RING POLYMERS

Aldemar Knossos Royal Hotel, Crete, September 25-27, 2017

ABSTRACTS (in order of appearance in the program)

ORAL PRESENTATIONS

Topological problems related to genome folding

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In the talk, I plan to review the solved and mostly unsolved problems of polymer physics which seems to be relevant for current understanding of genome folding.

Ring Dynamics: Current Status and Future Challenges

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The dynamics of circular or ring-like polymers has been a subject of investigation since the 1980s [1-5]. Creating a full understanding of ring dynamics remains an remains a challenge, partially because of the difficulty of making synthetic rings of sufficient size and purity to establish the nature of the entanglement dynamics, if entanglements even exist in these materials. Beyond the difficulty of molecular size, even extremely small amounts of linear impurities can impact the dynamics [4]. Hence, one of the major challenges to our understanding of ring dynamics is to make large molecular weight circular molecules of sufficient purity that the dynamics of the rings themselves can be determined. In the present work the current state of understanding of the dynamics of rings is outlined and current work from our group of collaborators [6] to make extremely large circular polymers using circular DNA in sufficient quantity and size to determine the dynamics of these materials will be shown. Early results will be presented and remaining challenges will be elucidated.

[1] J. Klein, *Macromolecules*, **19**, 105-118 (1986).
[2] J. Roovers, *Macromolecules*, **18**, 1359-1361 (1985)

[3] G.B. McKenna, G. Hadziioannou, P. Lutz, G. Hild, C. Strazielle, C. Straupe, P. Rempp and A.J. Kovacs, *Macromolecules*, **20**, 498-512 (1987).
[4] M. Kapnistos, M. Lang, D. Vlassopoulos, W. Pyckhout-Hintzen, D. Richter, D. Cho, T. Chang and M. Rubinstein, *Nat. Matls.*, Published online: 26 October 2008; doi:10.1038/nmat2292 (2008).
[5] Y. Doi, K. Matsubara,Y. Ohta, T. Nakano, D. Kawaguchi, Y.Takahashi, A. Takano and Y. Matsushita, *Macromolecules*, **48**, 3140−3147 (2015).
[6] Y. Li, K.-W. Hsiao, C. A. Brockman, D. Y. Yates, R. M. Robertson-Anderson, J.A. Kornfield, M. J. San Francisco, C. M. Schroeder and G. B. McKenna, *Macromolecules*, **48**, 5997-6001 (2015).

Designing Cyclic and Topological Polymer Constructions by Innovative Synthetic Protocols

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Cyclic (ring) and multicyclic polymer chain architectures are topologically intriguing and have inspired expanding research interests. A class of *multicyclic* polymer topologies, including three subclasses of *spiro-*, *bridged-* and *fused-*forms, are particularly unique not only from the topological geometry viewpoint but also from their programmed folding structures of biopolymer relevance. We have so far demonstrated an *electrostatic self-assembly and covalent fixation* (ESA-CF) protocol as a powerful synthetic approach, where ion-paired linear or non-linear polymer self-assemblies are employed as key intermediates. As a showcase example, we have recently achieved the ESA-CF construction of a topologically significant *fused*-tetracyclic $K_{3,3}$ graph polymer, known as a prototypical non-planar graph in topological geometry, and remarkably identified in cyclic polypeptides (cyclotides) of diverse biofunctions, by using a uniform-size dendritic polymer precursor having six cyclic ammonium salt end groups carrying two units of a trifunctional carboxylate counteranions. Moreover, a variety of multicyclic polymer topologies of the three subclasses and their hybrid-forms, including a triply-*fused* tetracyclic and a quadruply-*fused* pentacyclic forms (unfolded tetrahedron-graph, and "shippo"-form, respectively) have been constructed through the ESA-CF process in conjunction with a tandem alkyne-azide addition, i.e., *click*, and olefin metathesis, i.e., *clip*, reactions.

[1] *Topological Polymer Chemistry: Progress of cyclic polymers in synthesis, properties and functions*, Y. Tezuka ed., World Scientific, Singapore, 2013.
[2] Heguri H, Yamamoto T, and Tezuka Y, *Angwew. Chem. Int. Ed..*, **54**, 8688 (2015).

[3] Suzuki T, Yamamoto T, and Tezuka Y, *J. Am. Chem. Soc*., **136**, 10148 (2014).
[4] Tomikawa Y, Yamamoto T, Tezuka Y, *Macromolecules*, **49**, 4076 (2016).

New simulation studies on large polymer ring melts and their implications for chromosome organization

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Nonconcatenated polymer rings in a melt segragate and form distinct territories. Though this is well known by know there are still many questions concerning dynamics[1]. The current work tries to reveal these issues by looking at (a) much larger systems of many more rings based on a simple coarse grained model and (b) by studiying melts of very large rings. In the latter case the problem of validation of equilibration is of special concern.

Beyond that we study the relevance of melts of ring polymers for several problems concerning the chromosome organization in the cell nucleus. In interphase cell nucleus chromosomes occupy distinct territories, exhibit specific positioning and their transcriptionally active and passive segments are spatially segregated. While a melt of ring polymers reflects the territorial behavior due to topological constraints [1], a small partial activity on linear polymers can contribute to the positioning and segregation [2,3]. Here we combine these two models in a melt of partly active rings. This allows us to study the interplay between the equilibrium territorial structure and nonequilibrium microphase separation in the steady-state.

 [1] J. Halverson, J. Smrek, K. Kremer and A Grosberg, From a melt of rings to chromosome territories: the role of topological constraints in genome folding Rep. Prog. Phys. 77 022601 (2014)
[2] N. Ganai, S. Sengupta, and G. I. Menon, Chromosome positioning from activity-based segregation, Nucleic Acids Res. 42, 4145 (2014).
[3] J. Smrek, K. Kremer, Small Activity Differences Drive Phase Separation in Active-Passive Polymer Mixtures, PRL, (2017)

Polymer flow and polymer topology: linear chains, rings and knots flow differently

