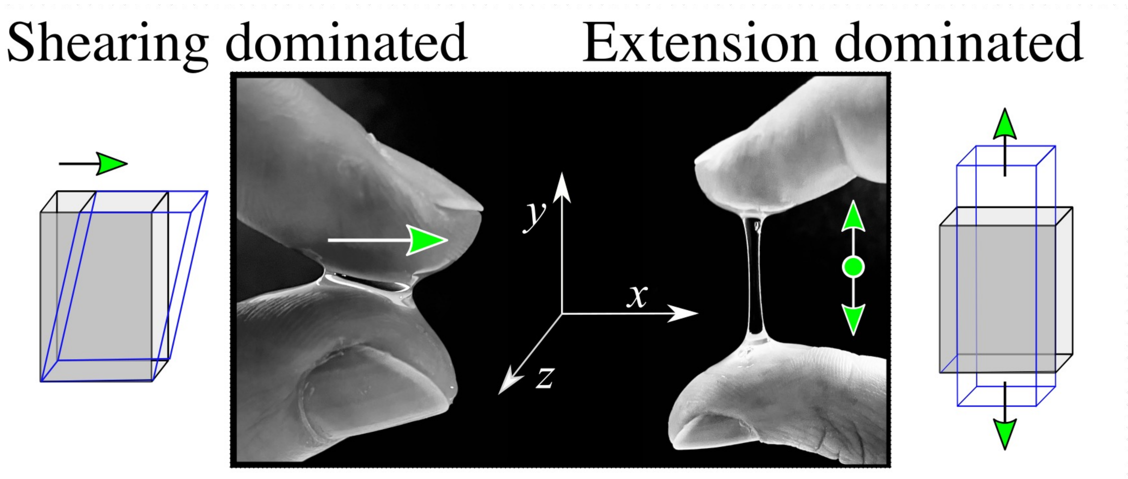
Microstructural dynamics and rheology of worm-like diblock copolymer nanoparticles under shear and extensional flows

Vincenzo Calabrese,[a] Csilla György,[b] Simon J. Haward,[a] Thomas J. Neal,[b] Steven P. Armes,[b] Amy Q. Shen[a]

[a] *Micro/Bio/Nanofluidics Unit, Okinawa Institute of Science and Technology Graduate University, Okinawa, Japan*

[b] *Dainton Building, Department of Chemistry, The University of Sheffield, Sheffield, South Yorkshire S3 7HF, U.K*

(1) Introduction



Tactility and customer perception of cosmetic formulations are strongly connected with the extensional response of the fluid. For example, extensional dominated flows can lead to "stringiness", which is undesirable for many cosmetic formulations.

(2) Test Fluid

We investigate the shear and extensional flow behavior of dispersions composed of two worm-like nanoparticles (WLNP) with comparable cross-sectional diameters, similar persistence lengths but differing contour lengths and thus differing flexibility. We obtain an experimental quantification of the role of shearing and planar extensional flows at aligning short and stiff WLNP (S-WLNP, ★) and relatively long and flexible WLNP (L-WLNP, ●).

