

# Supporting Information

## Viscoelastic Response of Double Hydrophilic Block

## Copolymers for Drug Delivery Applications

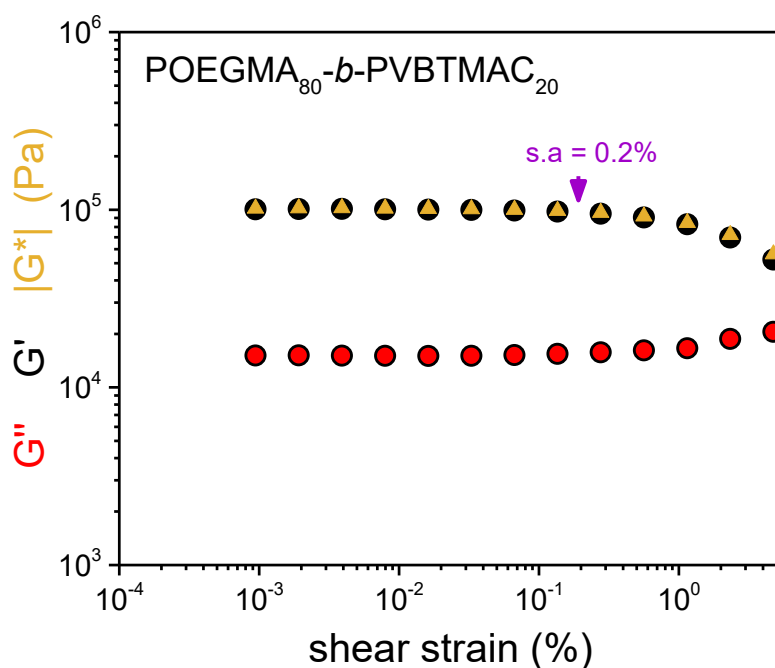
*Achilleas Pipertzis,<sup>1\*</sup> Angeliki Chroni,<sup>2</sup> Stergios Pispas,<sup>2</sup> Jan Swenson<sup>1</sup>*

*<sup>1</sup>Department of Physics, Chalmers University of Technology, 41296, Gothenburg, Sweden*

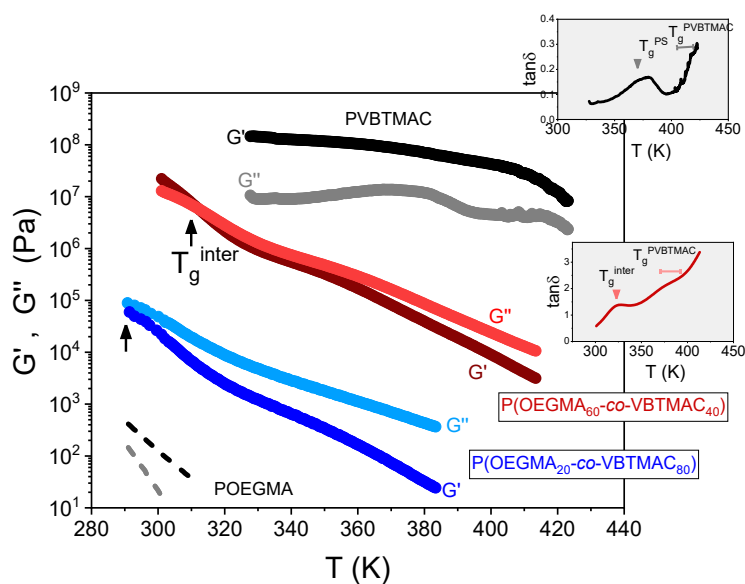
*<sup>2</sup>Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos  
Constantinou Ave., 11635 Athens.*

