## Supplementary Information: Chain dynamics in polyisoprene stars with arms linked by dynamic covalent bonds to the central core

Beatriz Robles-Hernández<sup>\*a,b</sup>, Nikolaos Patelis<sup>c</sup>, Arantxa Arbe<sup>b</sup>, Konstantinos Ntetsikas<sup>c</sup>, Saibal Bhaumik<sup>c</sup>, Nikos Hadjichristidis<sup>\*c</sup>, Ángel Alegría<sup>a,b</sup>, and Juan Colmenero<sup>b,d</sup>

 <sup>a</sup> Departamento de Polímeros y Materiales Avanzados: Física, Química y Tecnología (UPV/EHU), 20018 San Sebastián, Spain.
 <sup>b</sup> Centro de Física de Materiales (CFM-MPC), CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, E-20018 Donostia San Sebastián, Spain.
 <sup>c</sup> Polymer Synthesis Laboratory, Chemistry Program, KAUST Catalysis Center, Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), 23955 Thuwal, Saudi Arabia.
 <sup>d</sup> Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, E-20018 San Sebastián, Spain.

e-mails: beatriz.robles@ehu.eus, Nikolaos.Hadjichristidis@kaust.edu.sa

### S.1 Materials

sec-Butyllithium (s-BuLi, 1.4 M in cyclohexane, Sigma-Aldrich) was used as the initiator. It was purified by filtration through a glass filter (Synthware 60 mL, fine) under vacuum, then diluted to the desired concentration in purified benzene using custom-made glass apparatuses and high vacuum techniques.<sup>1</sup> Methanol (MeOH, 99%, Sigma-Aldrich), the terminating agent, and methyltrichlorosilane (CH<sub>3</sub>SiCl<sub>3</sub>, Sigma-Aldrich, 99%), the linking agent, were treated with calcium hydride (CaH<sub>2</sub>, 95%, Sigma-Aldrich) overnight and subsequently distilled into glass ampoules. The dry methyltrichlorosilane was further diluted in the desired concentration with purified benzene. Benzene (99.8%, Sigma-Aldrich) and toluene (99.8%, Sigma-Aldrich) were dried over CaH<sub>2</sub> overnight, followed by distillation into calibrated roundbottom flasks containing n-butyllithium (n-BuLi, 1.6 M in hexanes, Sigma-Aldrich) and styrene. The orange color confirmed the high purity of the solvents. Tetrahydrofuran (THF, 99%, Sigma-Aldrich) was purified in a three-step process: first, it was refluxed over metallic sodium under an argon atmosphere for several hours, followed by treatment with CaH<sub>2</sub> for 24 hours under vacuum, and finally, distilled into a calibrated round-bottom flask containing a potassium/sodium alloy (3:1 by mass). The bright, deep blue color confirmed the high purity of the THF. Ethylene oxide (99.5%, Sigma-Aldrich) was dried under vacuum over CaH<sub>2</sub> and *n*-BuLi at 0 °C, then distilled into glass ampules and stored at -20 °C. Isoprene (Sigma-Aldrich, 99%) was dried over CaH<sub>2</sub> (Sigma-Aldrich, 95%) overnight. Afterward, it was distilled into a flask with *n*-BuLi (twice), and left to react at -5 °C for 30 minutes each time. Tris(2-aminoethyl)amine (TAEA, 97%, thermo scientific), tert-butyl acetoacetate (TBAA, 98%, Sigma-Aldrich), and aniline (99%, Acros Organics) were stored in a glove box under an argon atmosphere and used as received. The antioxidant 2,6-di-tert-butyl-4-methylphenol (Sigma-Aldrich) (BHT) was used as received.

