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## Stress maximum and steady extensional flow of branched polymer melts

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Monday 11:15 Founders Ballroom A

SI4

**Microrheology of phospholipid monolayers at the air-water interface**KyuHan Kim<sup>1</sup>, Siyoung Q. Choi<sup>1</sup>, Joseph A. Zasadzinski<sup>2</sup>, and Todd M. Squires<sup>1</sup><sup>1</sup>Chemical engineering, University of California Santa Barbara, Santa Barbara, CA 93106, United States; <sup>2</sup>Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, United States

We report systematic measurements of the rheological properties of phospholipid monolayers at an air-water interface. Using microfabricated, ferromagnetic microbuttons as new rheological probes, we have measured both the linear and nonlinear viscoelastic responses of phospholipid monolayers as a function of both surface pressure and frequency. Visualization of the interfacial monolayers using fluorescence microscopy revealed that the interlocked, spiral liquid crystalline domains give rise to a viscoelastic solid response, analogous to a two-dimensional emulsion. The measured viscoelastic moduli qualitatively agreed with predictions based on a two-dimensional concentrated emulsion model. In addition, small amounts of cholesterol added to the phospholipids dramatically changed the domain structure as well as rheological responses of the monolayers. The observed rheological phenomena have important implications for replacement human lung surfactants in which the role of cholesterol remains hotly debated.

Monday 11:40 Founders Ballroom A

SI5

**Phases and phase transitions of a phosphatidylethanolamine monolayer studied by interfacial active microrheology**Prajnaparamita Dhar<sup>1</sup> and Joseph A. Zasadzinski<sup>2</sup><sup>1</sup>Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045, United States; <sup>2</sup>Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, United States

The reorientation of a magnetic Nickel nanorod was used to study the surface viscosity of a DiMyristoyl PhosphatidylEthanolamine (DMPE) monolayer at the air-water interface. Surface viscosity and surface pressure were measured as a function of the molecular area. Our results indicate that the surface viscosity undergoes a sudden order of magnitude change at the surface pressure corresponding to a phase transition from a liquid expanded (LE)-liquid condensed (LC) coexistence phase to a liquid condensed (LC) phase. On further increase of surface pressure, the change in surface viscosity is gradual within the LC region. Further, while no measurable elasticity is detected in the LC region, onset of elasticity is noted at the surface pressure corresponding to the LC-Solid(S) transition previously recorded using synchrotron X-ray scattering. This indicates that the solid phase in the monolayer is primarily elastic. The increased sensitivity of our measurements is primarily due to the nanometer dimensions of our probe. Therefore, we conclude that increased sensitivity of interfacial microrheology can be used as a useful tool to monitor changes in the lateral molecular organization in phospholipid films.

**Symposium MB****Rheology of Polymer Melts and Blends**

Organizers: Joao Maia and Avraam I. Isayev

Monday 10:00 Founders Ballroom B

MB1

**Stress maximum and steady extensional flow of branched polymer melts**Qian Huang<sup>1</sup>, Anne L. Skov<sup>1</sup>, Henrik K. Rasmussen<sup>2</sup>, David M. Hoyle<sup>3</sup>, Thomas C. McLeish<sup>3</sup>, Oliver Harlen<sup>4</sup>, David Hassel<sup>5</sup>, Tim D. Lord<sup>5</sup>, Malcolm R. Mackley<sup>5</sup>, and Ole Hassager<sup>1</sup><sup>1</sup>Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark; <sup>2</sup>Department of Mechanical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark; <sup>3</sup>Department of Chemistry, University of Durham, Durham, United Kingdom; <sup>4</sup>Department of Mathematics, University of Leeds, Leeds, United Kingdom; <sup>5</sup>Department of Chemical Engineering, University of Cambridge, Cambridge, United Kingdom

A stress maximum during start-up of kinematically steady extensional flow was reported by Meissner in 1985 for low density polyethylene (LDPE) [Meissner 1985]. Subsequently observations of a steady stress following a stress maximum was reported for two LDPE melts (Lupolen3020D and Lupolen1840D) [Rasmussen et al., 2005]. Steady stress following a stress maximum has also been reported for a model branched (Pompom) polystyrene of known architecture [Nielsen et al., 2006]. However the rheological significance of the stress maximum as well as the existence of steady flow conditions following the maximum is still a matter of some debate [Wang 2009].

We here report observations of stress in extensional flows observed in a Filament Stretching Rheometer (FSR) [Bach et al. 2003] and a Cross-Slot Extensional Rheometer (CSER) [Auhl et al. 2011]. The FSR describes the transient stress in start-up of kinematically steady flow, while the CER describes kinematically steady flow. The steady stress values measured by the FSR after the stress maximum compare favorably with the steady stress values observed in the CER thereby giving credence to both methods. To cast further light upon the rheological processes involved in the stress maximum we report measurements of stress relaxation and reverse flow before and after the stress maximum. The measurements reveal a loss of elasticity associated with the maximum.

