## Dielectric study on the well-resolved sub-Rouse and JG $\beta$ -relaxations of poly(methylphenylsiloxane) at ambient and elevated pressures

Wenkang Tu,<sup>1,2</sup>\* K. L. Ngai,<sup>3,4</sup>, Marian Paluch,<sup>1,2</sup> and Karolina Adrjanowicz<sup>1,2</sup>\*

<sup>1</sup> Institute of Physics, University of Silesia, 75 Pulku Piechoty 1, 41-500 Chorzow, Poland

<sup>2</sup> Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1a,

41-500 Chorzow, Poland

<sup>3</sup> State Key Lab of Metastable Materials Science and Technology, and College of Materials Science and Engineering, Yanshan University, Qinhuangdao, Hebei 066004 China

<sup>4</sup> CNR-IPCF, Largo B. Pontecorvo 3, I-56127, Pisa, Italy

\* Corresponding authors: Wenkang Tu (<u>wenkang.tu@smcebi.edu.pl</u>), Karolina Adrjanowicz (<u>kadrjano@us.edu.pl</u>)



Figure S1 Temperature (a) and pressure (b) dependences of structural relaxation times obtained during isobaric and isothermal measurements for PMPS 2.5k. Solid lines in panels (a) and (b) represent the fits to the VFT equation and its pressure counterpart. Panel (c) reveals the pressure dependence of the glass transition temperatures. The dashed line represents the fit to the Andersson and Andersson equation<sup>1</sup>. The red solid point marks the  $T_g$  value at a pressure of 250 MPa.



Figure S2 (a) Pressure dependences of structural relaxation times obtained during isothermal measurements for PMPS 27.8k. Solid lines represent the fits to the pressure counterpart of the VFT equation. Panel (b) reveals the fit to the Andersson and Andersson equation. Blue solid circle marks the  $T_g$  value at a pressure of 250 MPa.



Figure S3. The wine symbols are the relaxation times of the Rouse mode and the  $\alpha$ -relaxation determined by rheology for PMPS with  $M_w$ = 29.6 kg/mol from Alexandris et al.<sup>2</sup> The dashed lines represent the fits in terms of the VFT equation. The cyan symbols are the relaxation times of the sub-Rouse mode and the  $\alpha$ -relaxation determined by PCS for PMPS with  $M_w$ = 28.5 kg/mol.<sup>3</sup> The blue symbols are the relaxation times of the sub-Rouse mode, the  $\alpha$ -relaxation, and the  $\beta$ -relaxation of PMPS with  $M_w$ = 27.8 kg/mol. The magenta symbols are the relaxation times of the sub-Rouse mode, the  $\alpha$ -relaxation, and the  $\beta$ -relaxation of PMPS with  $M_w$ = 27.8 kg/mol confined in 20 nm AAO pore.<sup>4</sup>



Figure S4 Pressure dependences of the dielectric strengths,  $\Delta \varepsilon_{\alpha}$ ,  $\Delta \varepsilon_{\alpha'}$ , and  $\Delta \varepsilon_{\beta}$  determined for the samples of (a) PMPS 2.5k at *T*= 283 K and (b) PMPS 27.8k at *T*= 303 K during isothermal measurements.

## **References:**

- Andersson, S. P.; Andersson, O. Relaxation Studies of Poly(Propylene Glycol) under High Pressure. *Macromolecules* 1998, *31* (9), 2999–3006. https://doi.org/10.1021/ma971282z.
- (2) Alexandris, S.; Papadopoulos, P.; Sakellariou, G.; Steinhart, M.; Butt, H. J.; Floudas, G. Interfacial Energy and Glass Temperature of Polymers Confined to Nanoporous Alumina. *Macromolecules* 2016, 49 (19), 7400–7414. https://doi.org/10.1021/acs.macromol.6b01484.
- (3) Boese, D.; Momper, B.; Meier, G.; Kremer, F.; Hagenah, J.-U.; Fischer, E. W. Molecular Dynamics in Poly(Methylphenylsiloxane) As Studied by Dielectric Relaxation Spectroscopy and Quasielastic Light Scattering. *Macromolecules* 1989, 22, 4416–4421. https://doi.org/10.1021/ma00202a005.
- (4) Adrjanowicz, K.; Winkler, R.; Chat, K.; Duarte, D. M.; Tu, W.; Unni, A. B.; Paluch, M.; Ngai, K. L. Study of Increasing Pressure and Nanopore Confinement Effect on the Segmental, Chain, and Secondary Dynamics of Poly(Methylphenylsiloxane). *Macromolecules* 2019, 52 (10), 3763–3774. https://doi.org/10.1021/acs.macromol.9b00473.