1. Introduction / Description of the project

The way that polymers penetrate into nanometer size pores is of fundamental interest and important for many applications. This is the case, for instance, that a biopolymer is experiencing when migrating through a narrow passage towards to its target with profound importance in cell biology. Similarly, nanopores in lab-on-a-chip devices selectively transport biomolecules for detection and separation applications. When a polymer melt gets into contact with the opening of a thin pore the capillary force is strong and drags the chains into the pore. Within POLYCONF we followed the dynamics of capillary flow of polymer melts into nanopores under conditions where the molecular dimensions ($2R_g$) approach the pore diameter (d). Despite recent work in understanding capillary rise in nanopores at the onset of POLYCONF - this field was still at its infancy. As *model* confining systems in 2d we chose self-ordered nanoporous aluminum oxide (AAO) because AAO templates contain arrays of discrete-isolated, parallel, cylindrical nanopores that are uniform in length and diameter.

Within POLYCONF we explored (i) the kinetics of polymer imbibition. In addition we investigated the (ii) dynamics under confinement by combining experiment, theory and simulation.

Scientifically this research proposal addressed the following questions:

(1) How do polymers penetrate in thin pores? What is the origin of the defects in capillary imbibition observed occasionally?

(2) What is the origin of the observed reversal in capillary rise with polymer molecular weight?

(3) How do polymer mixtures, polymer blends and copolymers penetrate into thin pores? What is the role of thermodynamics on imbibition, *i.e.*, in the case of blends and copolymers how the product χN (χ is the interaction parameter and N the total degree of polymerization) enters the imbibition process?

(4) Can we make a semi-crystalline or a glassy polymer to flow within nanopores?

(5) Can we predict the local and global dynamics of polymers under 2-d confinement?

(6) Can we control processes such as adhesion, welding and melt processing by obtaining a better understanding of polymer/substrate interfaces?

Within POLYCONF in order to address these issues we employed different but complementary techniques (dielectric spectroscopy as a function of temperature and pressure as well as in-situ measurements of the dielectric function, differential scanning calorimetry, reflection microscopy, optofluidics as well as several surface characterization techniques).

2. The Research Team

The **research team** had a broad experience in experiment, theory and simulation. Apart from the PI, 1 post-doc, 2 graduate students, 2 post-graduate students, several undergraduate students and four external collaborators with experience in polymer theory (Masao Doi, Beijing), self-consistent field theory (SCFT) calculations (Jiajia Zhou, Beijing), atomistic simulations (Vaggelis Harmandaris, Crete) and on surface properties (Hans-Juergen Butt, Mainz) were employed.

3. Results

The main results from this work with reference to the scientific questions are as follows:

(1) With respect to the mechanism of capillary imbibition in nanopores, we have shown that this is controlled by two factors. The first one is the strong capillary force that forces chains to overcome the entropic barrier and enter the pores, and the second is polymer adsorption. The dead-layer effect discussed by M. Doi is central to the adsorption behavior. The latter is also responsible for polymer chains staying within the pores.

(2) With respect to the origin of the observed reversal in capillary rise with polymer molecular weight, we have shown that this reflects the strength of adsorption and the configuration of chains.

(3) With respect polymer blends, we have demonstrated that shorter chains enter first into nanopores and only latter are followed by the longer chains. We have further proposed that this difference in the imbibition kinetics can be employed, e.g. by industry, in separating long from short chains (e.g. like in GPC) and in the absence of solvent (unlike GPC).

(4) With respect to the possibility to induce flow by nanoconfinement we have demonstrated that a semi-crystalline polymer can flow. The drag force is so strong that can drive a semicrystalline polymer within the templates without melting the crystals.

(5) Can we predict the local and global dynamics of polymers under 2-d confinement? To this end, we can clearly predict both the local segmental and global chain dynamics in type-A polymers within nanopores. This resulted from extensive kinetic studies near the Tg, but also at higher temperatures by following the adsorption of chains.

(6) The results obtained within this period suggest means of controlling the interfacial interactions in homopolymers and their blends of importance in the design of polymer interfaces with controlled physical processes such as to adhesion and melt processing (even for semicrystalline polymers),

and with respect to the simulations:

(7) A new machine-learned atomistic force-field, based on extensive ab initio density functional theory calculations of cis-1,4 polybutadiene (cPB) melt, well above Tg, and confined between alumina (001) substrates was constructed. This resulted in an accurate atomistic description of the polymer structure at the vicinity of the interface providing a plethora of structural and dynamical information.

4. Publications

As a result, 33 **papers** have been published in refereed journals, 12 of which exactly on the subject and 21 in related fields. The 12 publications most closely related to the project are shown below:

[1] C.-H. Tu, J. Zhou, H.-J. Butt, and G. Floudas
Adsorption Kinetics of *cis*-1,4-Polyisoprene in Nanopores by *In Situ* Nanodielectric Spectroscopy.
Macromolecules 54, 6267-6274, 2021.

[2] C.-H. Tu, J. Zhou, M. Doi, H.-J. Butt, G. Floudas
Interfacial Interactions During *In Situ* Polymer Imbibition in Nanopores
Phys. Rev. Lett. 125, 127802, 2020.