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Modifications of the topological state of polymers are extremely interesting and relevant operations for a vast domain of scientific inquiry ranging from knot theory and polymer science all the way to materials science and biophysics, where cyclic and knotted DNA plays a key role in biological processes. Recent work has demonstrated that joining the two ends of a linear chain to form a cyclic (ring) polymer has a number of significant consequences in the structural [1,2] and rheological [3] properties of concentrated or semidilute solutions of the same. Accordingly, a number of questions arise regarding the behavior of linear, cyclic and knotted ring polymers under flow: how does the topology of the dissolved polymer affect its orientational resistance, as well as its rotation-, tumbling- or tank-treading motion under Couette flow? What consequences does shear flow have for knot localization along a sheared polymer? Can one make use of the different flow properties of various polymer topologies to build microfluidic devices that act as filters/separators of topologically different polymers? By applying hybrid (MPCD/MD) simulation techniques that take into account the hydrodynamics, we address the questions above for polymers of varying topologies, knotedness and stiffness and we analyze quantitatively the influence of polymer topology on single-polymer properties under flow [4]. Polymer properties under Poiseuille flow will also be analyzed and on this basis concrete suggestions for the construction of topology-separating microfluidic devices will be presented [5].
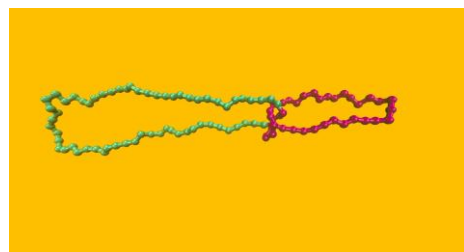

Fig. 1: A knotted ring polymer carrying a 3_1-knot under shear flow. The knotted part is rendered with magenta color.

[1] M. Z. Slimani, P. Bacova, M. Bernabei, A. Narros, C. N. Likos, and A. J. Moreno, ACS Macro Letters **3**, 611 (2014).
[2] P. Poier, S. A. Egorov, C. N. Likos and R. Blaak, Soft Matter **12**, 7983 (2016).
[3] M. Kapnistos et al., Nature Materials **7**, 997 (2008).
[4] M. Liebetreu and C. N. Likos, in preparation (2017).
[5] L. Weiß, A. Nikoubashman, and C. N. Likos, in preparation (2017).

Influence of Knots within Cyclic Polystyrene on the segmental dynamics and Glass temperature

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Molecular topology affects the glass temperature and polymer segmental dynamics. Here we study cyclic polystyrene structures, all with a similar molecular weight, designed with a number of irreversible knots located at strategic sites to control the shape of the polymer coil. For this purpose we employ dielectric spectroscopy and temperature modulated TM-DSC. To quantify the effect of topology we define (i) the number of branching points in the vicinity of a knot and (ii) the loop molecular weight. Glass temperature increases with the number of constrained segments and decreases with the loop molecular weight. In addition there exist small changes in fragility (or steepness index) with topology. The steepness index decreases with the number of constrained segments and increases with the loop molecular weight. The role of the polar triazol units at the coupling points is discussed.

Knot Energy, Complexity, and Mobility of Knotted Polymers

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The Newtonian energy E_N *of an object* is defined by the energy required to charge a conductive object of arbitrary shape and scales inversely to the self-capacity C, a basic measure of object size and shape. It is known that C is minimized for a sphere for all objects having the same volume, and that c increases as the symmetry of an object is reduced at fixed volume. Mathematically similar energy functionals have been related to the average knot crossing number (m), a natural measure of knot complexity and correspondingly we find E_N to be directly related to both (m) and the Stokes friction coefficient of knotted DNA. To establish this relation, we employ molecular dynamics simulations to generate knotted polymeric configurations having different length and stiffness, and minimum knot crossing number values m. We then compute EN for all these knotted polymers using the path-integration program ZENO and find that the average Newtonian knot energy (E_N) is directly

proportional to (*m*). Finally, we calculate the ratio of the hydrodynamic radius, radius of gyration, and the intrinsic viscosity of semi-flexible knotted polymers in comparison to the linear polymeric chains since these ratios should be useful in characterizing knotted polymers experimentally.

Loose Trees and Threadings: A Recipe for Topological Glasses

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The structure and dynamics of ring polymers in the melt are among the last big mysteries in Polymer Physics. In this talk I will show that one can gain insight into their local conformations by computing maps of intra-chain contacts. This strategy, often used for proteins and chromosomes, leads to patterns and motifs that can be mainly associated with tight branches and loose loops: both strong candidates for the formation of inter-ring threadings. By exploiting the abundance of these architecture-specific topological constraints I will show that one can drive the formation of a "topological glass" (at T>T_g) in a dense solution of ring polymers by "pinning" a small fraction of the rings. These findings not only strongly motivate the experimental design of the first topological glass but also shed light into the role of threadings in the dynamics of ring polymers in the melt.

Insights from MD simulations to structure and dynamics of unconcatenated ring melts

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It is now generally supposed that unconcatenated rings in the melt state become compact for very large rings, i.e. $R_g \sim N^{1/3}$ [1]. However, this asymptotic behavior is approached very slowly and all chain lengths currently realizable in simulations or experiments are governed by strong crossover phenomena [2,4]. It is an open question to what extent rings are self-similar at the sub-chain level. We will present results from large scale molecular dynamics simulations for bead-spring models with different rigidities and different densities to gain new insights into the structure and dynamics of unconcatenated rings. Our analysis is

inspired from two-dimensional polymer monolayers where the linear chains cannot overlap and take on compact conformations very different from the 3d case [2]. This analysis suggests that molten unconcatenated rings may be marginally compact objects [2,5]. The analogy to 2D melts helps also to understand the strongly sub-diffusive center-of-mass motion due to viscoelastic hydrodynamic interactions [3]. For long rings with some rigidity, we eventually show strong evidence of a temporary "glassy" state due to multiple threading between overlapping rings.

[1] T. Vettorel, A.Y. Grosberg, and K. Kremer. Phys. Biol. 6 (2009) 025013.
J.D. Halverson et al. Rep. Prog. Phys. 77 (2014) 022601.
[2] H. Meyer, N. Schulmann, J.E. Zabel, and J. Wittmer. Comput. Phys. Commun. 182 (2011) 1949.
[3] H. Meyer and A.N. Semenov. PRL 109 (2012) 248304.
[4] S. Obukhov, A. Johner, J. Baschnagel, H. Meyer, and J.P. Wittmer. EPL 105 (2014) 48005.
[5] M. Dolgushev, J.P. Wittmer et al. Soft Matter 13 (2017) 2499.