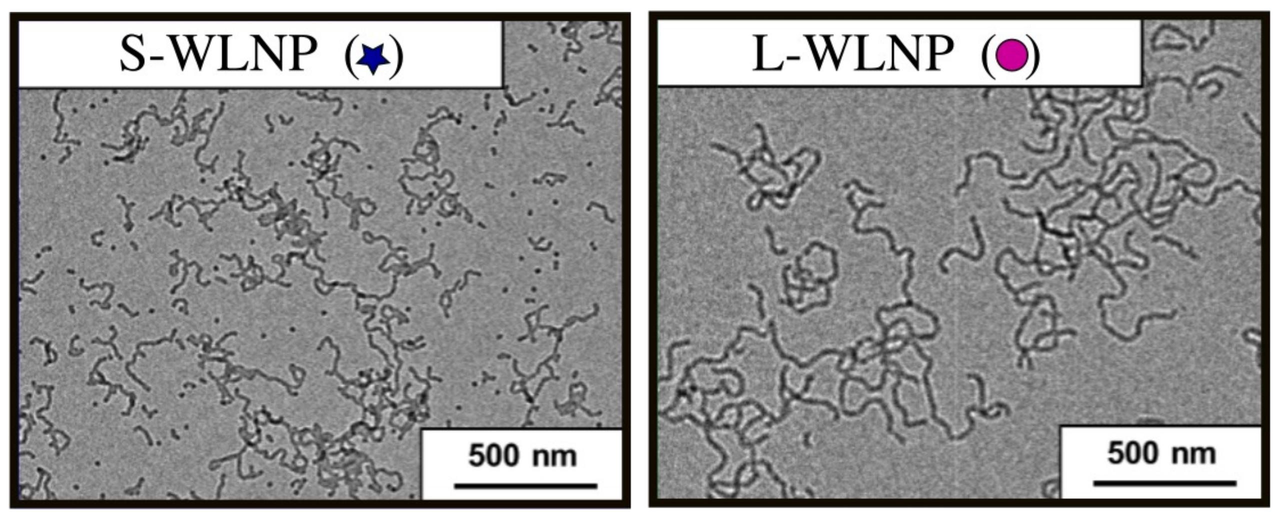


Fig. 1 Transmission electron microscopy images for S-WLNP and L-WLNP.

(4) Shear *vs*. extensional flow

Microfluidic experiments. Schematic representation of microfluidics devices used to assess the effect of shearing and extensional flows at aligning the WLNP.

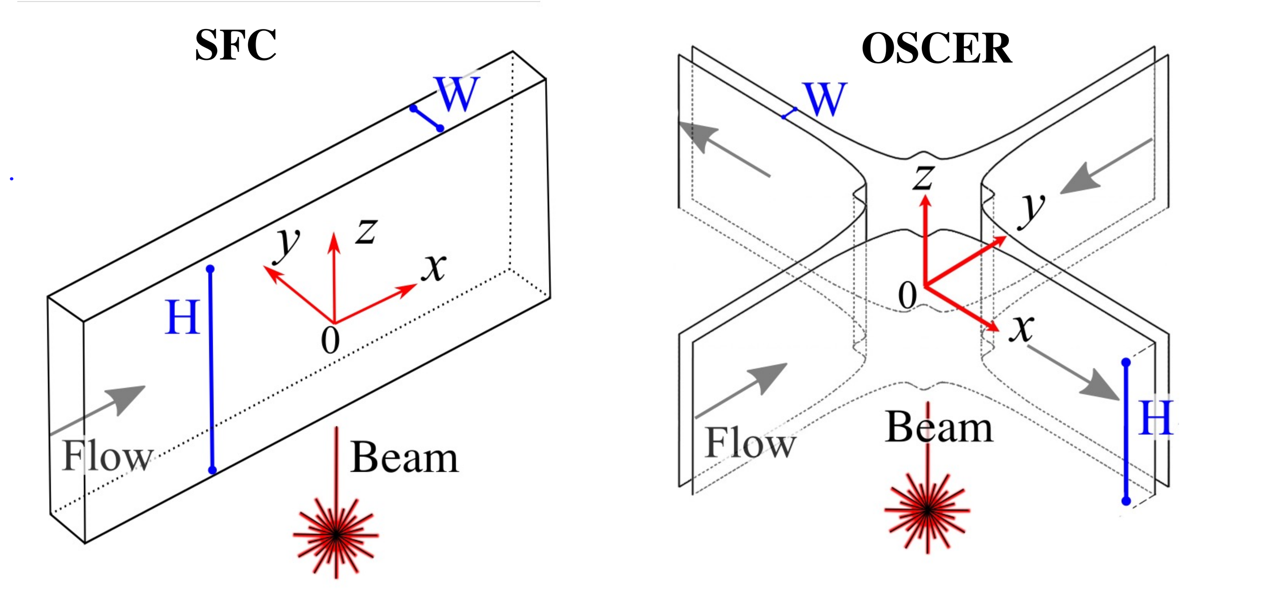


Fig. 2 Shearing-flow dominated channel (**SFC**) and the optimized cross-slot extensional rheometer (**OSCER**) used to assess the effect of shearing and extensional flows at aligning the WLNP.

