each monomer was determined by differential scanning calorimetry, DSC, as the temperature of the onset, T_{on} , of the glass to supercooled liquid transition, obtained with a heating rate of 10 °C/min (see Ref. [15] for a discussion on the accuracy of T_{on} , T_{mid} and T_{end}). Fig. 6 presents the thermograms thus obtained for the three monomers.

The onset temperatures of the glass transition calorimetric signal are -92 , -87 and -83 °C, respectively, for DEGDMA, TrEGDMA and TeEGDMA, being in close agreement, for all monomers, with the T_g values determined by extrapolating the VFT fit of the dielectric data to 100 s (the glass transition temperature of TeEGDMA, -83 °C, is also in perfect agreement with -81.7 °C of Ref. [20]). The heat capacity jumps, ΔC_p , of the calorimetric glass transition, are very high and well defined being equal to 209 ± 19 , 256 ± 23 and 316 ± 40 J k $^{-1}$ mol $^{-1}$ for $n = 2, 3$ and 4 , respectively.

The differential scanning calorimetry technique can be used for the estimation of the fragility index, since it allows the determination of the activation energy through the dependence of the glass transition temperature on the heating/cooling rate, $|q|$. According to Moynihan et al. [21,22], the dependence of T_g on $|q|$ is given to a high degree of approximation by

$$\frac{d \ln |q|}{d(1/T_g)} = \frac{-\Delta H^*}{R}, \quad (7)$$

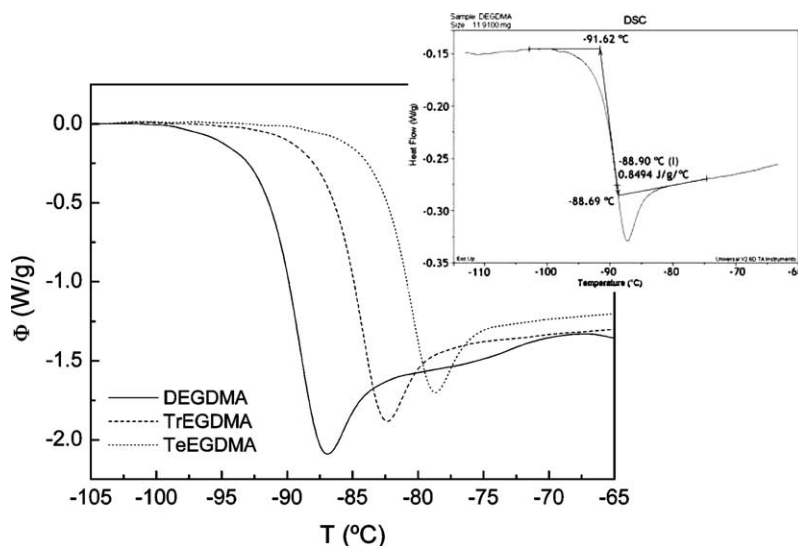


Fig. 6. DSC heating curves for DEGDMA, TrEGDMA and TeEGDMA obtained at a heating rate of 10 °C min $^{-1}$ (the curves were displaced to make coincide the initial heat flow, Φ , values); the inset shows for DEGDMA, how the onset temperature, T_{on} , is determined.

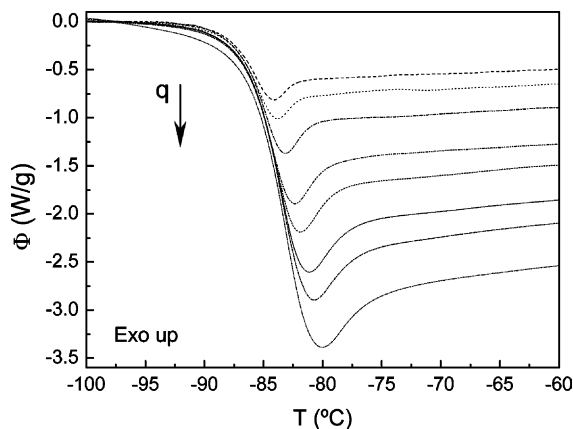


Fig. 7. Variation of the onset of the calorimetric glass transition signal for TrEGDMA obtained at 4, 5, 7, 10, 12, 15, 17 and 20 °C min $^{-1}$; the curves were shifted in order to make coincide the initial heat flow, Φ , values.

where ΔH^* is the activation energy (more properly, the activation enthalpy) for structural relaxation.

Therefore, in order to determine the activation energy for the glass transition process through calorimetric experiments, we performed several assays at different heating rates.

Fig. 7 presents the deviation of T_{on} of the glass transition with the heating rate, from 5 (upper thermogram) to 20 °C/min for the TrEGDMA monomer.

