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## **Electronic Supplementary Information: Mechanical relaxation of functionalized carbosilane dendrimer melts**

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This electronic supplementary information contains the details about the molecular dynamics simulations of melts of functionalized dendrimers considered in this study and about the method used for the calculation of their mechanical relaxation moduli.

The mechanical relaxation is studied by adapting the method used in Ref.<sup>1</sup> Here we recall it briefly and provide the information that specific for this study. This method allows overcoming the difficulty of covering a huge region of time scales inherent for the mechanical relaxation. The main feature of the method is the superposition of relaxation curves obtained for dynamical systems subjected to different internal frictions. The dynamics is studied by molecular dynamics simulations performed in the GROMACS package.<sup>2</sup> The dendrimers are modeled in the united atoms framework within Gromos53a6 force-field<sup>3</sup> and placed in the periodic boxes containing 27 macromolecules each. This force-field gives densities of carbosilane dendrimer melts that are very close to the experimental ones.<sup>4,5</sup> At the preliminary stage of equilibration of the systems, V-rescale thermostat of the GROMACS package was used, which was triggered every 0.1 ps, and Berendsen barostat at 1 atm and  $\tau_p = 1$  ps. The systems are maintained at the temperature of 600 K by means of the Langevin thermostat in the GROMACS package:

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = -\frac{m_i d\vec{r}_i}{\tau_T dt} + \vec{F}_i + \vec{w}_i,$$

where  $m_i$  and  $\vec{r}_i$  are the mass and the coordinate vector of *i*th atom,  $\vec{F}_i$  is the external force acting on the *i*th atom,  $1/\tau_T$  is the weighted friction constant [1/ps], and  $\vec{w}_i$  is a noise process with  $\langle w_i(t)w_j(t+s) \rangle = 2(m_i/\tau_T)k_BT\delta(s)\delta_{ij}$ . The Langevin thermostat has been used at different values of the coupling constant  $\tau_T = 0.005$ , 0.05, 0.5 ps in order to vary the friction in the systems. For the highest value of  $\tau_T$ , we have simulated ten replicas to have a better statistics at long times. Before using the final trajectories (of 600 ns for G2, 1000 ns for G3, 2000 ns for G4), the systems were equilibrated (in NPT ensemble with Berendsen barostat<sup>6</sup> with 1 atm and thermostat actuation each ps (i.e.  $\tau_p =$ 1 ps) during 50 ns for G2, 100 ns for G3, 600 ns for G4).

The dynamical modulus G(t) is calculated from the fluctuations of the stress tensor  $\hat{P} = (P_{\alpha\beta})_{7}$ 

$$G(t) = \frac{V}{30k_B T} \sum_{(\alpha\beta)} \left( 6 \left\langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \right\rangle + \left\langle N_{\alpha\beta}(t) N_{\alpha\beta}(0) \right\rangle \right)$$

Here *V* is the box volume, T is the temperature,  $k_B$  is the Boltzmann constant,  $N_{\alpha\beta} = P_{\alpha\alpha} - P_{\beta\beta}$ , and the sum runs over components ( $\alpha\beta$ ) = xy, yz, zx of the stress tensor

$$\hat{P} = \frac{1}{V} \left( \sum_{i} m_{i} \vec{v}_{i} \otimes \vec{v}_{i} + \sum_{i < j} \vec{r}_{ij} \otimes \vec{F}_{ij} \right)$$

It is calculated in GROMACS based on the microscopic characteristics: the mass  $m_i$  and the velocity  $\vec{v}_i$  of the united atom group *i*, the force exerted  $\vec{F}_{ij}$  from the group *j* to *i* having the distance  $|\vec{r}_{ij}|$  between them. The resulting G(t) obtained for different values of the parameter  $\tau_T$  are superimposed based on the rotational relaxation autocorrelation function,

$$P_1^{rot}(t) = \langle \vec{u}(t) \cdot \vec{u}(0) \rangle$$

where  $\vec{u}(t)$  is the unit vector connecting two silicon atoms, one from the periphery and another one is the core. The exponential tail of the function  $P_1^{\text{rot}}(t)$  is characterized through the time  $\tau_{rot}$  (see Table S1). The  $P_1^{\text{rot}}(t)$  related to different  $\tau_T$  can be perfectly rescaled based on  $\tau_{rot}$ ; the same happens for G(t), see Figure S1. Also we provide the additional parameters of FD and CSD in Table S2.

**Table S1.** The rotational relaxation time,  $\tau_{rot}$ , for FD of various generations G for different values of the parameter  $\tau_T$  characterizing the Langevin thermostat (in ps of GROMACS package).

System	$\tau_T = 0.005 \text{ ps}$	$ au_T = 0.05  ext{ ps}$	$ au_T = 0.5  ext{ ps}$
G2	40.528 ns	4.335 ns	0.685 ns
G3	140.622 ns	17.234 ns	2.560 ns
G4	483.914 ns	55.400 ns	8.033 ns

**Table S2.** The molecular weight, M, the radius of gyration,  $R_g$ , and density in the simulation cell for FD and CSD.

System	Density, g/cm <sup>3</sup>		M, g/mol		$R_{g}$ , nm		$D*10^{10}, m^2/s$	
	FD	CSD	FD	CSD	FD	CSD	FD	CSD
G2	0.634	0.669	2131.604	1964.288	0.874	0.872	1.70	1.70
G3	0.634	0.694	4746.252	4241.280	1.141	1.118	0.50	0.54
G4	0.641	0.667	9973.832	8763.008	1.441	1.394	0.18	0.14



**Figure S1.** (a)-(c) Normalized shear-stress relaxation modulus  $[G(t)] \equiv G(t)/G(0)$  for a melt of FD (G2, G3, and G4, respectively), calculated from simulations employing the Langevin thermostat with different values of the parameter  $\tau_T$ . The curves are rescaled with  $\tau_{rot}$  (Table S1) that are obtained from (d) the rotational autocorrelation function  $P_1^{\text{rot}}(t)$ .

## References

- 1 M. Dolgushev, D. A. Markelov and E. Lähderanta, Linear Viscoelasticity of Carbosilane Dendrimer Melts, *Macromolecules*, 2019, **52**, 2542–2547.
- 2 M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess and E. Lindahl, GROMACS: High performance molecular simulations through multi-level parallelism from laptops to supercomputers, *SoftwareX*, 2015, **1**–**2**, 19–25.
- 3 C. Oostenbrink, A. Villa, A. E. Mark and W. F. Van Gunsteren, A biomolecular force field based on the free enthalpy of hydration and solvation: The GROMOS force-field parameter sets 53A5 and 53A6, *J. Comput. Chem.*, 2004, **25**, 1656–1676.

- 4 N. K. Balabaev, M. A. Mazo and E. Y. Kramarenko, Insight into the Structure of Polybutylcarbosilane Dendrimer Melts via Extensive Molecular Dynamics Simulations, *Macromolecules*, 2017, **50**, 432–445.
- 5 A. N. Shishkin, D. A. Markelov and V. V. Matveev, Molecular dynamics simulation of poly(butyl)carbosilane dendrimer melts at 600 K, *Russ. Chem. Bull.*, 2016, **65**, 67–74.
- 6 H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola and J. R. Haak, Molecular dynamics with coupling to an external bath, *J. Chem. Phys.*, 1984, **81**, 3684–3690.
- J. Ramírez, S. K. Sukumaran, B. Vorselaars and A. E. Likhtman, Efficient on the fly calculation of time correlation functions in computer simulations, *J. Chem. Phys.*, 2010, **133**, 154103.