Correspondence: Achilleas Pipertzis

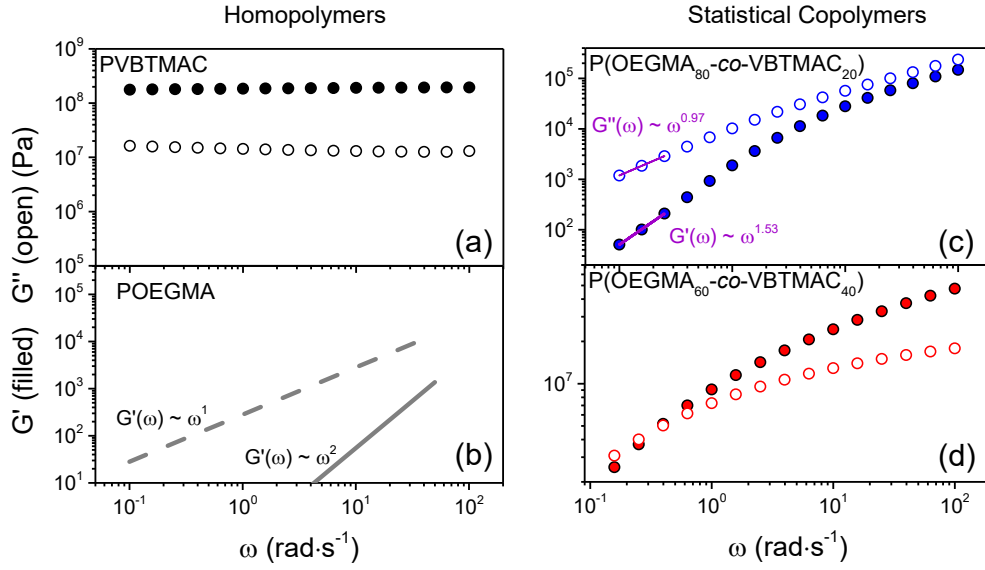
Email: [achilleas.pipertzis@chalmers.se](mailto:achilleas.pipertzis@chalmers.se)



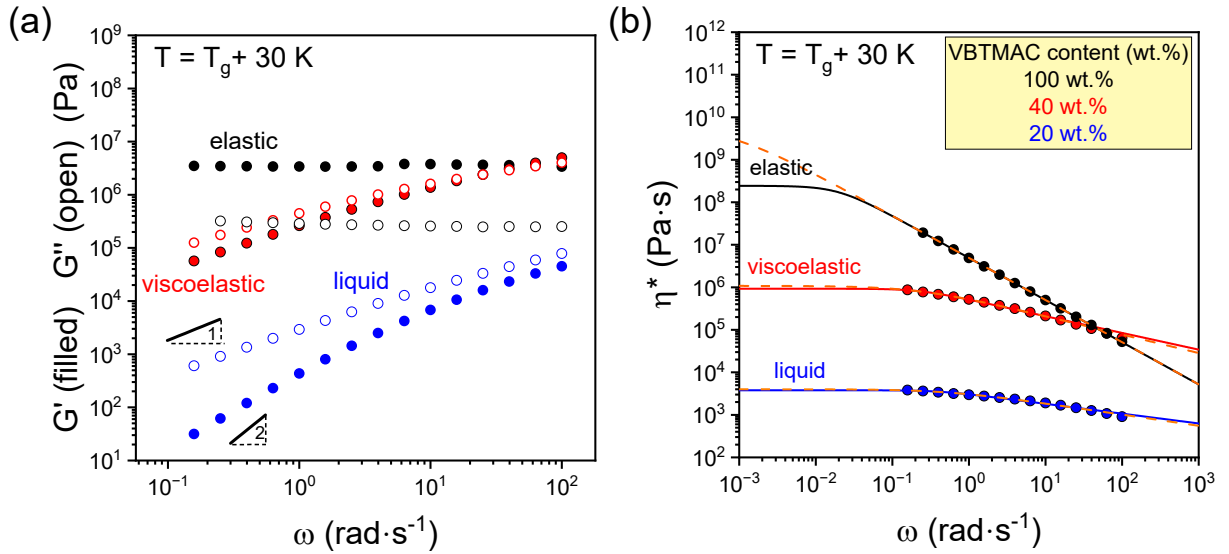
**Figure S1.** Absolute value of the shear storage modulus as a function of the shear strain amplitude presented on a log-log scale. The vertical arrow shows the used strain amplitude into the linear viscoelastic regime.