Marginally compact hyperbranched macromolecular trees

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This contribution presents our studies [1,2] on fractal hyperbranched trees with a Gaussian chain statistics, which are marginally compact. Marginal compactness means that in the $d = 3$ dimensional space the average size of the trees follows $R \sim N^{1/d}$ (where N is the molecular mass of the tree), and at the same time for their surface A the relation $A \sim N$ holds. In various studies it was argued that unknotted and unconcatenated rings in a melt might adopt increasingly compact configurations due to the mutual repulsion caused by the topological constraints. In particularly, this implies that their form factor $F(q)$ shows a $F(q) \approx N/[R(N)q]^d \sim N^0/q^3$ behavior. We show that albeit the self-contact density ρ_c diverges for marginally compact objects logarithmically with the molecular weight N, this issue can be overcome by introducing linear spacers. Indeed, the spacers of length S yield a $\rho_c \sim \log(N/S)/S^{1/2}$ behavior, so that the strong decay with S bits rapidly the logarithmic divergence [1]. Another recipe for suppression of the self-contact density ρ_c is introduction of local stiffness [2]. The

compactness leaves its fingerprints also in the dynamics. In particular, the relaxation time of a subchain of mass $n \approx N/p$ scales as $\tau \sim (N/p)^{5/3}$ that then reveals itself, e.g., in the decay rate of the dynamic structure factor, $\Gamma_q \sim N^0 q^5$, or in the temporal scaling $t^{2/5}$ of the monomeric mean-square displacement.

[1] M. Dolgushev, J. P. Wittmer, A. Johner, O. Benzerara, H. Meyer, and J. Baschnagel, *Soft Matter* **13**, 2499—2512 (2017).
[2] M. Dolgushev, A. L. Hauber, P. Pelagejcev, and J. P. Wittmer, *Phys. Rev. E* **96**, 012501 (2017).

Single polymer dynamics of ring polymers in dilute and semi-dilute solutions

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Recent advances in polymer science have allowed for the synthesis of chains with complex architectures such as combs, stars, dendrimers, and rings. Despite recent progress, we still lack a complete molecular-level understanding of chain dynamics in these materials. A major challenge lies in understanding how nonlinear chain topologies affect nonequilibrium dynamics, in both dilute and entangled solutions. In this talk, I will discuss three recent projects that focus on single molecule studies of ring polymers in dilute and semi-dilute solutions. In the first effort, we interrogate the dynamics of single ring polymers in ultra-dilute solutions using a combination of simulation, theory, and experiment. Inspired by recent experimental results by Li et al. (Macromolecules 2015), we show that the architectural constraints imposed by the ring topology result in surprising effects on the dynamic properties of polymers as they are driven out of equilibrium. In particular, ring constraints lead to a shifted coil-stretch transition that occurs at larger values of the dimensionless flow strength (Weissenberg number, Wi) compared to linear chains, which is driven by coupling between intramolecular hydrodynamic interactions (HI) and chain architecture. In addition, a large loop conformation is observed for ring polymers in extensional flow at intermediate to large Wi, which is caused by intramolecular HI. In a second effort, we use single polymer techniques to investigate the dynamics of single ring polymers in background solutions of semi-dilute unentangled DNA in extensional flow, including polymer relaxation from high stretch and transient stretching dynamics in flow. For solutions of pure linear polymers, our results show a decrease in average transient chain extension at the same flow strength

compared to dilute solutions. For ring polymers in a background of semi-dilute linear polymers, we observe strikingly large fluctuations in steady-state polymer extension in extensional flow. This intriguing behavior occurs due to the interplay between polymer topology and intermolecular interactions, leading to chain "threading" in flow. Finally, we present recent results on the longest relaxation time of ring polymers in semi-dilute unentangled and entangled solutions consisting of mixtures of linear and ring polymers ranging from equal mixtures to pure solutions of each. For solutions of pure linear polymers, our results show a power-law scaling of the longest polymer relaxation time that is consistent with scaling arguments based on the double cross-over regime, both in the unentangled and entangled regime. For ring polymers, we aim to determine the unique scaling properties that arise to due to the ring topology. Overall, our work aims to provide a molecular-level understanding of the role of polymer topology on bulk rheological properties using single polymer techniques.

Effects of entanglements and crowding on the dynamics of ring DNA

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Unlike most synthetic polymers, DNA naturally occurs in ring form. Ring DNA serves as the genome for prokaryotic cells, and is used widely in molecular biochemistry to store and replicate specific base pair sequences. In the cell, ring DNA is often forced to function in highly entangled states and crowded environments. DNA has also been shown to be a model polymer to elucidate the molecular dynamics arising in entangled polymer systems. Yet, the diffusion and conformational dynamics of ring DNA in highly concentrated systems remain poorly understood. Here, we use fluorescence microscopy, single-particle tracking, and image analysis to track the position, size and shape of single fluorescent-labeled ring DNA molecules diffusing in crowded and entangled systems. We reveal a range of steady-state molecular transport properties and conformational dynamics that are highly dependent on the characteristics and concentrations of the surrounding molecules. We compare ring dynamics to that of their linear counterparts, and specifically explore transport phenomena in ring-linear blends and cell-mimicking crowded environments.

The theory of localization in crumpled interphase chromosomes

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With reptation times of the order of centuries, large chromosomes cannot equilibrate their knot- and link-free topological state. Structural relaxation under this constraint leads to crumpled chain conformations resembling those of long, non-concatenated ring polymers in the melt state. The statistics of crumpled chains differs significantly from the ideal random walk behavior of equilibrated, topologically unconstrained chains under comparable environmental conditions. Here we formulate a generalized Gaussian model for crumpled polymers, which uses as input the chain statistics observed in extensive computer simulations of topologically constrained chains. We then explore the consequences of quenched random localisation to predict statistical aspects of the cell-state specific folding of interphase chromosomes. In particular, we ask why it makes sense to compare the predictions of the annealed ring ensemble to sequence-averaged biological data.

Cyclic polymers: an examination of cyclic purity

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The study of cyclic polymers has been hindered by the presence of trace impurities that in some cases yield significant perturbations in physical properties measurements. In the last 15 years, a number of improvements have been made regarding the synthesis of cyclic polymers, but limitations remain in the ability to both isolate cyclic polymers from non-cyclic impurities and rapidly assess topological purity. Two recent efforts in our labs investigate the presence of impurities in click "ring closure" cyclic polystyrene and zwitterionic "ring expansion" cyclic polyethers. The use of chromatographic techniques, coupled with MALDI-TOF MS analysis, has proven invaluable for identification of trace impurities that provide significant insight into the formation of cyclic impurities.

Separation of cyclic and linear oligo(oxyethylene)s based on kinetically-controlled intercalation into graphite oxide: a calorimetric study

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Large-scale purification of cyclic polymers from linear polymer contaminants remains being a challenging task. The methods most routinely used are solvent fractionation, preparative size-exclusion chromatography and liquid chromatography at the critical conditions. The first method often requires multiple step purification in detriment of the yield, whereas the chromatographic methods are expensive and generate pure cyclic polymer in small scale. Alternative methods include chemical immobilization via selective trapping by end-group reaction at the surface of solid supports [1].

