Supporting Information

Dielectric Relaxation as a Probe To Verify the Symmetrical Growth of Two-Arm Poly(glycidyl phenyl ether) Initiated by t-BuP4/Ethylene Glycol

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1. Synthesis of 1-arm PGPE

1-arm PGPE samples were synthesized by ring-opening polymerization of GPE with tetrabutylammonium azide (N$_3$NBu$_4$) as initiator according to our previous work.$^1$ Samples of $M_n < 6$ kg/mol were synthesized by method A, and samples of $M_n > 6$ kg/mol were synthesized by method B, as explained below. Table S1 summarizes the molecular characteristics of obtained polymers.

**Method A.** In a typical experiment, N$_3$NBu$_4$ (200 mg; $7.03 \times 10^{-4}$ mol) was transferred to a round bottom flask equipped with a magnetic stirrer in a glovebox and dissolved in 1 mL of toluene. Then, GPE (2 mL; $1.47 \times 10^{-2}$ mol) was added, the flask sealed with a stopcock and the reaction stirred at room temperature for 20 h. The reaction was stopped by addition of HCl (60 µL in 0.5 mL of methanol). The solvent was evaporated under reduced pressure; the product was redissolved in THF and purified by two precipitations in cold methanol.

**Method B.** In a typical experiment, GPE (2 mL; $1.47 \times 10^{-2}$ mol) was transferred to a round-bottom flask containing 7 mL of toluene and equipped with a magnetic stirrer in a glovebox. Then, 0.96 mL of iBu$_3$Al solution (1.1 mol/L in toluene) was added to the reaction flask. Finally, N$_3$NBu$_4$ (200 mg; $7.03 \times 10^{-4}$ mol) was dissolved in 2 mL of toluene and added to the reaction flask. The flask was sealed and cooled down to -30 °C during the first 15 min to reduce the initial polymerization rate. After this, the reaction was stirred for 4 h at room temperature. The reaction was stopped with 1 mL of ethanol. The solvent was evaporated under reduced pressure and the polymer was redissolved in THF and precipitated in cold methanol twice and dried under vacuum.

| Entry (1-arm) | $M_n$ (SEC) (kDa) | $D$ | Method |
|--------------|------------------|-----|--------|
| I            | 4.4              | 1.06| A      |
| II           | 5.5              | 1.05| A      |
| III          | 7.4              | 1.27| B      |
| IV           | 13.6             | 1.27| B      |
| V            | 21.2             | 1.08| B      |

Table S1. Molecular characteristics of 1-arm PGPE polymers.
2. 2D-NMR spectroscopy

Figure S1. $^1$H - $^{13}$C HSQC spectrum (acetone-$d_6$) of PGPE synthesized by initiation with $t$-BuP$_4$ / ethylene glycol in the absence of $i$-Bu$_3$Al (Entry 3, Table 1).

3. Structures assigned to MALDI–ToF MS signals

Table S2. Structures assigned to MALDI–ToF MS signals.

| Name  | Structure | Mass          |
|-------|-----------|---------------|
| EG    | ![Structure](image1.png) | (nx150) + 62  |
| EG-prop | ![Structure](image2.png) | (nx150) + 138 |
| W     | ![Structure](image3.png) | (nx150) + 18  |
4. Analysis of dielectric relaxations

We evaluated the temperature dependence of the dielectric relaxations (segmental and normal mode) of all the samples presented in this work, as well as 1-arm PGPE samples previously reported by us.\(^1\) Figure S2 shows the relaxation plots of two representative samples, namely 1-arm PGPE sample (Entry IV, Figure S2a) and 2-arm PGPE (Entry 3, Figure S2b). In these plots, solid circles represent the segmental relaxation and empty triangles the normal mode relaxation.

As stated in the main manuscript, both relaxations were fitted following the Williams-Landel-Ferry (WLF) equation:
The WLF equation is mathematically equivalent to the Vogel-Tamman-Fulcher (VFT) equation.\textsuperscript{2, 3} The VFT equation was used already by us to describe the segmental relaxation of PGPE in a previous work,\textsuperscript{4} and can be written as:

\[ \tau = \tau_0 \exp\left[\frac{D \cdot T_0}{T - T_0}\right] \]  

Eq. S2

where \( \tau \) is the relaxation time evaluated at the maximum of the relaxation peak, \( \tau_0 \) is a pre-exponential factor, \( D \) a parameter related with the dynamic fragility of the polymer, and \( T_0 \) the so-called Vogel temperature. Considering that equations S1 and S2 are equivalent, it is possible to find a relation among their parameters. Briefly, taken \( T_{\text{ref}} = T_g \), Eq. S1 can be written as:

\[ \tau = \tau_s(T_g) \exp\left[-\frac{C_1 \cdot (T - T_g + C_2) - C_1 C_2}{C_2 + T - T_g}\right] \]

or

\[ \ln \tau = \ln \tau_s(T_g) - C_1 + \frac{C_1 C_2}{C_2 + T - T_g} \]  