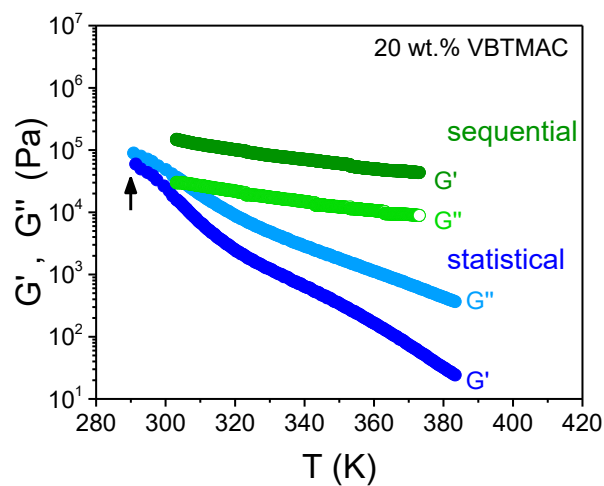
**Figure S2.** Temperature dependence of the storage and loss shear moduli for the PVBTMAC homopolymer (black symbols), P(OEGMA<sub>60</sub>-co-VBTMAC<sub>40</sub>) (red symbols) and P(OEGMA<sub>80</sub>-co-VBTMAC<sub>20</sub>) (blue symbols) upon heating with a rate of 5 K·min<sup>-1</sup>. **(Insets)** Loss factor as a function of temperature. The vertical arrows and horizontal lines indicate the interfacial and PVBTMAC glass transition temperatures, respectively.



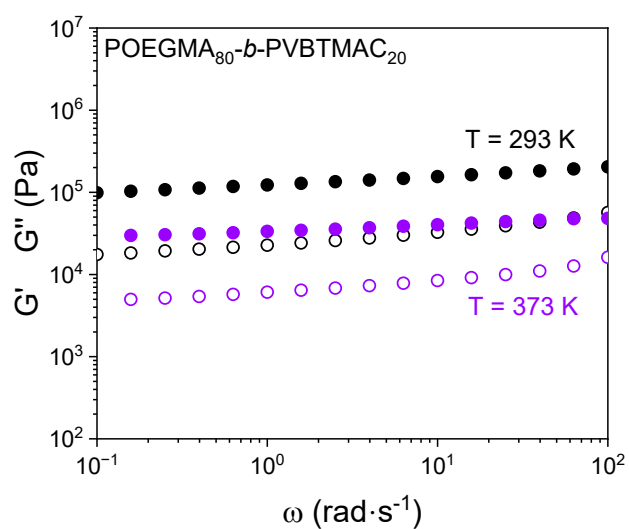
**Figure S3.** Angular frequency dependence of the storage (filled symbols or solid lines) and loss (open symbols or dashed lines) shear moduli for (a) PVBTMAC, (b) POEGMA, (c) P(OEGMA<sub>80</sub>-co-VBTMAC<sub>20</sub>) and (d) P(OEGMA<sub>60</sub>-co-VBTMAC<sub>40</sub>), at a temperature of 293 K.