In the present study we provide an alternative to current methods to separate linear and cyclic chains, which does not require of chemical reactions, and which is based on the distinct intercalation kinetics of both architectures into the interlayer space of graphite oxide (GO). As a proof of concept we selected a series of linear and cyclic penta(ethyleneoxide)s and evaluated their kinetic parameters of intercalation in GO by means of in situ x-ray diffraction experiments. Then, we established a calorimetric method to evaluate the separation efficiency of both compounds in GO. We made use of the total absence of glass transition of the intercalated oligomers [2] to monitor the evolution of the glass transition of the non-intercalated liquid as a function of time. This unique property of the intercalated (and confined) phase in GO [2] allowed us to quantify the enrichment of the non-intercalated material in the cyclic component [3]. As a result we obtained fractions enriched in the cyclic component in amounts as high as 99 wt%, demonstrating the potential use of GO as a sieving material for large-scale purification of cyclic polymers contaminated with linear impurities.

[1] Haque, F.; Alegria, A.; Grayson, S.; Barroso-Bujans, F. Macromolecules 2017, DOI: 10.1021/acs.macromol.6b02755.
[2] Barroso-Bujans, F.; Cerveny, S.; Alegria, A.; Colmenero, J. Macromolecules 2013, 46, 7932-7939.
[3] Barroso-Bujans, F.; Alegria, A., submitted.

Microscopic dynamics and threadings in ring polymers: A detailed computer simulation study

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Due to the absence of chain ends and their loop topology, microscopic mechanisms and processes such as reptation through an effective confining tube, contour length fluctuations and constraint release do not directly apply to polymer rings. This has triggered significant research work over the past decade in an effort to elucidate several aspects of the unique properties of this class of polymers with techniques such as small angle neutron scattering (SANS), neutron spin echo (NSE), and pulse-field gradient NMR and rheology.[1-2]

In this work, we will present results from long atomistic molecular dynamics (MD) simulations for the density, microscopic structure, conformation and local and segmental dynamics of pure ring and linear poly(ethylene oxide) (PEO) melts, ranging in molar mass from ~500 g/mol to ~30,000 g/mol.[3] Our simulation results will be compared with recent experimental data for the chain center-of-mass self-diffusion coefficient, the normalized single-chain dynamic structure factor and the viscosity. We have also carried out a detailed normal mode analysis which allowed us to check the degree of consistency of ring PEO melt dynamics with the ring Rouse model. This revealed a strong reduction of the normalized mode amplitudes for the smaller mode numbers, combined with an undisturbed spectrum of Rouse relaxation rates.[3]

In a second step, representative configurations from the accumulated MD trajectories were subjected to a detailed geometric analysis using triangulation and 3-d vector calculus to identify threadings between ring polymers. Our analysis[4] has revealed a variety of single and multiple penetrations in all systems, whose relative number increases with increasing MW. These ring-ring inter-penetrations constitute strong ring-ring topological interactions and persist for times significantly longer than the characteristic ring average orientational relaxation time τ_{ring}. We will show that these interpenetrations, together with the additional ring-linear threadings due to remaining linear impurities, can explain the appearance of slow relaxation modes observed experimentally in entangled rings.[4] Finally, we will highlight recent efforts aimed at computing the rheological properties of ring PEO melts and the dependence of their viscometric functions on ring molecular weight.

[1] M. Kapnistos et al., *Nat. Mater.* **2008**, *7*, 997.
[2] S. Gooßen et al., *Phys. Rev. Lett.* **2014**, *113*, 168302.
[3] D.G. Tsalikis et al., *Macromolecules* **2017**, *50*, 2565-2584.
[4] D.G. Tsalikis, V.G. Mavrantzas, D. Vlassopoulos, *ACS Macro Lett.* **2016**, *5*, 755.

Re-examination of terminal relaxation behavior for high molecular weight ring polystyrenes

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For high molecular weight (M) ring polymers with low contamination of linear chains, recent viscoelastic tests revealed broad terminal relaxation associated with no clear entanglement plateau. This relaxation behavior is qualitatively similar to that deduced from molecular models for entangled ring polymers, but quantitatively different. In this study, the linear viscoelastic relaxation of the high-M ring polystyrene (PS) sample (R-240; M = 244 kg/mol) have experimentally re-examined, especially for two points; the purity of the samples after the viscoelastic test at high T and the molecular origin of the viscoelastic stress. For the first point, the R-240 samples contaminated with linear PS at low but different levels were prepared. The fraction w_L of the linear contaminant after the viscoelastic measurement was ranging from 0.7% to 4.9%, and the extrapolation of the modulus data to $w_L = 0$ gave the data for the "ideally" pure ring melt. This pure ring melt exhibited broad terminal relaxation that started faster but completed slower compared with the model prediction, indicating that the ring relaxation is not well described by the current models even in the absence of linear contaminant. For the second point, rheo-optical measurements were conducted for the R-240 samples with w_L = 4.6 and 1.0%. These samples obeyed the stress-optical rule and their stress-optical coefficient was indistinguishable from that for linear PS samples, revealing that the stress of the ring PS chains reflects the orientational anisotropy of the chains as is the case also for linear chains. The relaxation behavior of the pure ring PS melt is discussed on the basis these findings, with the focus being placed on the ring-ring threading not considered in the models.

Threading Dynamics of Ring Polymer Melts Revealed by Dynamically Constrained Lattice Model

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Topological constraints of ring polymers force themselves to be in a threading configuration, which is believed to be a main reason for abnormally slow diffusion observed in a melt phase. In this work, we construct a lattice model that incorporates threading configurations using dynamic constraints, based on the idea of separation of length scales, and investigate a link between the structural correlation and its dynamic behavior via Monte Carlo simulations. We discover that the hierarchical threading configurations render the whole system to exhibit abnormally slow dynamics before the free translational diffusion process takes place. By analyzing statistical distributions of timescales of threading configurations, we find that the decoupling between internal structural relaxation and diffusion is crucial to understand the threading effects on the dynamics of a ring melt. In particular, in the limit of low threading probability, both the diffusion coefficient D and timescale τ_{diff} exhibit scaling relationships, $D \sim N^{-2}$ and $\tau_{\text{diff}} \sim N^{8/3}$, where N is the degree of polymerization. As N increases, both quantities exhibit more precipitous behaviors, which are qualitatively well described by our mean-field type analysis. Our model also shows a significant breakdown of Stokes-Einstein relation which can be taken as a strong evidence for the topological glass.