The T_{on} dependence on the heating rate for the three monomers is presented in Fig. 8. The activation energy values (calculated from the slope of the activation plot according to Eq. (7)), and fragility indexes (calculated from Eq. (6) with $E_a(T_g) = \Delta H^*$), are included in Table 1.

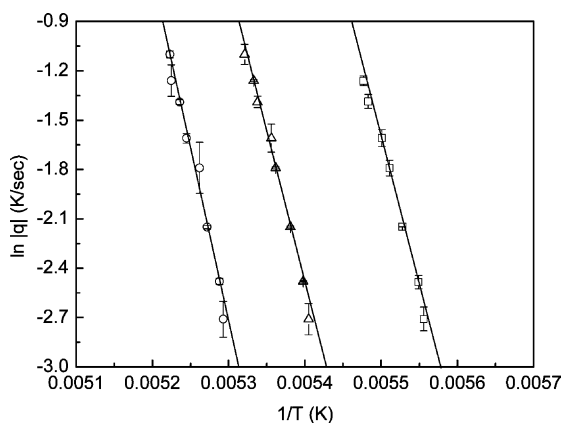


Fig. 8. Activation plots (logarithm of the heating rate as a function of $1/T_{on}$) of the calorimetric glass transition signal for DEGDMa (circles) TrEGDMa (triangles) and TeEGDMa (squares).

Finally, the TeEGDMa monomer shows crystallization when heated above -20 °C. Fig. 9 shows, above the glass transition, the crystallization endothermic peak centered at 2.9 °C for a heating rate of 12 °C/min, which was absent in the previous cooling run. Due to the large C_p value (37×10^3 JK $^{-1}$ mol $^{-1}$) associated with the crystallization, almost 100 times greater than the C_p value associated with the glass transition, it is not possible to observe both processes in the same heat flow scale.

This particular type of crystallization that occurs when the material is heated from below its glass transition, i.e., from the amorphous solid state, rather during cooling from above their melting point, it is known by cold crystallization.

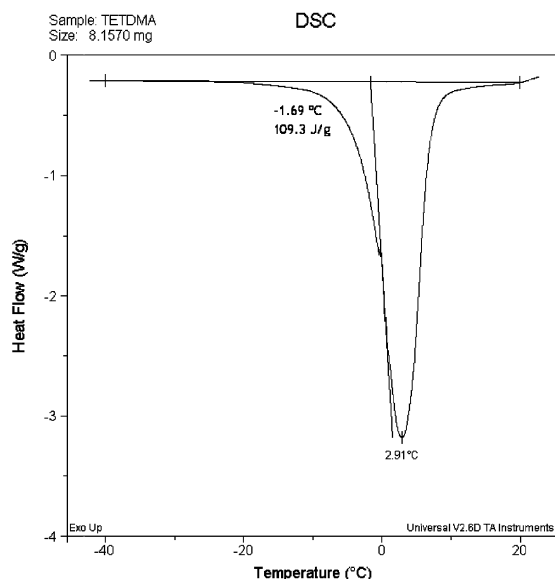


Fig. 9. Endothermic peak obtained in the heating mode at 12 °C/min from -100 up to 20 °C (only the peak region is shown) corresponding to the cold crystallization of TeEGDMa; the peak was absent in the previous cooling mode.

4. Discussion

The dielectric data revealed a rather intense relaxation process related to the glass transition, for all the three monomers studied. The shape characteristics of this α process are similar for all the materials, mainly in the lower temperature region, making it possible to build a master curve. Since the α_{HN} shape parameter is close to 1 for all monomers, the relaxation behavior is equivalent to describe the α peak with the empirical Davidson–Cole equation [23] (Eq. (1) with $\alpha_{HN} = 1$). The width parameter ($\alpha_{HN} \cdot \beta_{HN}$) increases with the temperature for $T > -70$ °C in DEGDMa and in TrEGDMa. The same behavior is found in a series of polyalcohols for threitol and xylitol [10]. By other side, the loss curves of the more fragile TeEGDMa monomer, maintain a low width $\alpha_{HN} \cdot \beta_{HN}$ parameter (around 0.40) in all temperature range. The tendency to increase the width of the α peak (lower $\alpha_{HN} \cdot \beta_{HN}$ values) when the fragility increases, is in accordance with the strong correlation between fragility and non-exponentiality observed in a large number of supercooled liquids [4,9,10].

Additionally, by analyzing separately the α_{HN} and β_{HN} values for TeEGDMa, the lower β_{HN} means that the loss curves of this molecule present asymmetry in all temperature range. Despite the applicability of the Davidson–Cole function to many systems, it seems likely that in a given system two or more discrete relaxations may be present, which results in a broadening of the loss curves at the high-frequency side [24]. Indeed, a high-frequency flank is observed in the higher monomer when the data are plotted in the logarithmic scale (as in Figs. 1(a) and 3), which, as pointed out by a referee, appears excess wing as found in some glass formers [25–28]. Brand et al. [27] argue that the excess wing is not a separate feature in the spectra of glass formers; instead, in ethanol, glycerol and propylene carbonate where the authors detected this high frequency flank, it can be ascribed to a second relaxation peak, submerged under the a peak. More work has to be done to clarify these findings in our results.