[3] M.M. Elmahdy, D. Gournis, A. Ladavos, Ch. Spanos, G. Floudas

H-Shaped Copolymer of Polyethyne and Poly(ethylene oxide) under Severe Confinement: Phase State and Dynamics.
Langmuir 36, 4261-4271, 2020.
[4] P. Kardasis, N. Kalafatakis, M. Gauthier, D. Vlassopoulos, and G. Floudas
Layers of Distinct Mobility in Densely Grafted Dendrimer Arborescent Polymer Hybrids
Phys. Rev. Lett. 126, 207802, 2021.
[5] C.-H. Tu, J. Zhou, H.-J. Butt, and G. Floudas
Adsorption Kinetics of *cis*-1,4-Polyisoprene in Nanopores by *In Situ* Nanodielectric Spectroscopy.
Macromolecules 54, 6267-6274, 2021.
[6] Panagiotis Kardasis, Angelos Oikonomopoulos, Georgios Sakellariou, Martin Steinhart, and George Floudas
Effect of Star Architecture on the Dynamics of 1,4-cis-Polyisoprene under Nanometer Confinement
Macromolecules 54, 11392-11404, 2021.
[7] C.-H. Tu, L. Veith, H.-J. Butt, G. Floudas
Ionic Conductivity of a Solid Polymer Electrolyte Confined in Nanopores
Macromolecules 55, 1332-1341, 2022.
[8] Kardasis, P.; Sakellariou, G.; Steinhart, M.; Floudas, G.
Nonequilibrium Effects of Polymer Dynamics under Nanometer Confinement: Effects of Architecture and Molar Mass.
J. Phys. Chem. B. 126, 5570−5581, 2022.
[9] Patsalidis, N.; Papamokos, G., Floudas, G.; Harmandaris, V.
Understanding the Interaction between Polybutadiene and Alumina via Density Functional Theory Calculations and Machine-Learned Atomistic Simulations.
J. Phys. Chem. C 126, 39, 16792–16803, 2022.
[10] Zhang, J.; Lei, J.; Tian, W.; Zhang, G.; Floudas, G.; Zhou J.
Capillary Filling of Polymer Chains in Nanopores.
Macromolecules 2023, 56, 2258-2267.
[11] Tu, C.-H.; Steinhart, M.; Berger, R.; Kappl, M.; Butt, H.-J.; Floudas, G.
When crystals flow.
Science Advances 2023, 9, eadg8865
[12] Patsalidis, N.; Papamokos, G.; Floudas, G.; Harmandaris, V. Structure and Dynamics of a Polybutadiene Melt Confined between Alumina Substrates.
Macromolecules 2023, 56, 6552−6564.

Invited talks at international conferences given by the PI (APS March Meeting 2021; Bordeaux Polymer Conference 2022; ACS Fall Meeting Chicago, 2022; 11th International Conference on Broadband Dielectric Spectroscopy and its Applications, San Sebastian 2022; 5th Int. Workshop on Dynamics in Confinement, Grenoble 2022; 9th International Discussion Meeting on Relaxations in Complex Systems, Chiba, Japan, August 2023) and several contributed talks by the POLYVONF collaborators.

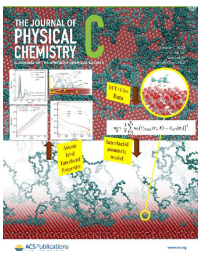
Seminars were given by the PI at Universities and Research Centers (Osaka Metropolitan University, Dept. of Chemistry, August 2023; University of Crete, Dept. of Materials Science and Technology, March 2021; FORTH-IESL, December 2020; University of Massachusetts at Lowell, September 2020, University Wuppertal, GDCh Kolloqium, 2020).

Advertisement. Results from the current investigation published in Phys. Rev. Lett. 125, 127802, 2020 on "the way that Macromolecules penetrate narrow pores" was **advertised** on the webpage of the Max Planck Institute for Polymer Research, https://www.mpip-mainz.mpg.de/en/press/pr-2020-17 as well as in popular science periodicals in

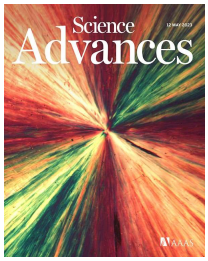
Germany, https://www.innovations-report.com/physics-and-astronomy/shall-they-go-with-the-flow/.

Cover pages. The research on (a) the simulation results of confined polymers, and (b) the flow of a confined semi-crystalline polymer made the respective cover pages of *J. Phys. Chem B*. and *Science Advances* as shown below:

[a] Patsalidis, N.; Papamokos, G., Floudas, G.; Harmandaris, V. Understanding the Interaction between Polybutadiene and Alumina via Density Functional Theory Calculations and Machine-Learned Atomistic Simulations.
J. Phys. Chem. C 126, 39, 16792–16803, 2022.



[b] Tu, C.-H.; Steinhart, M.; Berger, R.; Kappl, M.; Butt, H.-J.; Floudas, G. When crystals flow.
Science Advances 2023, 9, eadg8865.



5. Impact and added value

Results from POLYCONF provided understanding of the mechanism that control polymer imbibition into nanopores. They provide opportunities for possible exploitation, in areas such as coatings, sensors, membranes and possibly in organic electronic devices. Given the current challenges related e.g. to sensors and membranes, the fundamental understanding brought by POLYCONF on the effects of polymer adsorption and the non-equilibrium polymer dynamics near Tg, will have an important impact in their future design. In addition, the research was important for the career development of young scientists. The truly interdisciplinary team provided a fertile environment for science, learning and possible innovation. POLYCONF was an excellent vehicle for the development of two UoI graduate students, 2 post-graduates and several undergraduates with exceptional technical and strong communication skills as continuously honed by studying the literature, discussing results in one-on-one meetings with the PI, presenting at group meetings and at national and international conferences, and by publishing papers in scientific journals.