Eq. S3

Comparing eq S1 and S3, we get:

\[ C_1 = \ln \left[\frac{\tau_s(T_g)}{\tau_0}\right] \]

\[ C_2 = T_g - T_0 = \frac{T_g}{C_1 D + 1} \]

Then, taking the relaxation time at \( T_g, \tau_s(T_g) = 100 \text{ s} \), and knowing \( \tau_0 = 10^{-14} \text{ s} \) from our previous work,\textsuperscript{4} we find \( C_1 = 36.84 \). Considering this value, and taking and \( D = 6.1, \textsuperscript{4} \) we obtain \( C_2 = 0.1421 \cdot T_g \). Substituting these values in eq 1, the WLF equation used to fit the temperature dependence of the segmental relaxation in this work was:

\[ \tau_\alpha = 10^2 \text{ s} \exp\left[-\frac{36.84 \cdot (T - T_{g\cdot \text{BDS}})}{T - 0.86 T_{g\cdot \text{BDS}}}\right] \]  

Eq. S4

Please beware that under this approximation, the only free fitting parameter is the dynamic glass transition temperature \( T_{g\cdot \text{BDS}} \).
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Figure S2. Relaxation plot for (a) 1-arm PGPE sample ($M_n = 13.6$ kg/mol) synthesized with tetrabutylammonium azide (Entry IV), and (b) 2-arm PGPE sample ($M_n = 5.4$ kg/mol) synthesized with $i$-Bu$_4$P$_4$/ethylene glycol in the absence of $i$-Bu$_3$Al (Entry 3). Empty triangles represent the normal mode relaxation and solid circles the segmental relaxation. Continuous lines are the fits of the WLF equation to the normal mode and segmental relaxation.

Table S3. Fitting parameters of Eqs. S1 and S4 for 1-arm PGPE and 2-arm PGPE samples. Here, $C_1$ and $C_2$ refer exclusively to those found for the NM relaxation.

| Sample         | $M_n$ (kg/mol) | $T_{g-BDS} \pm 1$ (K) | $C_1$ | $C_2$ (K) | $\tau_{NM}(T_{g-BDS})$ (s) |
|----------------|----------------|-----------------------|-------|-----------|-----------------------------|
| 1-arm (Entry IV) | 13.6           | 280                   | 30.0 ± 0.1 | 34.8 ± 0.7 | 25120                       |
| 2-arms (Entry 3)  | 5.4            | 277                   | 30.0   | 34.8      | 1100                        |

The normal mode relaxation was fitted using eq. S1. The corresponding WLF parameters were found by fitting the data of a representative 1-arm PGPE sample (Figure S2, Table S3), fixing $T_{REF} = T_{g-BDS}$. We applied the found $C_1$ and $C_2$ NM parameters to every other sample presented in this work. For example, in Figure S2 and Table S3, we present the results for a 2-arm PGPE sample, showing good agreement.

In the main manuscript, Table 2 summarizes the results obtained for the investigated PGPE samples of this work. Table S4, shown below, presents the results found for 1-arm PGPE samples.\(^1\)
Table S4. Relaxation time of the NM at the dynamic glass transition temperature

| Entry (1-arm) | \( T_{g-BDS} \pm 0.5 \) (K) | \( \tau_{NM}(T_{g-BDS}) \) (s) | \( \tau_{NM}(T_{g-BDS})/M_n^2 \) (s/kg^2mol^-2) |
|---------------|-----------------------------|-----------------------------|----------------------------------|
| I             | 273.0                       | 2820                        | 147                              |
| II            | 276.0                       | 3160                        | 103                              |
| III           | 277.0                       | 7940                        | 144                              |
| IV            | 279.0                       | 25100                       | 136                              |
| V             | 280.0                       | 79400                       | 177                              |

5. About the applicability of the Rouse model

In the main manuscript, we analyzed the NM relaxation peak using a sum of Cole-Cole functions that resembled the Rouse model expectation (eq 5 in the manuscript). We made emphasis that this equation is not the exact application of the Rouse model but in the case when \( b_{NM} = 1 \). We found that for our samples, the best fit was obtained with a \( b_{NM} = 0.80 \). In the following lines, we clarify how the description of the NM relaxation peak using a Cole-Cole function with a shape parameter value \( b_{NM} = 0.8 \) approximates quite well to a situation where there exists a set of chains each one described by the Rouse model. The different Rouse modes components decay with exponential functions, but having distinct Rouse times \( (\tau_R) \) following a log-Gaussian distribution function around a center value \( (\tau_1) \).