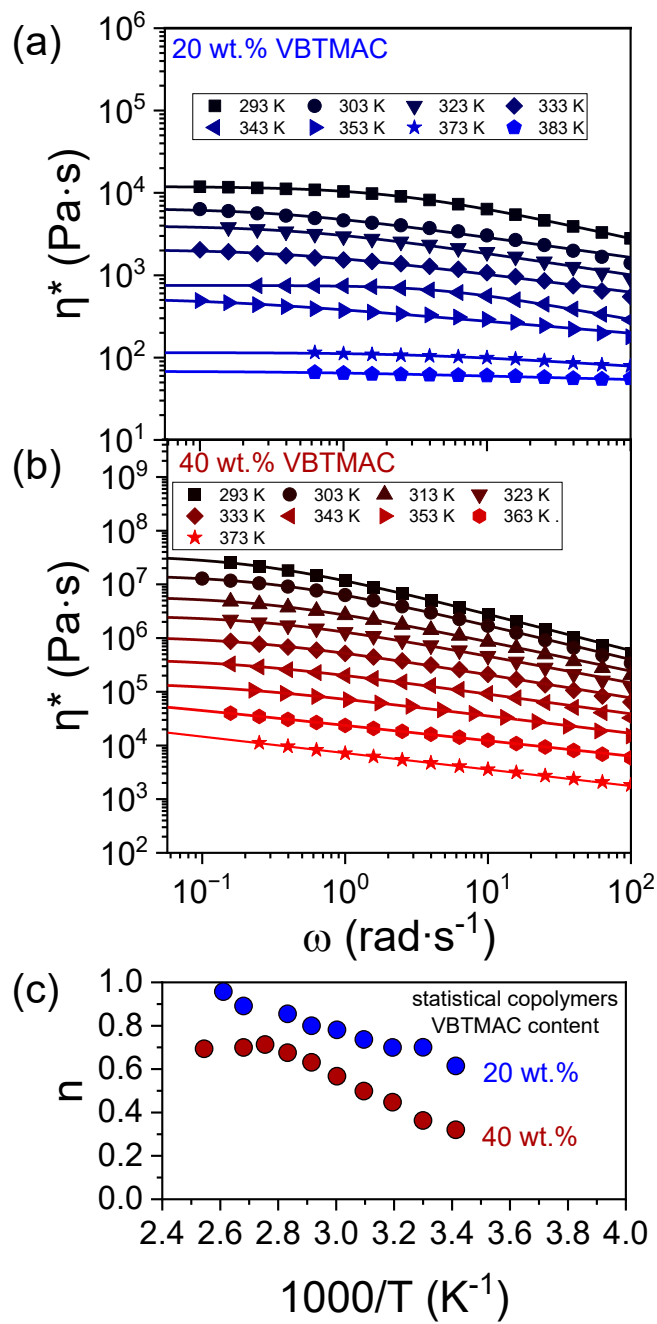
**Figure S4.** Angular frequency dependence of (a) the storage (filled symbols) and loss (open symbols) shear moduli and (b) complex viscosity of P(OEGMA<sub>80</sub>-co-VBTMAC<sub>20</sub>) (blue symbols), P(OEGMA<sub>60</sub>-co-VBTMAC<sub>40</sub>) (red symbols) and the PVBTMAC homopolymer (black symbols) at a temperature of 293 K. Lines with slopes 1 and 2 are also shown in (a). The solid and dashed lines in (b) represent fits by Eq. 1 and Eq. 2 of the main manuscript, respectively.