The cooperative process is more mobile in DEGDMa relative to TrEGDMa since both have almost the same activation energy, and the relaxation process is deviated to higher frequencies/lower temperatures in the lower monomer (cf. Fig. 1(b)). Also the glass transition occurs at lower temperatures. For the greater TeEGDMa molecule, the relaxation process is located at lower frequencies/higher temperatures. This same behavior is observed in dielectric measurements of polyalcohols [10], poly(propylene glycol) oligomers [9] and poly(ethylene glycol) methacrylate macromonomers with $n = 7$ and 12 [29], where the dielectric loss peaks of the higher molecular weight materials are located at higher temperatures.

The dielectric strength values are quite high due to the dipole moments of both C=O groups and ethylene glycol moiety. $\Delta\epsilon$ remains almost constant in the entire temperature range where the relaxation process was detected for all the monomers, the difference being constant between consecutive monomers and close to 3. This value can be attributed to the dipolar contribution of each additional ethylene glycol moiety. Moreover, it can be concluded that the configuration adopted by the whole molecule when approaching the glassy state is almost the same in the three materials.

The temperature dependence of the relaxation times reveals an increasing curvature and, consequently, an increasing activation energy and fragility values, with increasing n (di \approx tri<tetra). The increase of m with the molecular weight is also observed in related materials [9,10,29].

The accordance between activation energies and fragility indexes determined by DRS and DSC only holds when Arrhenius behavior is assumed for $n = 2$ and $n = 3$. Table 1 summarizes the data for the three monomers obtained by both DRS and DSC techniques.

By other side, the accordance in what concerns the T_g values, is better between DSC and the extrapolation of VFT behavior for $\tau = 100$ s. The E_a and m values for DEGDMA and TrEGDMA, determined by assuming VFT behavior, are higher than the calorimetric estimates. The same is true for TeEGDMA, which has a higher fragility index, as was expected from its greater departure from the Arrhenius behavior. In this monomer the DSC and DRS techniques strongly disagree in estimating m . While the estimated calorimetric fragility index is 52, the value of m obtained from the VFT fit of the dielectric data is 78. This erroneous prediction for more fragile materials by using DSC technique is already described in the literature [21,30]. The non-Arrhenius behavior near T_g produces a large $\Delta H^* = E_a(T_g)$, which decreases the effect of the heating rate on T_g , and thus, a greater error is found in the estimation of $E_a(T_g)$ [30].

Anyway the m values indicate that both DEGDMA and TrEGDMA are quite strong liquids, since their fragility indexes are not very far from glycerol ($m = 53$ [7], 57 [10]) indicated in the literature as one of the strongest low molecular weight organic glass formers known. The fragility of the higher monomer is identical to fragile materials as the polyalcohol threitol ($m = 79$ [10]) and m -toluidine ($m = 79$ [7], 83 [31]).

The values of ΔC_p at the glass transition, which are a measure of the degrees of freedom released on heating from the glassy state to the supercooled liquid, are unusually high by comparing with organic glass formers and polymers, being of the same order of ionic liquids that have, in the liquid state, an appreciable mobility [15].

Finally, the higher ethylene glycol dimethacrylate monomer, crystallizes on heating with the maximum of the endothermic peak close to 3 °C anticipated by an onset around -10 °C. This temperature region agrees with the anomalous behavior found for this monomer in dielectric measurements (remember the inset in Fig. 2) where a step in ϵ'' , obtained also in increasing temperature steps, is observed above -10 °C.

5. Conclusions

The relaxation processes related with the glass transition of DEGDMA, TrEGDMA and TeEGDMA were characterized dielectrically. The mobility of the cooperative process decreases with molecular weight, M_w , while the width of the relaxation peak, glass transition temperature and fragility increases with the M_w increase. The temperature dependence of the relaxation times is nearly Arrhenius type in DEGDMA and TrEGDMA, and VFT type in TeEGDMA as usually found in fragile glass formers. The fragility indexes estimated by both DSC and DRS techniques increase with n , but their values only agree when Arrhenius behavior is assumed. In spite of the differences between the two techniques, the fragility indexes indicate rather strong liquids with m values comparable to glycerol. The ΔC_p , values associated with the calorimetric glass transition are quite high, being comparable with the values found for ionic liquids, which are characterized by a high mobility in the liquid state.

Acknowledgements

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