Flow induced birefringence (FIB) experiments performed in the SFC and OSCER for representative values of flow velocity ($|U|$). The normalized birefringence ($\Delta n/\phi$) is relatively high in the regions with high deformation rates.

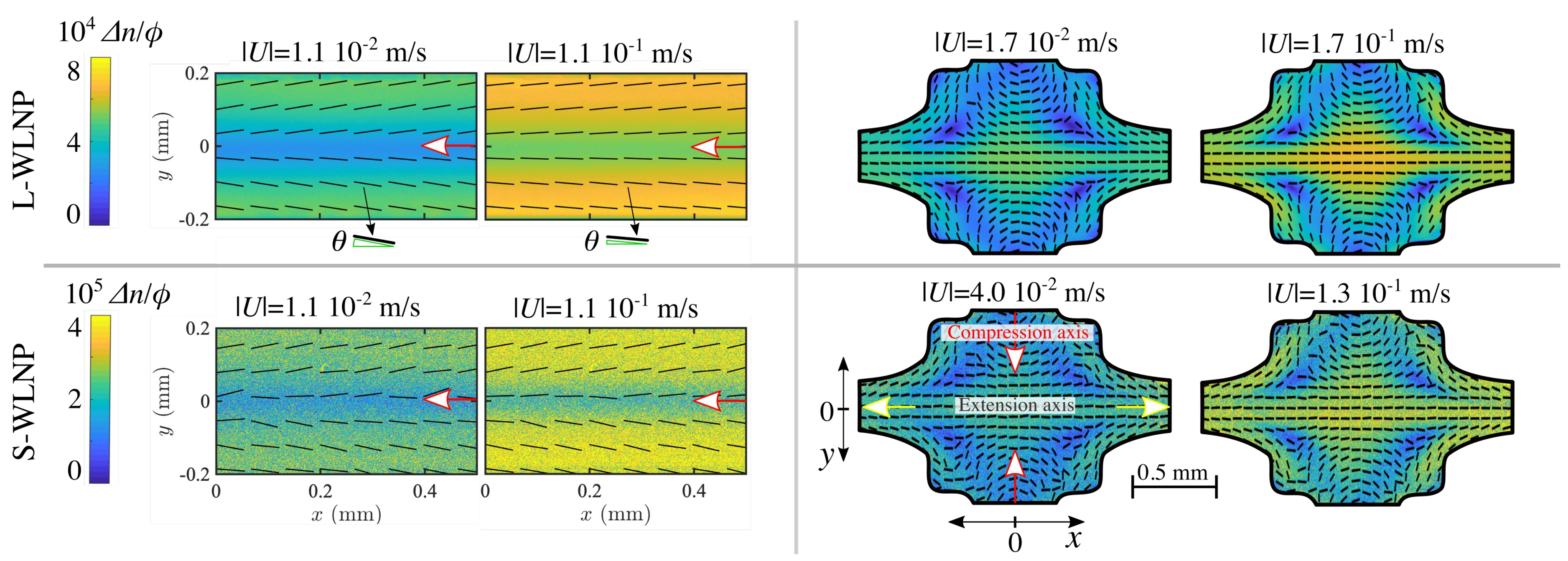


Fig. 3 FIB experiments in the shearing-flow dominated channel (**SFC**) and the optimized cross-slot extensional rheometer (**OSCER**). The normalized birefringence ($\Delta n/\phi$) is illustrated by the contour plot while the direction of the slow optical axis, θ, is indicated by the solid line. The arrows indicate the flow direction.