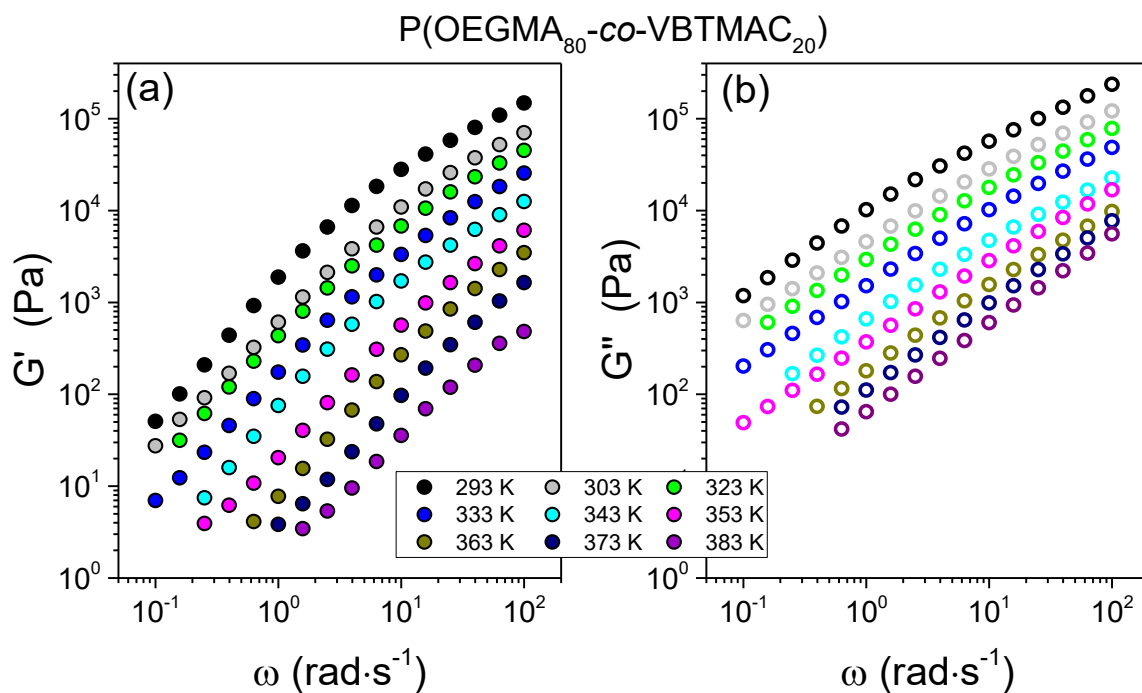
**Figure S5.** Temperature dependence of the storage (filled symbols) and loss (open symbols) shear moduli for P(OEGMA<sub>80</sub>-co-VBTMAC<sub>20</sub>) (blue symbols) and POEGMA<sub>80</sub>-b-VBTMAC<sub>20</sub> (green symbols) upon heating with a rate of 5 K·min<sup>-1</sup>.



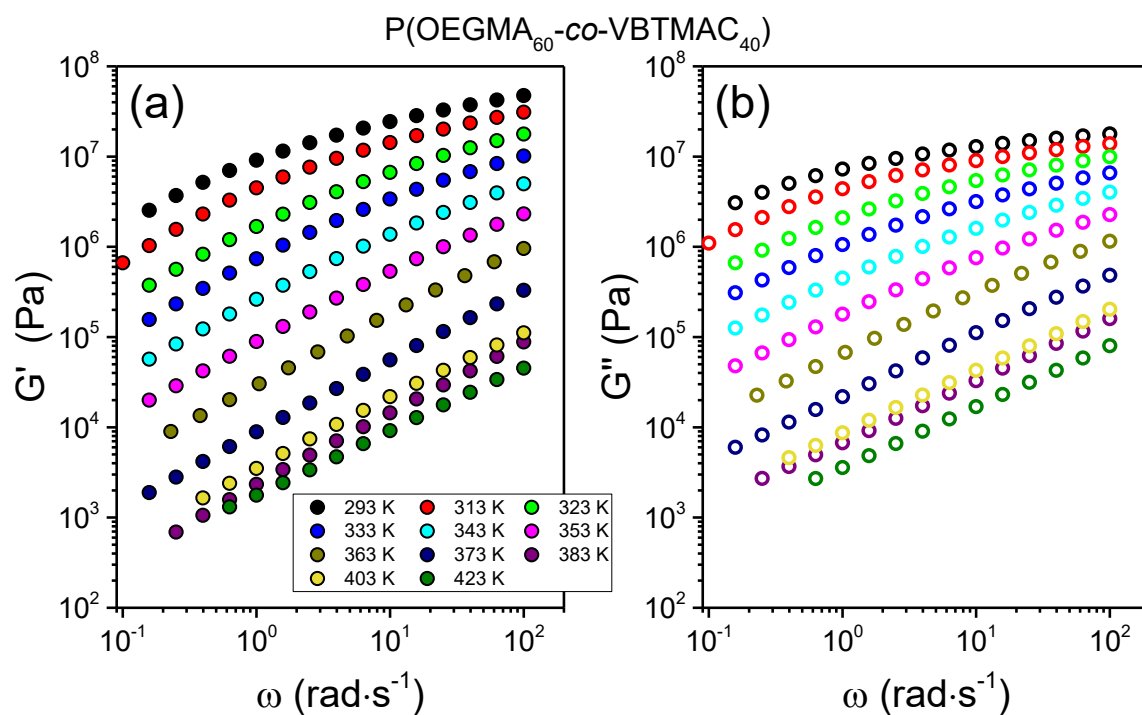
**Figure S6.** Dynamic frequency sweeps for the diblock copolymer with 20 wt.% of PVBTMAC at the temperatures  $T = 293$  K (black) and  $T = 373$  K (purple).