#### S.2 Instrumentation

Size exclusion chromatography (SEC) analysis and dispersity ( $D = M_w/M_n$ ) estimation of the samples was performed in a Malvern GPCmax VE2001 system equipped with a refractive index detector, an isocratic pump, and Styragel HR2, HR4, HR5 columns in series (300 mm × 8 mm). Tetrahydrofuran (THF) was served as the eluent with a flow rate of 1 mL/min at 35 °C. The system was calibrated with polyisoprene standards. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy measurements in solution were conducted in a Bruker ADVANCE III 500 MHz spectrometer at room temperature (25 °C). All the samples were diluted in chloroform-*d* (CDCl<sub>3</sub>) before the measurements. The chemical structure of all the samples and the number-average molecular weight ( $M_n$ ) of the precursors ( $\omega$ -hydroxy functionalized polyisoprenes (PI-OH),  $\omega$ -functionalized acetoacetate polyisoprenes (PI-AcAc)) were determined by their respective spectra. Tetramethylsilane (TMS) was used as a reference for the samples' chemical shifts ( $\delta$ ). Fourier-transform infrared (FT-IR) spectra were collected using a Thermo Scientific Nicolet instrument in ATR mode. Acetone was used to clean and dry the crystal surface before measurement. 160 scans were recorded for each sample and background, ranging from 4000 to 550 cm<sup>-1</sup>.

#### S.3 Synthetic methods

Synthesis of  $\omega$ -hydroxy functionalized polyisoprenes Three well-defined  $\omega$ -hydroxy functionalized polyisoprenes, with molecular weights 2, 5, and 11 kg/mol, labeled as PI<sub>2k</sub>-OH, PI<sub>5k</sub>-OH, and PI<sub>11k</sub>-OH respectively, were synthesized via anionic polymerization. The polymerizations were carried out in custom-made glass apparatuses using high vacuum and glass-blowing techniques.<sup>1–4</sup> All the  $\omega$ -hydroxy functionalized polyisoprenes were synthesized similarly to the following procedure. Isoprene (11 g, 0.16 mol) was dissolved in approximately 200 mL of benzene. Then, *sec*-butyllithium (*s*-BuLi, 2.2 mmol) was added as the initiator, and the polymerization was allowed to proceed at room temperature for 24 hours to ensure completion. Afterward, ethylene oxide (~ 1 mL, 20 mmol) was added, and after 12 hours, the

reaction was quenched with degassed methanol. The resulting PI-OH was precipitated into cold methanol and dried under a dynamic vacuum at 30 °C overnight. The  $M_n$  of all the samples and their microstructure were determined by <sup>1</sup>H NMR. The dispersity (D < 1.06) was estimated by SEC.

Synthesis of  $\omega$ -acetoacetate functionalized polyisoprenes In a dry 100 mL Schlenk round-bottom flask equipped with a Teflon stirrer, PI<sub>5k</sub>-OH (5 g, 0.97 mmol) was dissolved in approximately 30 mL of dry toluene under vacuum. The solution was heated at 75 °C for 20 min under stirring, then condensed. This procedure was repeated two additional times to remove any traces of water. The sample was then dried overnight under a dynamic vacuum. Following this, 40 mL of purified THF was distilled into the flask containing the PI<sub>5k</sub>-OH. *Tert*-butyl acetoacetate (9.7 mmol) was added to the solution, and the reaction was allowed to proceed under vacuum for 4 days at 65 °C. The progress of the acetoacetylation of the  $\omega$ -hydroxyl group was monitored by <sup>1</sup>H NMR. Afterward, the resulting  $\omega$ -acetoacetate functionalized polyisoprene (PI<sub>5k</sub>-AcAc) was precipitated into methanol. For further purification, the collected PI<sub>5k</sub>-AcAc was dissolved in 30 mL of fresh dry toluene and stirred for 20 min at 75 °C. Subsequently, the toluene was removed under vacuum, and the remaining PI<sub>5k</sub>-AcAc was dried overnight at 35 °C. This purification step was repeated to ensure the removal of any unreacted reagents and byproducts. The remaining samples (PI<sub>2k</sub>-AcAc, PI<sub>11k</sub>-AcAc) were functionalized using the same procedure and stored under vacuum at -20 °C.