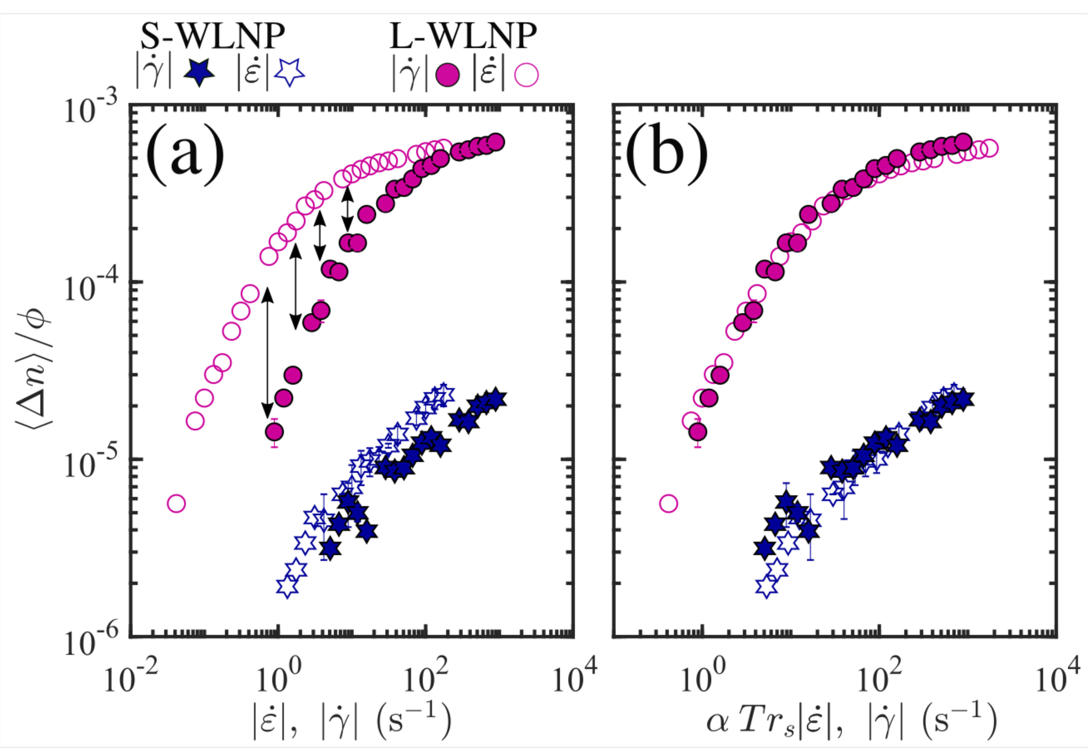


Fig. 4 **(a)** Normalized mean birefringence ($\langle\Delta n\rangle/\phi$) as a function of the shear rate, $|\dot{\gamma}|$, and extension rate $|\dot{\varepsilon}|$. In **(b)** $|\dot{\varepsilon}|$ is scaled by $\alpha Tr_s|\dot{\varepsilon}|$.

When comparing quantitatively the effect of shear and extension at aligning the S-WLNP and L-WLNP three main observations can be drawn.
(i) The extensional deformation rate is generally more effective at inducing the alignment of the WLNP.
(ii) The dynamics of alignment in shear and extension are self-similar. The curves in **Fig. 4a** can be superimposed by adopting a scaling factor to the extension rate $|\dot{\varepsilon}|$ as $\alpha Tr_s|\dot{\varepsilon}|$, where Tr_s is the Trouton ratio of the solvent in a planar extensional flow ($Tr_s = 4$) and α is an empirical shifting parameter (**Fig. 4b**).
(iii) The difference between shear and extensional flows is more pronounced for the more flexible L-WLNP.

(3) Characterization

The S-WLNP and L-WLNP dispersed in mineral oil display a qualitatively similar shear thinning behaviour that is well captured by the Cross model (solid lines). However, for a given volume fraction (ϕ), the longer L-WLNP have a greater viscosity.