Closed Loops: Their Impact on Melt Surface Fluctuations and Surface Segregation in Blends

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Creating cycles in polymer chains has implications for both the surface fluctuations of melts and the thermodynamics of surface segregation in blends. Since surface fluctuations are important for determining wetting/dewetting, adhesion and tribology of thin melt films, we have investigated the variation in their behavior as chain topology is varied from linear to branched to cyclic and bicyclic (8-shaped). As films become thinner the surface fluctuation

dynamics become slower than expected from a hydrodynamic continuum theory (HCT) that works well for sufficiently thick films of unentangled chains. For cyclic chains, this slowing of fluctuations sets in at film thicknesses (relative to R_g) larger than in the case of linear chains. It is also observed that a "residual adsorbed layer" persisting after rinsing away most of the film is notably thicker for the case of the cyclic chain than for its linear analog. Star branched chains display behavior deviating from the HCT at still larger thicknesses. The design of architecture thus presents wide opportunities for engineering surface properties.

If time permits we will consider as well surface segregation in a blend of chains in which the two species differ only in topology, one being linear and the other a ring. Rationalizing the experimental results requires proper theoretical treatment of topologically driven surface segregation, which cannot be described using a conventional surface potential. We report a crossover in the surface segregation of blends of linear and cyclic polymers from control by a universal topological driving force for long chains to control by surface packing for short chains. For a 37k cyclic/linear polystyrene blend the surface is enriched in cyclic chains in quantitative agreement with self-consistent field theory. For a 2k cyclic/linear polystyrene blend the surface is enriched in linear chains, consistent with the Wall Polymer Reference Interaction Site Model theory.

On Segregation of Ring Polymers under Confinement

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High molecular weight linear polymers are heavily entangled in their melts and concentrated solutions, which indicates mutual overlapping and mixing with surrounding polymers. This is true in bulk 3-dimensional space, but the situation is more subtle in confined spaces. For example, a counter trend of segregation would take place in the polymer solutions confined in cylindrical cavity under certain conditions, which might be relevant to the bacterial chromosome segregation. In the presentation, I will first summarize the physics of polymer solution confined in cavity with various aspect ratios. I will then discuss how the result is affected by the topological constraint if the polymers are noncatenated rings based on the idea of topological volume[1-3].

[1] T. Sakaue, Phys. Rev. Lett. 106, 167802 (2011)

[2] T. Sakaue, Phys. Rev. E 85, 021806 (2012)
[3] T. Sakaue and C.-H. Nakajima, Phys. Rev. E 93, 042502 (2016)

Interfacial and topological effects on the glass transition in free-standing polystyrene films

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I will discuss the very recent results of the united-atom molecular-dynamics computer simulations of atactic polystyrene (PS), for the bulk and free-standing films of 2 nm – 20 nm thickness, and for both linear and cyclic polymers comprised of 80 monomers. Simulated volumetric glass-transition temperatures (Tg) [1,2] show a strong dependence on the film thickness below 10 nm [3]. The glass-transition temperature of linear PS is 13% lower than that of the bulk for 2.5 nm-thick films, as compared to less than 1% lower for 20 nm films. Our studies reveal that the fraction of the chain-end groups is larger in the interfacial layer with its outermost region approx. 1 nm below the surface than it is in the bulk. The enhanced population of the end groups is expected to result in a more mobile interfacial layer and the consequent dependence of Tg on the film thickness. In addition, the simulations show an enrichment of backbone aliphatic carbons and concomitant deficit of phenyl aromatic carbons in the interfacial film layer. This deficit would weaken the strong phenyl-phenyl aromatic interactions and, hence, lead to a lower film-averaged Tg in thin films, as compared to the bulk sample. To investigate the relative importance of the two possible mechanisms (increased chain ends at the surface or weakened π-π interactions in the interfacial region), the data for linear PS are compared with those for cyclic PS. For the cyclic PS the reduction of the glass-transition temperature is also significant in thin films, albeit not as much as for linear PS. Moreover, the deficit of phenyl carbons in the film interface is comparable to that observed for linear PS. Therefore, chain-end effects alone cannot explain the observed pronounced Tg dependence on the thickness of thin PS films; the weakened phenyl-phenyl interactions in the interfacial region seems to be an important cause as well [4]. I will also discuss the interface characteristics of polystyrene in free-standing thin films and on a graphite surface simulated employing an explicit all-atom force field [5].

(1) Ediger, M.D.; Forrest, J.A. Dynamics near free surfaces and the glass transition in thin polymer films: a view to the future. Macromolecules 2014, 47, 471-478.
(2) Barrat, J.-L.; Baschnagel, J.; Lyulin, A.V. Molecular dynamics simulations of glassy polymers. Soft Matter 2010, 6, 3430-3446.
(3) Hudzinskyy, D.; Lyulin, A.V.; Baljon, A.R.C.; Balabaev, N.K.; Michels, M.A.J. Strong confinement effects on glass transition temperature in atactic polystyrene films. Macromolecules 2011, 44, 2299-2310.
(4) A. V. Lyulin, N. K. Balabaev, A. R.C. Baljon, G. Mendoza, C. W. Frank and Do Y. Yoon, Interfacial and Topological Effects on the Glass Transition in Free-standing Polystyrene Films J. Chem. Phys., in print (2017).
(5) S. Lee, A. V. Lyulin, C. W. Frank, Do Y. Yoon, Interface Characteristics of Polystyrene Melts in Free-standing Thin Films and on Graphite Surface from Molecular Dynamics Simulations, Polymer, resubmitted (2017)

Dynamics and Relaxation of Linear and Ring Rouse Chains undergoing Reversible End-Association and Dissociation

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For dilute telechelic linear and ring Rouse chains undergoing reversible end-association and dissociation, the time (t) evolution equation was analytically formulated for the subchain bond vector, $\mathbf{u}(n,t;c)$ with n being the subchain index and the index c specifying the chain (c = L and R for the linear and ring chains). The end-association of the linear chain (*i.e.*, ring formation) occurs only when the ends of the linear chain come into close proximity. Because of this constraint for the ring formation, the time evolution equation for $\mathbf{u}(n,t;L)$ of the linear chain was formulated with a conceptually new, two-step expansion method: $\mathbf{u}(n,t;L)$ was firstly expanded with respect to its sinusoidal Rouse eigenfunction, $\sin(p\pi n/N)$ with p = integer and N being the number of subchains *per* chain, and then the series of odd sine modes is re-expanded with respect to cosine eigenfunctions of the ring chain, $\cos(2q\pi n/N)$ with q = integer, so as to account for that constraint. This formulation allowed analytical calculation of the viscoelastic relaxation function of the linear and ring chains. It turned out that the terminal relaxation of the ring and linear chains is retarded and accelerated, respectively, due to the motional coupling of those chains occurring through the reaction. This coupling breaks the ring symmetry (equivalence of all subchains of the ring chain), thereby leading to oscillation of the orientational anisotropy of the ring chain at long t with the subchain index n. Furthermore, the above formulation also enables analytical calculation of the dielectric relaxation function for

the linear and ring chains having non-inverted type-A dipoles. The ring is dielectrically inert, but its motion affects (accelerates and broadens) the dielectric relaxation of the linear chain.