Synthesis of vinylogous urethane 3-arm star PI Three 3-arm star PI, labeled as  $d-(PI_{2k})_3$ ,  $d-(PI_{5k})_3$ , and  $d-(PI_{11k})_3$ , were synthesized through vinylogous urethane chemistry. The preparation of the samples proceeded as follows. Dry  $PI_{5k}$ -AcAc (200 mg, 0.039 mmol) and TAEA (0.0133 mmol, 1.99  $\mu$ L) were added into a dry Schlenk tube equipped with a Teflon stirrer, under an argon atmosphere. The mixture was frozen, degassed, and diluted with a few mL of purified benzene, then allowed to react for 2 h under static vacuum at r.t. Afterward, the benzene was evaporated, and the reaction continued under dynamic vacuum at r.t for 5 days. The formation of the 3-arm star was monitored via <sup>1</sup>H NMR, SEC, and FT-IR measurements. Upon completion of the reaction, the samples were stored under vacuum at -20 °C.

Associative transamination reaction of 3-arm star PI The dynamic associative bonding exchange of the 3-arm star PI was evaluated through the reaction of  $d-(PI_{2k})_3$  (40 mg, ~ 0.02 mmol of DCBs) with a fivefold excess of aniline (0.1 mmol), based on the number of the DCBs in the 3-arm star PI. The reaction was performed at room temperature for 24 h in 1 mL of THF, followed by heating at 130 °C for 120 minutes. Subsequently, the THF was evaporated, and the sample was washed sequentially with MeOH and DMF to remove the excess aniline and the produced free TAEA, then dried under vacuum at 35 °C overnight. The dynamic nature of the system was confirmed by monitoring changes in molecular weight, as recorded by SEC.

Synthesis of 3-arm star PI through static covalent bonds Anionic polymerization, high vacuum techniques, and a chlorosilane coupling reaction were employed to synthesize a 3-arm star PI with  $M_n$  (PI-arm) of approximately 6 kg/mol. The synthesis proceeded as follows: 5.34 g of isoprene (Is, 78.3 mmol) was diluted in around 100 mL of benzene, followed by the addition of *sec*-BuLi (0.86 mmol). The reaction was allowed to proceed for 24 h at room temperature. At this point, an aliquot was extracted and terminated with methanol, and the  $M_n$  of the PI arm was estimated by SEC (calibrated with PI standards). Subsequently, 0.272 mmol of the coupling agent methyltrichlorosilane (CH<sub>3</sub>SiCl<sub>3</sub>) was added to ensure 5% excess of living arms. The system was left to react for one month at room temperature while the progress of the coupling reaction was monitored by SEC analysis of weekly aliquots. The excess of the living PI was terminated with degassed methanol, and the mixture was precipitated in cold methanol containing a small amount of BHT and dried under vacuum at 35 °C. The purification of the 3-arm star PI from the excess of linear PI was collected, precipitated into cold methanol with BHT, dried under vacuum at 35 °C, and stored at -20 °C.

Sampla	$M_{\rm n}$ <sup>a</sup>		DP <sup>a</sup>	1,4 microstructure <sup>a</sup>	3,4 microstructure <sup><i>a</i></sup>	
Sample	(g/mol)	$D^{\circ}$	(PI)	(mol %)	(mol %)	
PI <sub>2k</sub> -OH	1850	1.06	26	89.7	10.3	
PI <sub>5k</sub> -OH	5200	1.03	74	92.2	7.8	
PI <sub>11k</sub> -OH	11200	1.02	163	92.4	7.6	
PI <sub>6k</sub> arm	6300	1.03	91	93.0	7.0	

Table S.1 Molecular characteristics of  $\omega$ -hydroxy functionalized PI (PI-OH) and the linear precursor of the (PI<sub>6k</sub>)<sub>3</sub>

<sup>*a*</sup> Determined by <sup>1</sup>H NMR spectroscopy (500 MHz, chloroform-*d*, 25 °C) except the  $M_n$  of the PI<sub>6k</sub> arm, which was determined from SEC (THF, 35 °C, calibrated with PI standards).