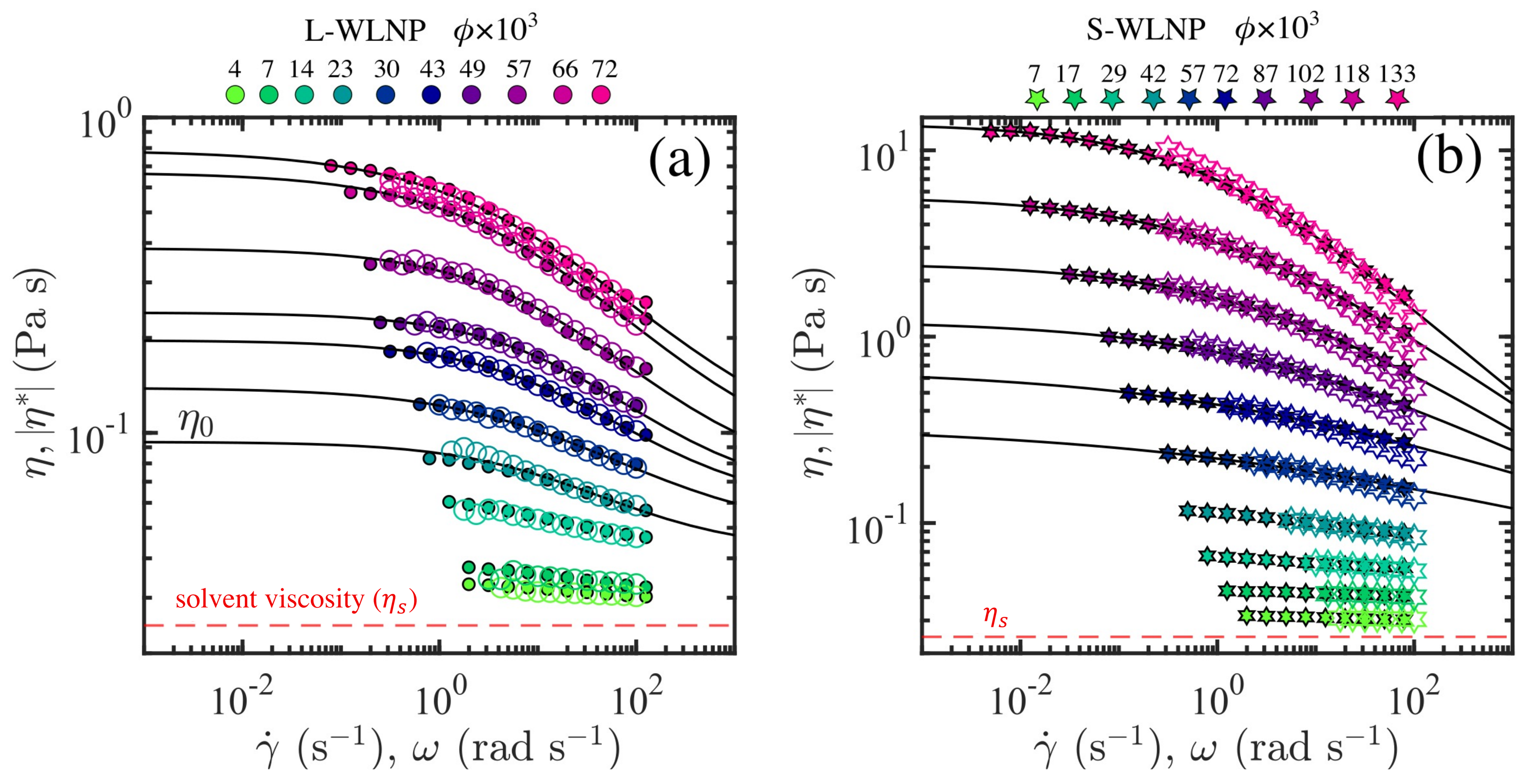


Fig. 2 Steady shear viscosity (η), and the magnitude of complex viscosity ($|\eta^*|$) as a function of shear rate ($\dot{\gamma}$) and angular frequency (ω), respectively.

(5) Alignment-rheology relationship

As rheological and structural properties are linked, we evaluate the shear viscosity response of the WLNP dispersions with the extent of particle alignment under shear flow. The viscosity follows an exponential decay with the increasing birefringence, $\langle\Delta n\rangle/\phi$, (see **Fig. 5b, c**).