Ring polymers: a local probe for entangling effects

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Small angle neutron scattering was used to study the structure and the entangling state of linear and cyclic polystyrenes of the same length in a blend of a linear matrix during a fast start-up flow. After stretching the samples to Hencky strains up to 2 in a filament stretching rheometer, followed by a fast quenching, strong anisotropic but different two-dimensional patterns were obtained, which are due to an affine deformation of the probe label and non-affine fluctuation parameters arising from topological entangling effects. Rheo-mechanical data in both linear and nonlinear regime were shown to be insensitive and were unable to detect any signature of the architecture of the label. With a modified Warner-Edwards description, the topological confinement is tested and for the linear probe the classical tube diameters are retrieved. Since the concept of tube for a ring polymer does not apply, pure constraint effects with the embedding linear chains are revealed. Mainly transversal motion remains. The smaller transversal values that the ring polymer probes agree with the unrelaxed short-time dynamics modulus before longitudinal relaxations along the tube profile set in for the linear analogue. The results favor the $1/3^{rd}$ loss of modulus between short and long times.

Extensional Rheology of Linear/Ring Polystyrene Blends

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In extensional flow at large Hencky strain, a stress overshoot has been observed for branched polymer melts, including commercial low-density polyethylene melts [e.g. 1, 2] and a model polystyrene melt [3]. The physics behind stress overshoot is not fully understood. However, stress overshoot has never been observed for linear polymer melts. Therefore one hypothesis is that it is related to branch points [3] and probably due to branch point withdrawal [4]. In this work, we report stress overshoot in extensional flow for symmetric linear/ring polystyrene (PS) blends which contain no branch points. The blends are made from 185kg/mol ring PS with weight fraction of 5%, 20%, and 30% in 185kg/mol linear PS, respectively. These blends are dominated by threading of rings by the linear chains, as revealed by linear and nonlinear shear measurements. We show that at fast stretch rates, stress overshoot is observed for all the samples at high Hencky strain values. The stress overshoot is more significant with increasing the fraction of ring PS. For the samples containing 20% and 30% ring PS, the maximum stress during stretching is higher than that for the pure linear PS. This is in agreement with the fact that the zero-shear-viscosity of these two samples is higher than the pure linear sample. Interestingly, no steady state following the overshoot is observed at the experimental time window. The above results suggest that in these blends linear-ring threads are released at large strains in fast extensional flow. The idea of entanglement stripping [5] might be the explanation for the stress overshoot observed here. This study may shed light into the nature of entanglements (linear-ring vs linear-linear).

[1] T. Raible, A. Demarmels, and J. Meissner, Polym. Bull. 1, 397–402 (1979)
[2] H. K. Rasmussen, J. K. Nielsen, A. Bach, and O. Hassager, J. Rheol. 49, 369–381 (2005)
[3] J. K. Nielsen, H. K. Rasmussen, M. Denberg, K. Almdal, and O. Hassager, Macromolecules 39, 8844-8853 (2006)
[4] M. H. Wagner and V. H. Rolon-Garrido J. Rheol. 52, 1049–1068 (2008)
[5] L. G. D. Hawke, Q. Huang, O. Hassager, and D. J. Read , J. Rheol. 59, 995–1017 (2015)

Dynamics of cyclic and linear polymer blends

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The absence of the chain ends in polymer rings results in a compact structure and dynamics distinctly different from most other polymer architectures: Slow lattice animal-like loop displacement are accompanied by fast relaxing subunits (loops) [1]. In blends of ring and linear polymers a tiny amount of linear chains may lead to dramatic changes in viscosity and diffusion properties [2]. Pulsed field gradient (PFG) NMR has proven to be an invaluable tool for monitoring molecular displacements in a broad range of length scales, from below 100 nm up to tens of micrometers at the time scale from tens of milliseconds to a few seconds. Experiments addressing translational diffusion and rheological properties of ring polymers and blends of rings and linear chains using PFG-NMR demonstrate a relatively clear picture for short chains [3,4]. Here, we report a PFG-NMR study of the translational mobility of cyclic poly(ethylene oxide) chains and their blends with linear matrices of different compositions. We focus on both, non-entangled and entangled linear matrix systems to elucidate the effect of topological interactions on the ring and chain dynamics. We demonstrate the effective combination of high resolution neutron spin-echo (NSE) spectroscopy that probes molecular dynamics up to hundreds of nanoseconds and explores the intrachain dynamics, with PFG-NMR operating on timescales several orders of magnitude longer measuring centre-of-mass diffusion. In particular, we focus on the long-range "threading" effects of the polymer matrix on ring dynamics in the blend.

[1] S. Goossen, A. R. Brás, M. Krutyeva, M. Sharp, P. Falus, A. Feoktystov, U. Gasser, W. Pyckhout-Hintzen, A. Wischnewski, D. Richter, Phys. Rev. Lett. 113, 2014, 168302
[2] J. Halverson, G. S. Grest, A. Y. Grosberg, K. Kremer, Phys. Rev. Lett. 108 (2012) 038301
[3] S. Nam, J. Leisen, V. Breedveld and H. W. Beckham, Polymer, 2008, 49, 5467–5473
[4] S. Nam, J. Leisen, V. Breedveld and H. W. Beckham, Macromolecules, 2009, 42, 3121–3128.

Unexpected Self-Diffusivity of Ring Tracers in Linear Matrices

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Equilibrium Monte Carlo simulations of large ring and linear probes in matrices of linear polymers, where the molar mass of the matrix chains is varied, show contrasting trends. As the matrix chain length is increased, the diffusivity of the linear probe decreases monotonically, while that of the ring probe varies non-monotonically. It initially increases with matrix molar mass, reaches a maximum, and then decreases with further increases in molecular weight. The phenomenon is fairly robust: it persists in tracer simulations, in which ring-ring interactions are completely eliminated. Differences in the short-time dynamics, and the entanglement structure of the linear and ring probes are analyzed. The role that threading plays is also investigated, by performing simulations of ring-linear blends in which the uncrossability of ring and linear polymer contours is switched on (non-crossing), or artificially turned off (crossing). The analysis suggests that the smaller matrix chains are able to infiltrate the space occupied by the ring probe more effectively, which is dynamically manifested as a larger frictional drag per ring monomer.