The orientational correlation function \( C(n,t;m) \) for a Rouse chain can be written as:\(^5\)

\[
C(n, t; m) \propto \frac{2}{N} \sum_{p \geq 1} \sin \frac{p \pi n}{N} \sin \frac{p \pi m}{N} \exp \left[ -\frac{p^2 t}{\tau_R} \right]
\]

Eq. S5

where \( N \) is the number of segments composing the polymer chain, and \( p \) the mode number. This function represents an orientation correlation of the \( n \)th and \( m \)th bond vectors at two separate times, and thus contains the information of the global chain motion.

The dielectric relaxation function for a melt of linear and monodispersed Rouse chains without dipole inversion can be calculated as:
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\[ \Phi(t) \propto \int_0^N dn \int_0^N dm \, c(n,t;m) \propto \sum_{p=\text{odd} \geq 1} \frac{8}{p^2 \pi^2} \exp \left[ - \frac{p^2 t}{\tau_R} \right] \quad \text{Eq. S6} \]

Now, if we consider a set of chains having different values of \((\tau_R)\) (certain polydispersity), but each one of them following the Rouse model, eq S6 transforms to:

\[ \Phi(t) \propto \sum_{p=\text{odd} \geq 1} \frac{8}{p^2 \pi^2} \phi_p(t), \quad \text{Eq. S7} \]

where \( \phi_p(t) = \int_0^\infty \exp \left[ - \frac{p^2 t}{\tau_R} \right] g(\tau_R) d\tau_R \)

Here \( g(\tau_R) \) is the Rouse time’s distribution function. The monodisperse case corresponds to \( g(\tau_R) \) equal to the Dirac’s delta distribution function, which allows recovering equation S6. In the frequency domain, \( \phi_p(t) \) in eq S7 becomes:

\[ \phi_p(\omega) \propto \int_0^\infty \frac{1}{1 + i\omega \tau_R/p^2} g(\tau_R) d\tau_R \quad \text{Eq. S8} \]

It is found that when \( g(\tau_R) \) is a log-Gaussian distribution function eq. S8 can be well approximated to a Cole-Cole function. So, we can write eq. S8 as:

\[ \phi_p(\omega) \propto \frac{1}{1 + (i\omega \tau_R/p^2)^b} \quad \text{Eq. S9} \]

Using this approach, eq. 5 of the main manuscript is suitable for describing the NM relaxation of polymers with chain dynamics following the Rouse model. Figure S3 shows how good is this agreement in the case of a log-Gaussian distribution function with a \( \sigma_{\log_{10}\tau_R} = 0.45 \), which implies \( b = 0.80 \), that we found by fitting the experimental data. Interestingly, if the log-normal distribution of molecular weights is assumed (as detailed in the equations 5-8 in ref 6), the corresponding polydispersity (D) will be 1.05, similar to that of the samples here considered.
Figure S3. Dielectric losses corresponding to a log-Gaussian distribution function (points) and Cole-Cole fit (continuous line). The distribution function had a $\sigma_{\log_{10} \tau_R} = 0.45$, resulting in a Cole-Cole shape parameter $b = 0.80$.

In an equivalent way, the dielectric relaxation function for a melt of linear and monodispersed Rouse chains with symmetric dipole inversion can be calculated as:

$$
\Phi(t) \propto \left\{ \int_0^{N/2} dn - \int_{N/2}^N dn \right\} \left\{ \int_0^{N/2} dm - \int_{N/2}^N dm \right\} C(n, t; m)
$$

Eq. S10

$$
\Phi(t) \propto \sum_{p=odd \geq 1} \frac{8}{p^2 \pi^2} \exp \left[ -\frac{p^2 t}{\tau_R/4} \right]
$$

For a polydisperse set of chains:

$$
\Phi(t) \propto \sum_{p=odd \geq 1} \frac{8}{p^2 \pi^2} \phi_p(t),
$$

Eq. S11

where $\phi_p(t) = \int_0^\infty \exp \left[ -\frac{p^2 t}{\tau_R/4} \right] g(\tau_R)d\tau_R$

In frequency domain, we get:

$$
\phi_p(\omega) \propto \int_0^\infty \frac{1}{1 + i\omega\tau_R/4p^2} g(\tau_R)d\tau_R
$$

Eq. S12

which in the case of a log-Gaussian distribution can be well approximated to:

$$
\phi_p(\omega) \propto \frac{1}{1 + (i\omega\tau_R/4p^2)^b}
$$

Eq. S13
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Again, we found that using this approach eq. 5 in the main manuscript is suitable for describing the NM relaxation of symmetrically dipole-inverted Rouse linear chains.

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