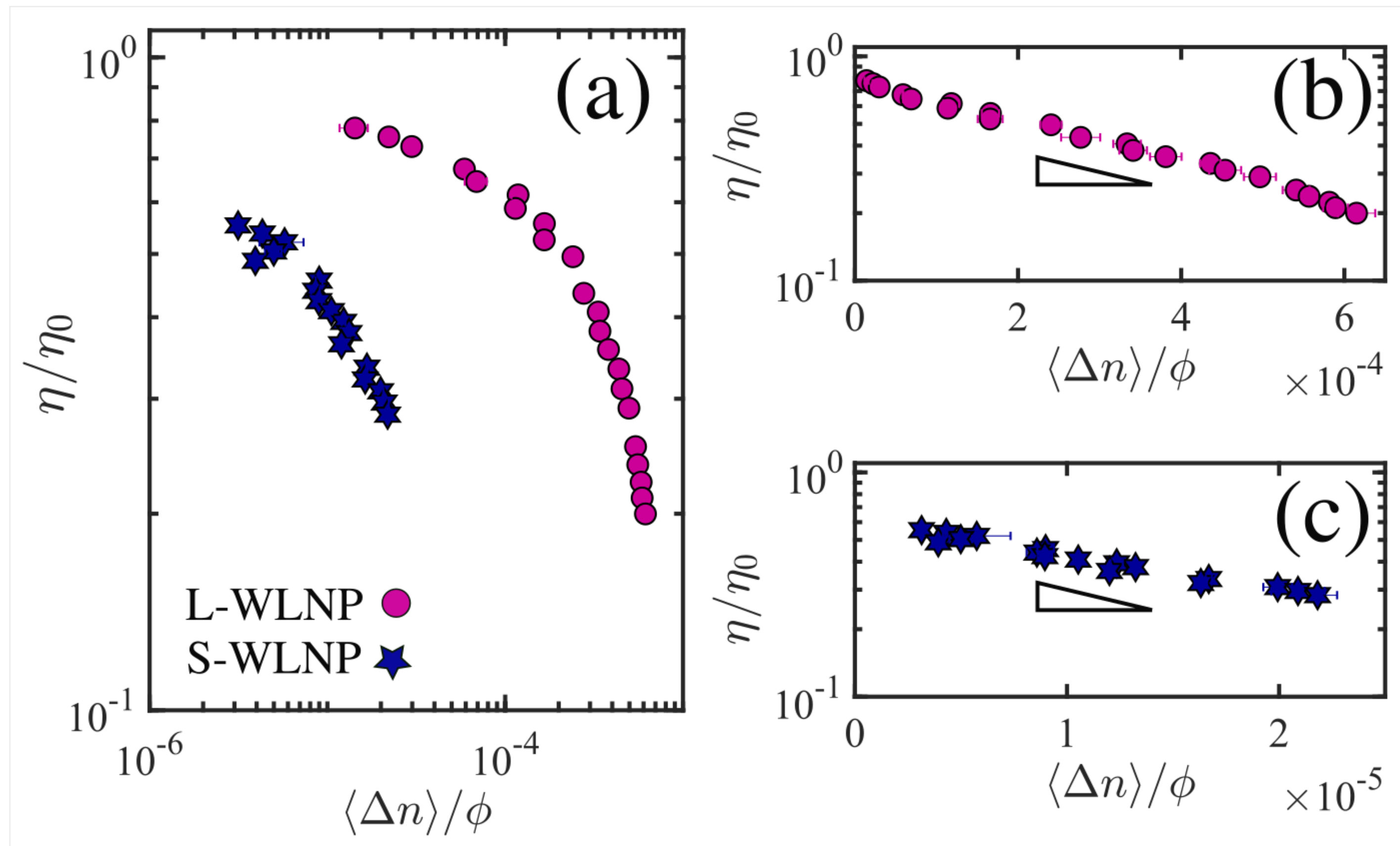


Fig. 5 **(a)** Normalized shear viscosity (η/η_0) as a function of the normalized mean birefringence ($\langle\Delta n\rangle/\phi$) obtained in shear.

(6) Conclusions

- Semi-flexible WLNP exhibits self-similar dynamics in shear and extensional flows.
- The onset of WLNP alignment is affected by the type of deformation rate.
- Extensional forces are more effective than shear forces at inducing WLNP alignment.

OKINAWA INSTITUTE OF SCIENCE AND TECHNOLOGY GRADUATE UNIVERSITY
沖縄科学技術大学院大学
1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan Phone. +81-98-966-8711
〒904-0495 沖縄県国頭郡恩納村字谷茶 1919-1 Phone. 098-966-8711
http ://www.oist.jp

References:
Calabrese et al. *Macromolecules*, **2022** (*Accepted*)
Calabrese et al. *Macromolecules*, **2021** *54* (9), 4176-4185