Microscopic dynamics and topology of polymer rings immersed in a host matrix of longer linear polymers: Results from a detailed molecular dynamics simulation study and comparison with experimental data

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Present-day research in the dynamics of ring polymers varies from experimentally sophisticated measurements of properties to new theoretical developments beyond the animal picture and computer simulations based upon either detailed, atomistic models or simpler but useful coarse-grained representations. Motivated by recent state-of-the art experimental measurements,[1] we have performed exhaustive molecular dynamics simulations of melt systems consisting of a small number of long ring poly(ethylene oxide) (PEO) molecules immersed in a host matrix of linear PEO chains and have studied microscopic dynamics and

topology as a function of molecular length of the host linear chains.[2] Consistent with neutron spin echo spectra [1], we have observed that the segmental dynamics of the probe ring molecules is controlled by the length of the host linear chains. In matrices of short, unentangled linear chains, probe rings exhibit a Rouse-like dynamics, and the spectra of their dynamic structure factor resemble those in their own melt. In contrast, in matrices of long, entangled linear chains, their dynamics is drastically altered. The corresponding dynamic structure factor spectra exhibit a steep initial decay for times up to the corresponding entanglement time τ_e of linear PEO at the same temperature and then approach constant, plateau values which are different for different wave-vectors and depend on the length of the host linear chains. A novel geometric analysis[3] reveals that rings suffer strong threadings by the host linear chains (in most cases, each ring is simultaneously threaded by a large number of linear chains), explaining the strong dynamic coupling between rings and linear chains.

[1] S. Gooßen, M. Krutyeva, M. Sharp, A. Feoktystov, J. Allgaier, W. Pyckhout-Hintzen, A. Wischnewski and D. Richter, Phys. Rev. Lett. 115, 148302, 115 (2015).
[2] G. D. Papadopoulos, D. G. Tsalikis and V. G. Mavrantzas, Polymers 8, 283 (2016).
[3] D. G. Tsalikis, V. G. Mavrantzas and D. Vlassopoulos, ACS Macro Letters 5, 755 (2016).

Viscoelastic properties of dumbbell-shaped polystyrenes in bulk

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In this study, we prepared dumbbell-shaped polystyrenes (PS) where rings are attached on both chain ends of a linear chain by anionic polymerization and interaction chromatography (IC) fractionation methods, and examined their viscoelastic properties in bulk. Two dumbbell PS samples, D-30/120/30 and D-30/240/30, possessing the same ring size (MR = 30×103) and different length of central linear chains (ML = 120 and 240×103), were successfully prepared. In dynamic oscillatory measurements, both dumbbell PS samples exhibited an extremely long entanglement plateau with essentially the same height of plateau modulus as linear PS, and do not reach the terminal relaxation region in our measurement range. This result suggests that the dumbbell chain spontaneously form intermolecular ring-linear penetration (i.e., one dumbbell chain threads the ring part of other molecules) as well as the normal linear-linear entanglements. In stress relaxation measurements, two dumbbell PS samples exhibit considerably slower terminal relaxation than high-M linear PS (M = 1.0×106). Moreover, a clear difference between D-30/120/30 and D-30/240/30 was observed in long t regime, i.e., D-30/240/30 exhibited much slower decay of the stress relaxation modulus G(t) than D-30/120/30. We discussed the relaxation behavior of dumbbell chains considering two mechanisms, i.e., the release of intermolecular threading and the motion the dumbbell molecule itself after release the threading.

Conformation of Ring Polystyrenes in Bulk and Solution

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The conformation of ring polymers in bulk and solution has gathered scientific interest because the topological constraints of ring chains (i.e., the absence of chain ends) definitely

affect their conformation. Recent theoretical and simulation studies[1,2] proposed that the ring chains in bulk exhibit the compact structures and their Flory scaling exponent ν follows the crossover from $\nu = 1/2$ (Gaussian) to $\nu = 1/3$ (collapsed) through $\nu = 2/5$ with increasing the ring chain lengths. Experimentally, Arrighi et al.[3] examined the radius of gyration R_g of poly(dimethylsiloxane) (PDMS) rings in bulk by using small-angle neutron scattering (SANS), and revealed that the rings exhibit the relationship $R_g \propto M_w^{0.42}$. However, they did not mention the details of sample characters (i.e., purity) and their samples, and their samples did not cover much wide molecular weight range. In this study, a series of hydrogenous and deuterated ring polystyrene (PS) samples covering a wide range of molecular weight ($20 \leq 10^{-3}M_w \leq 330$) with high purity were prepared, and their conformation in bulk and solution was examined by using SANS. We estimated R_g of the rings in bulk by Guinier analysis and discussed M_w dependence of R_g. Moreover, in the same manner, R_g of ring solutions was estimated, and their concentration c dependence was discussed.

(1) Sakaue, T. Phys. Rev. Lett. 2011, 106, 167802.
(2) Halverson J. D. et al. J. Chem. Phys. 2011, 134, 204904.
(3) Arrighi V. et al. Macromolecules 2004, 37, 8057.

Designing a topological filter: Transport of linear and ring polymers in micro-fluidic devices

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Ring polymers are an important class of biological and synthetic macromolecules. Due to the lack of free ends, they are expected to show distinct behaviour compared to their linear counterparts, as for example with respect to migration, rheology or disentanglement. This simulation study aims at adressing the question, whether those two are transported distinctly in micro-fluidic devices. Since many biological ring polymers are in aqueous solution, hydrodynamics is taken into account by a simulation method called Multi-Particle Collision Dynamics. Although a bare slit channel is not sufficient to separate them for all investigated rigidities, we propose a filter by decorating the channel walls with attractive spots. In doing so, ring polymers show up to an order of magnitude increase in transport compared to linear

chains. Moreover, those spots induce a reorientation of ring polymers close to the walls enabling them to perform a tank-treading motion along the patches. At the same time, and for intermediate driving pressure gradients along the channel, a crossover regime appears, in which the linear chains are transported faster than the rings due to incessant adsorption-desorption processes that are active for the former but absent for the latter. Our work demonstrates the possibility to employ micro-fluidic devices in order to achieve separation of topologically distinct states of polymeric macromolecules.

Polymer Ring Brushes investigated: a DPD simulation study

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Grafting polymers to a surface is of interest to many physiyochemical areas and applications, such as colloid stabilisation, wetting, adhesion, chromatography, biocompatibility and others. Recent experimental methods allow the production of well-defined surface-grafted polymer nanoparticle systems without free chain-ends [1], i.e., grafted polymer loops or rings. In the present investigation, equivalent situations are studied making use of computer simulations based on Dissipative Particle Dynamics [2,3] (DPD).

DPD is a highly efficient, coarse grained, method smoothly covering length scales from several nanometers up to the mesoscale region. In order to reproduce the behaviour of adsorbed polymers an attractive interaction between one (or in case of loops both) chain end(s) and the surface, represented by a soft wall, is introduced as well. Aim of the study is the comparison of properties of loops and rings to those of linear chains as functions of surface coverage free chain concentration and inter particle distance i.e : from isolated particles to polymers in slit like confinement.