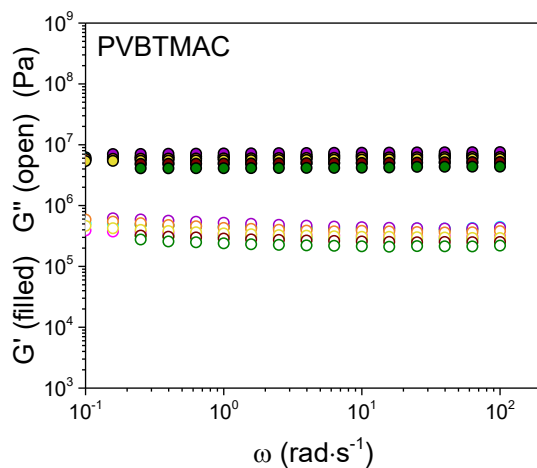
**Figure S7.** Angular frequency dependence of complex viscosity for **(a)** P(OEGMA<sub>80</sub>-*cO*-VBTMAC<sub>20</sub>) and **(b)** P(OEGMA<sub>60</sub>-*cO*-VBTMAC<sub>40</sub>) at different temperatures. The solid lines represent fits by the CM model (Eq. 2). **(c)** Inverse temperature dependence of the extracted power law index values.



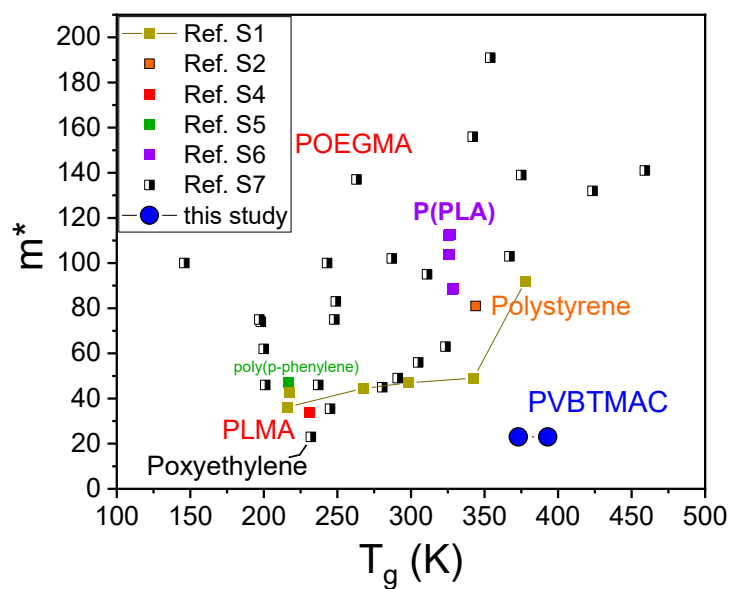
**Figure S8.** Angular frequency dependence of (a) storage and (b) loss moduli for the P(OEGMA<sub>80</sub>-co-VBTMAC<sub>20</sub>) statistical copolymer at the temperatures; 293 K (black), 303 K (gray), 323 K (green), 333 K (blue), 343 K (cyan), 353 K (magenta), 363 K (dark-yellow), 373 K (navy) and 383 K (purple), as indicated.