<sup>b</sup> Determined from SEC (THF, 35 °C, calibrated with PI standards).



Scheme S.1 General scheme of the synthesis of (a) PI-OH and (b) 3-arm star PI via static covalent bonds.

**Table S.2** Molecular characteristics of  $\omega$ -acetoacetate functionalized polyisoprenes (PI-AcAc)

Sample	$M_{\rm n}^{\ a}$ (g/mol)	$D^{b}$	DP <sup><i>a</i></sup> (PI)	1,4 microstructure <sup>a</sup> (mol %)	3,4 microstructure <sup><i>a</i></sup> (mol %)
PI <sub>2k</sub> -AcAc	1850	1.06	26	89.7	10.3
PI <sub>5k</sub> -AcAc	5200	1.03	74	92.2	7.8
PI <sub>11k</sub> -AcAc	11200	1.02	163	92.4	7.6

<sup>*a*</sup>  $M_n$ , DP and (1,4-, 1,2-) microstructure of polymers are similar to the PI-OH precursors depicted in Table S.1. <sup>*b*</sup> Determined from SEC (THF, 35 °C, calibrated with PI standards).



**Scheme S.2** General scheme of the acetoacetylation reaction between the  $\omega$ -hydroxy functionalized PI-OH and *t*-butyl acetoacetate, resulting in  $\omega$ -acetoacetate functionalized polyisoprene (PI-AcAc).



**Scheme S.3** Schematic representation of associative substitution reactions. (a) General mechanism, (b) Pl vinylogous urethane 3-arm star with aniline, in THF at 130 °C under vacuum.



**Scheme S.4** Schematic representation of the condensation reaction between PI-AcAc and tris(2-aminoethyl)amine (TAEA), under vacuum at room temperature, resulting in a 3-arm star PI d-(PI)<sub>3</sub>.



**Figure S.1** SEC traces of (a) PI-OH (2, 5, 11 kg/mol) and (b) the corresponding PI-AcAc (2, 5, 11 kg/mol) in THF at 35 °C, calibrated with PI standards.



**Figure S.2** SEC traces in THF at 35 °C of the arm  $Pl_{6k}$  aliquot (black) and the corresponding 3-arm star Pl (red)  $(Pl_{6k})_3$  with static covalent bonds, after fractionation.



**Figure S.3** Study of the dynamic associative behavior of the vinylogous urethane 3-arm star PI. SEC traces (in THF at 35 °C) of 3-arm star d-( $PI_{2k}$ )<sub>3</sub> (black trace) and d-( $PI_{2k}$ )<sub>3</sub> reacted with aniline at room temperature and at 130 °C (red trace).



Figure S.4  $^{1}$ H NMR spectra (500 MHz, CDCl<sub>3</sub>, DMSO, 25  $^{\circ}$ C) of (a) *tert*-butyl acetoacetate, (b) TAEA.



Figure S.5 <sup>1</sup>H NMR spectra (500 MHz,  $CDCI_3$ , 25 °C) of (a)  $PI_{2k}$ -OH, (b)  $PI_{5k}$ -OH and (c)  $PI_{11k}$ -OH.



Figure S.6 <sup>1</sup>H NMR spectra (500 MHz,  $CDCI_3$ , 25 °C) of (a)  $PI_{2k}$ -AcAc, and (b) d-( $PI_{2k}$ )<sub>3</sub>.



Figure S.7 <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>, 25  $^{\circ}$ C) of (a) Pl<sub>5k</sub>-AcAc and, (b) d-(Pl<sub>5k</sub>)<sub>3</sub>.



Figure S.8  $^1\text{H}$  NMR spectra (500 MHz, CDCl\_3, 25  $^\circ\text{C})$  of (a) Pl\_{11k}-AcAc and, (b) d-(Pl\_{11k})\_3.