The results show that with increasing grafting density, loops and rings become more and more rodlike in structure and increase the layer thickness in the same way as linear chains do. A rise in concentration of free polymer chains results into a compression of the brush. Decreasing the inter particle distance leads to an increase in pressure exerted by the grafted polymer on the wall. A comparioson of the structural effects and possible interpenetration for linear chains and rings will be shown in detail.

[1] R. Rotzoll, P. Vana, J. Polym. Sci. Part A: Polym. Chem. 46, 7656 (2008)

[2] R.D. Groot, P.B. Warren, J. Chem. Phys. 107, 4423 (1997)
[3] M.M. Nardai, G. Zifferer, J. Chem. Phys. 131, 124903 (2009)

Linear and nonlinear shear rheology of ring melts and ring-linear mixtures

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We present systematic linear and nonlinear shear rheological data with selected well-characterized purified polystyrene rings (with Z~11 entanglements) and their mixtures with linear polymers of different molar masses and high fractions. Our main findings are: (i) confirmation of the slow mode in pure rings; (ii) rings act as viscosity enhancers of entangled linear polymers; (iii) entangled rings exhibit much weaker shear thinning compared to their linear analogues. Their thinning slope of about -0.6 is confirmed by MD simulations ; (iv) in the accessible range of experimental shear rates (using cone-partitioned plate setup) there is no rheological signature of tumbling for rings, akin to linear chains ; (v) preliminary data on normal stresses suggest that the ratio N2/N1 for rings is larger compared to linear polymers.

Synthesis of regioregular cyclic poly(glycidyl phenyl ether)

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Cyclic polymers have proven to display altered physical and self-assembly properties respect to their linear counterparts. In particular, control over stereochemistry in cyclic polymers has shown to have impact on the structure of stereocomplexes. For instance, the formation of polypseudorotaxane-type" structures has been proposed in cyclic+linear stereoregular poly(methyl methacrylate)s, which depart from the triple-helix stereocomplexes observed for their linear analogs.1 Isoregic structures are generated by the formation of head-to-tail or tail-to-head linkages during polymerization. In the ring-opening polymerization (ROP) of

monosubstituted epoxides, regio-errors [head-to-head and tail-to-tail] can frequently occur. For that reason, in ROP, regio-control is requisite prior to stereo-control.

Poly(glycidyl phenyl ether) (PGPE) is obtained from ROP of glycidyl phenyl ether (GPE). We previously observed that ROP of GPE with B(C6F5)3 through a ring-expansion strategy leads to the formation of aregic cyclic PGPE.2 To generate isoregic cyclic structures, the ring-closure strategies offer much greater versatility.

In this study we explore different strategies to synthesize regioregular cyclic PGPE. We first obtained linear isoregic α(ω)-azido-ω(α)-alkyne-PGPEs and then proceeded to cyclization by using copper-catalyzed azide-alkyne "click" reactions. To synthesize linear PGPE we used anionic ROP initiators (tetrabutyl ammonium azide and alcohol/phosphazene) and performed end-group modification. We investigated the effect of polymer concentration, solvent and feed rate to find the optimum conditions for the synthesis of cyclic PGPE. We used strategies such as "click scavenging" of linear impurities with alkyne(azido)-modified-silica gel, and post-modification reactions to provide evidence of topological purity. The regicity of synthesized polymers was evaluated by 13C NMR and the topological purity by MALDI-ToF MS. Techniques such as 1H NMR, FTIR, GPC-MALS and DSC were routinely used to characterize the obtained products.

(1) Ren, J. et al. Angew. Chem. Int. Ed. 2014, 53, 459
(2) Gambino, T. et al. Macromolecules 2016, 49, 1060

Ring shaped polymers via anionic polymerization

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Ring-shaped polymers have received considerable attention due to their unique endless molecular topology. The absence of free chains end restricts their topology and affects their macromolecular motion. Thus, ring polymers possess properties that significantly distinguish them from their linear counterparts. In this work, monodispersed ring and linear polystyrene

(PS) with identical molar mass were synthesized by anionic polymerization. Different series of PS samples (linear precursor and ring polymer of the same molar mass) were prepared, with an average molecular weight of the linear precursor ranging from 5K to 148K. The approach followed for the formation of ring shaped PS is based on a bimolecular ring closer reaction under extreme dilute conditions. The method involves first the formation of living PS dicarbanion using naphthalene potassium as initiator. Next, part of the 'living PS dianion' reacts with a bifunctional electrophile (the dibromo-p-xylene), to form ring PS via an intermolecular coupling. The linear PS precursor was obtained by purring methanol in the remaining living PS chains. All the reactions were carried out in tetrahydrofuran (THF), a good solvent for PS, to obtain unknotted ring PS. The linear PS and the crude product after cyclization were characterized by size exclusion chromatography (SEC). After ring closer reaction the isolated product was purified by fractional precipitation to remove linear chains that were deactivated during the synthesis and PS of higher molecular weight formed by intermolecular coupling. By fractional precipitation nearly pure ring PS was obtained. Finally, the samples were further purified by liquid chromatography at the critical condition (LCCC), to remove any traces of the linear precursors.

The Intrinsic Mechanical Nonlinearity $3Q_0$ of Linear Polymer Melts varying Mn, Monomer and PDI

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Medium amplitude oscillatory shear (MAOS) in combination with Fourier Transformation of the mechanical stress signal (FT rheology) was utilized to investigate the influence of molecular weight, molecular weight distribution and the monomer on the intrinsic nonlinearity $^3Q_0(\omega)$. Nonlinear master curves of $^3Q_0(\omega)$ have been created, applying the time-temperature superposition (TTS) principle. These master curves showed a characteristic shape with an increasing slope at small frequencies, a maximum $^3Q_{0,max}$ and a decreasing slope at high frequencies. $^3Q_0(De)$ master curves of monodisperse polymers were evaluated and quantified with the help of a semi-empiric equation, derived from predictions from the pom-pom and molecular stress function (MSF) models. This resulted in a monomer independent

description of the nonlinear mechanical behavior of linear, monodisperse homopolymer melts, where $^3Q_0(\omega,Z)$ is only a function of the frequency ω and the number of entanglements Z. For polydisperse samples, $^3Q_0(\omega)$ showed a high sensitivity within the experimental window towards an increasing PDI. At small frequencies, the slope of $^3Q_0(\omega)$ decreases until approximately zero as a plateau value is reached, starting at a PDI around 2 and higher.