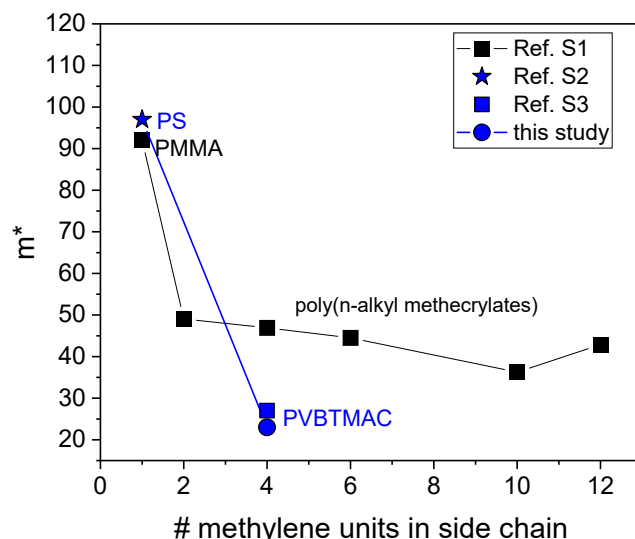
**Figure S9.** Angular frequency dependence of shear (a) storage and (b) loss moduli for the statistical copolymer with 40 wt.% VBTMAC content at the temperatures 293 K (black), 313 K (red), 323 K (green), 333 K (blue), 343 K (cyan), 353 K (magenta), 363 K (dark-yellow), 373 K (navy), 383 K (purple), 403 K (yellow) and 423 K (olive).



**Figure S10.** Angular frequency dependence of shear (a) storage (filled symbols) and loss moduli (open symbols) for the PVBTMAC homopolymer, at the temperatures 323 K (green), 343 K (cyan), 353 K (magenta), 363 K (dark yellow), 383 K (purple), 393 K (orange), 403 K (yellow), 413 K (wine) and 423 K (olive).



**Figure S11.** Fragility at  $T_g$  as a function of glass transition temperature for the PVBTMAC homopolymer (blue symbols). Data from common polymers are included, taken from Refs [S1, S2-S7], as indicated.



**Figure S12.** Fragility,  $m$ , plotted as a function of the number of methylene units on the side chain of polystyrene (blue star), PVBTMAC (blue circle and square) and the family of poly(*p*-alkyl methacrylates) (black symbols), taken from Refs [S1-S3].

## References

- (S1) Floudas, G.; Štěpánek, P. Structure and dynamics of poly (n-decyl methacrylate) below and above the glass transition. *Macromolecules* **1998**, *31* (20), 6951-6957.
- (S2) Pipertzis, A.; Hossain, M. D.; Monteiro, M. J.; Floudas, G. Segmental dynamics in multicyclic polystyrenes. *Macromolecules* **2018**, *51* (4), 1488-1497.
- (S3) Pipertzis, A.; Chroni, A.; Pispas, S.; Swenson, J. Molecular Dynamics and Self-Assembly in Double Hydrophilic Block and Random Copolymers. *The Journal of Physical Chemistry B* **2024**, *128* (45), 11267-11276.
- (S4) Pipertzis, A.; Skandalis, A.; Pispas, S.; Floudas, G. Nanophase Segregation Drives Heterogeneous Dynamics in Amphiphilic PLMA-*b*-POEGMA Block-Copolymers with Densely Grafted Architecture. *Macromolecular Chemistry and Physics* **2024**, *225* (19), 2400180.
- (S5) Mierzwa, M.; Floudas, G.; Neidhöfer, M.; Graf, R.; Spiess, H. W.; Meyer, W. H.; Wegner, G. Constrained dynamics in supramolecular structures of poly (p-phenylenes) with ethylene oxide side chains: A combined dielectric and nuclear magnetic resonance investigation. *The Journal of chemical physics* **2002**, *117* (13), 6289-6299.
- (S6) Hu, M.; Xia, Y.; McKenna, G. B.; Kornfield, J. A.; Grubbs, R. H. Linear rheological response of a series of densely branched brush polymers. *Macromolecules* **2011**, *44* (17), 6935-6943.
- (S7) Qin, Q.; McKenna, G. B. Correlation between dynamic fragility and glass transition temperature for different classes of glass forming liquids. *Journal of Non-Crystalline Solids* **2006**, *352* (28-29), 2977-2985.