Figure S.9  $^1\text{H}$  NMR spectra (500 MHz, CDCl3, 25  $^\circ\text{C})$  of the (Pl\_{6k})\_3.



Figure S.10 FT-IR spectra of the PI-OH 2, 5, and 11 kg/mol.



Figure S.11 FT-IR spectra of (a) *t*-butyl acetoacetate and (b)  $\omega$ -acetoacetate functionalized polyisoprenes (PI-AcAc).

# S.4 Dielectric characterization of linear PI and PI stars with static bonds

Figure S.12 shows the dielectric loss curves at several temperatures above  $T_g$  for the linear PI with  $M_n = 6$  kDa (hereafter, LPI<sub>6k</sub>). At the lowest represented temperature (210 K, blue symbols) only the  $\alpha$ -relaxation —besides a much weaker  $\beta$ -relaxation at higher frequencies— is detected, and as the temperature increases the normal mode enters the experimental window as a more intense peak at lower frequencies.



Figure S.12 Dielectric loss curves at several temperatures above  $T_{\rm g}$  for LPI<sub>6k</sub>.

The dielectric relaxation data of the linear PI has been described as a sum of two relaxation processes plus a power law term to account for the DC conductivity and other low-frequency effects:

$$\boldsymbol{\varepsilon}^{*}(\boldsymbol{\omega}) - \boldsymbol{\varepsilon}_{\infty} = \boldsymbol{\varepsilon}_{\mathrm{NM}}^{*}(\boldsymbol{\omega}) + \boldsymbol{\varepsilon}_{\alpha}^{*}(\boldsymbol{\omega}) - i\frac{\boldsymbol{\sigma}_{\mathrm{DC}}}{\boldsymbol{\omega}\boldsymbol{\varepsilon}_{0}}.$$
 (S.1)

The low-frequency mode was described using a Rouse-like description of the normal mode<sup>5</sup> as a superposition of Cole-Cole relaxation processes:  $^{6-9}$ 

$$\varepsilon_{\rm NM}^*(\omega) = \Delta \varepsilon_{\rm NM} \left(\sum_{k:\rm odd} \frac{1}{k^2}\right)^{-1} \sum_{k:\rm odd} \frac{1/k^2}{1 + (i\omega\tau_1/k^2)^{a_{\rm NM}}},\tag{S.2}$$

where  $\Delta \varepsilon_{\rm NM}$  is the dielectric strength of the normal mode,  $\tau_1$  is the relaxation time of the first mode and  $a_{\rm NM}$  is the symmetric broadening of the modes. This broadening corresponds to a distribution of relaxation times around the peak's maximum, accounting for the dispersity D of the samples. Contributions from  $k \ge 9$  did not affect the description of our data. Notice that the Rouse model is recovered when  $a_{\rm NM} = 1$  (superposition of Debye processes), and in that case  $\tau_1 = 2\tau_{\rm Rouse}$ , the slowest relaxation time.<sup>10</sup>

The  $\alpha$ -relaxation has been described using the Havriliak-Negami (HN) function, <sup>11,12</sup>

$$\varepsilon_{\alpha}^{*}(\omega) = \frac{\Delta \varepsilon_{\alpha}}{\left[1 + \left(i\omega\tau_{\alpha}\right)^{a_{\alpha}}\right]^{b_{\alpha}}},\tag{S.3}$$

where  $\Delta \varepsilon_{\alpha}$  is the dielectric strength of the  $\alpha$ -relaxation,  $\tau_{\alpha}$  is its HN time, and  $a_{\alpha}$  and  $b_{\alpha}$  are the symmetric and asymmetric broadening of the process, respectively. The condition  $0 < a_{\alpha} \leq 1$ ,  $a_{\alpha}b_{\alpha} < 1$  is satisfied.

The spectra of a PI-based 3-arm star with a statically bonded core and a  $M_n$  per arm of 6 kDa (hereafter,  $(PI_{6k})_3$ ) were also recorded. In this case, there is an excess of intensity at frequencies slightly above the NM peak maximum. This leads to a data description with three relaxation processes, similar to the analysis made for the DCB stars:

$$\boldsymbol{\varepsilon}^{*}(\boldsymbol{\omega}) - \boldsymbol{\varepsilon}_{\infty} = \boldsymbol{\varepsilon}_{\mathrm{NM}}^{*}(\boldsymbol{\omega}) + \boldsymbol{\varepsilon}_{\mathrm{mid}}^{*}(\boldsymbol{\omega}) + \boldsymbol{\varepsilon}_{\alpha}^{*}(\boldsymbol{\omega}) - i\frac{\boldsymbol{\sigma}_{\mathrm{DC}}}{\boldsymbol{\omega}\boldsymbol{\varepsilon}_{0}}, \tag{S.4}$$

where the mid-frequency relaxation has been described using a Cole-Cole function.

The fitting parameters obtained from the analysis of the data from the two samples using eqs. S.1 and S.4 are collected in Table S.3 for T = 250 K. As shown in Fig. S.13, the description of the data obtained from this analysis is very good.



Figure S.13 Dielectric permittivity of (a)  $LPI_{6k}$  and (b)  $(PI_{6k})_3$  at T = 250 K. Solid symbols account for  $\varepsilon'$  and open symbols for  $\varepsilon''$ . Solid lines are the description of the data using eqs. S.1 and S.4: black lines for the whole response; the resolved modes (just for  $\varepsilon''$ ) are also represented: normal mode (light green),  $\alpha$ -relaxation (yellow), and additional process for the  $(PI_{6k})_3$  sample (purple).

The frequency of the maximum of the dielectric losses is related to the HN relaxation time by <sup>13</sup>

$$f_{\max} = \frac{1}{2\pi\tau_{\alpha}} \left[ \sin\left(\frac{a_{\alpha}\pi}{2+2b_{\alpha}}\right) \right]^{1/a_{\alpha}} \left[ \sin\left(\frac{a_{\alpha}b_{\alpha}\pi}{2+2b_{\alpha}}\right) \right]^{-1/a_{\alpha}}.$$
 (S.5)

**Table S.3** Fitting parameters obtained at T = 250 K using eqs. S.1 and S.4 for the dielectric data description depicted in Fig. S.13

<i>α</i> -relaxation					Normal mode		
Sample	$\Delta \varepsilon_{lpha}$	$f_{\alpha}^{\max}$ (Hz)	$a_{\alpha}^{*}$	$b_{\alpha}^{*}$	$\Delta \epsilon_{ m NM}$	$f_{\rm NM}$ (Hz)	$a_{\rm NM}*$
LPI <sub>6k</sub>	0.076	259307	0.55	1	0.084	36	0.91
(PI <sub>6k</sub> ) <sub>3</sub>	0.094	176514	0.55	1	0.085	7.8	0.88

\* These parameters have been kept constant with temperature, as well as the ratio  $\Delta \varepsilon_{\alpha} / \Delta \varepsilon_{\rm NM}$  in the (PI<sub>6k</sub>)<sub>3</sub>.

The frequencies of the maximum of the relaxation peaks obtained from the analysis are represented in Fig. S.14 for both samples. The temperature dependence of the frequencies for all the processes was described using the Vogel-Fulcher-Tamman (VFT) law:<sup>14</sup>

$$f_{\max}(T) = f_{\infty} \exp\left(-\frac{DT_0}{T - T_0}\right),\tag{S.6}$$

with  $f_{\infty}$  a pre-exponential factor, *D* the fragility parameter, and  $T_0$  the Vogel temperature. Table S.4 collects the parameters used to describe the data. As can be observed, the description using similar values of  $f_{\infty}$  and *D* for relaxation processes with the same origin but corresponding to a different sample are very good.



**Figure S.14** Arrhenius plot of the frequencies of the maximum of the relaxation processes for  $LPI_{6k}$  (solid symbols) and  $(PI_{6k})_3$  (empty symbols). Lines are fits to the VFT law (Eq. S.6).

In Fig. S.15 we have represented the loss curves obtained in three previously investigated PI-based vitrimeric systems<sup>15</sup> along with that recorded for the  $d-(PI_{11k})_3$  at a temperature where the frequency of the maxima of the segmental relaxation is approximately the same for all the samples. As can be observed, the timescale of the DCB-related relaxation process is very similar for the stars and the vitrimers, despite the DCB chemistry not being the same: the vitrimers have imine bonds while the stars have vinylogous urethane bonds. Also, the dependence on the temperature of this relaxation process is very similar in both, PI-based vitrimers and star-shaped DCB stars. On the other hand, the slower relaxation detected in the vitrimers shows a distinct temperature dependence, consistent with that found in other dynamic covalent networks.

#### Table S.4 VFT fitting parameters

		LPI <sub>6</sub>	k	(PI <sub>6k</sub> ) <sub>3</sub>		
Mode	D	$\log(f_{\infty}(\text{Hz}))$	<i>T</i> <sub>0</sub> (K)	$\log(f_{\infty}(\mathrm{Hz}))$	<i>T</i> <sub>0</sub> (K)	
$\alpha$ -relaxation	7.8	12.4	167	12.4	168.8	
Normal mode	7.8	8.4	167	8.0	168.8	



**Figure S.15** Dielectric loss curves of  $d-(Pl_{11k})_3$  at 250 K and of three PI-based vitrimers of different molecular weight at 260 K.

#### References

- [1] N. Hadjichristidis, H. Iatrou, S. Pispas and M. Pitsikalis, *Journal of Polymer Science Part A: Polymer Chemistry*, 2000, **38**, 3211–3234.
- [2] K. Ntetsikas, V. Ladelta, S. Bhaumik and N. Hadjichristidis, ACS Polymers Au, 2023, 3, 158–181.
- [3] S. Bhaumik, K. Ntetsikas, N. Patelis, K. Peponaki, D. Vlassopoulos and N. Hadjichristidis, *Macro-molecules*, 2024, 57, 1751–1760.
- [4] S. Bhaumik, K. Ntetsikas and N. Hadjichristidis, *Macromolecules*, 2020, 53, 6682–6689.
- [5] P. E. Rouse, *The Journal of Chemical Physics*, 1953, **21**, 1272–1280.
- [6] S. Arrese-Igor, A. Alegría and J. Colmenero, *Physical Review Letters*, 2014, 113, 078302.
- [7] S. Arrese-Igor, A. Alegría and J. Colmenero, ACS Macro Letters, 2014, 3, 1215–1219.
- [8] T. Gambino, A. M. D. Ilarduya, A. Alegría and F. Barroso-Bujans, *Macromolecules*, 2016, 49, 1060– 1069.
- [9] J. Ochs, D. E. Martínez-Tong, A. Alegria and F. Barroso-Bujans, *Macromolecules*, 2019, 52, 2083–2092.

- [10] M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford: Oxford University Press, 2003.
- [11] S. Havriliak and S. Negami, *Journal of Polymer Science Part C: Polymer Symposium*, 1966, **14**, 99–117.
- [12] S. Havriliak and S. Negami, Polymer, 1967, 8, 161–210.
- [13] R. Diaz-Calleja, *Macromolecules*, 2000, **33**, 8924.
- [14] *Broadband Dielectric Spectroscopy*, ed. F. Kremer and A. Schönhals, Springer-Verlag Berlin Heidelberg, 2003.
- [15] A. Alegría, A. Arbe, J. Colmenero, S. Bhaumik, K. Ntetsikas and N. Hadjichristidis, *Macromolecules*, 2024, 57, 5639–5647.