References: Meissner, J. (1985), Chem. Engr. Commun., 33:159-180. Bach, A., et al. (2003), J. Rheol., 47:429-441. Nielsen, J. K., et al., (2006), Macromolecules, 39(25):8844-8853. H.K.Rasmussen et al. (2005) J. Rheol. 49(2), 369-381. Y. Wang and S-Q. Wang, J. Rheol.(2009) 53, 1389-1401. D. Auhl et al. J. Rheol. (2011), 55, 1-XXX (in press)

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Monday 10:25 Founders Ballroom B

MB2

**Molecular weight and rate effects in uniaxial extension of polymer melts**

Shiwang Cheng and Shi-Qing Wang

*Department of Polymer Science, University of Akron, Akron, OH 44325, United States*

A previous PTV study of SBR melts [Macromolecules 42, 6261 (2009)] has indicated strong macroscopic motions after step shear, which suggest that the elastic yielding resulted in localized breakdown of the entanglement network. We carry out a systematic parallel study to determine how similar nonlinear responses may occur upon uniaxial extension of the entangled polymer melts. We will show whether the previously observed [Phys. Rev. Lett. 99, 237801 (2007)] specimen breakup after step extension can occur involving Hencky rate lower than the Rouse relaxation rate and can show up only after a period longer than the Rouse time.

Monday 10:50 Founders Ballroom B

MB3

**What and where is the strain hardening and softening**

Shi-Qing Wang, Yangyang Wang, Hao Sun, and Gengxin Liu

*Department of Polymer Science, University of Akron, Akron, OH 44325, United States*

It is commonly accepted today that some entangled polymer melts show "strain hardening" in uniaxial extension but only strain softening in simple shear. A famous example is LDPE, which was described as showing strain hardening in extension and softening in shear (Phys. Today, August 2008, p. 40). We demonstrate that true strain hardening in non-crystalline melts can only occur in the limit of finite chain extensibility, often leading to rupture. Much of strain hardening discussed in the literature on extensional rheology of polymeric liquids arises from a straightforward geometric compactification that has no other physical meaning. This geometric exaggeration of the true stress is greater when the sample resists more to yielding, i.e., when it can be stretched more before the extension ends in either non-uniform stretching (necking) or specimen failure. We found no true strain hardening for commercial LDPE. Moreover, in the nonlinear regime, LDPE specimen never reaches the point of fully developed flow state before it breaks up. The same is true for most linear melts as well. Thus, it is never really instructive and insightful to represent the mechanical response in terms of the Cauchy (true) stress.

Monday 11:15 Founders Ballroom B

MB4

**Microscopic theory of the dynamic tube confinement potential for entangled liquids of rigid macromolecules**

Daniel M. Sussman<sup>1</sup> and Kenneth S. Schweizer<sup>2</sup>

*<sup>1</sup>Department of Physics, University of Illinois, Urbana, IL 61801, United States; <sup>2</sup>Dept. of Materials Science, University of Illinois, Urbana, IL 61801, United States*

We present a first-principles theory of the slow quiescent dynamics of a solution of infinitely thin, non-rotating rods. As objects with trivial equilibrium structure, entanglement dynamics are determined solely by bond uncrossability and macromolecular connectivity. Our work builds on the theory of Szamel, which exactly enforces uncrossability at the two-rod level in conjunction with a self-consistent renormalization to account for many-particle effects. This approach predicts the emergence of tube localization and long-time reptative diffusion above a critical density, consistent with simulations and the Doi-Edwards asymptotic scaling laws. The dynamic confinement potential for lateral motion is constructed based on local equilibrium and nonlinear Langevin equation ideas. In contrast with the usual tube model, distinct anharmonicities are predicted that severely soften (but do not destroy) the transverse confining forces. The spatial nature of the confinement potential is analyzed in detail, and shown to quantitatively agree with recent experiments on entangled F-actin solutions that observe highly nongaussian features in the transverse displacement distribution (long exponential tails). The theory also allows for an investigation of the strong effect of orientational alignment on tube confinement and dynamics, as relevant to rods under strong flows or quiescent nematic liquid crystals. Finally, our approach is extended to other macromolecular architectures. For solutions of non-reptating rigid crosses we propose rare local density fluctuations on the polymer size scale control macroscopic transport and result in an exponential decay of the diffusion constant with density, in agreement with recent simulations. Inspired by primitive paths ideas, a mapping between the rigid macromolecules and flexible chains/stars is proposed. This allows ab initio predictions to be made for the tube diameter, critical degree of entanglement, and transport properties of chain polymer solutions and melts.

Monday 11:40 Founders Ballroom B

MB5

**Microscopic theory of nonlinear rheology, relaxation and yielding in entangled polymer liquids**

Kenneth S. Schweizer<sup>1</sup> and Daniel M. Sussman<sup>2</sup>

*<sup>1</sup>Dept. of Materials Science, University of Illinois, Urbana, IL 61801, United States; <sup>2</sup>Department of Physics, University of Illinois, Urbana, IL 61801, United States*

We have developed a first-principles theory of the entanglement dynamics of a solution of infinitely thin, non-rotating rods based solely on bond uncrossability and macromolecular connectivity. Tube localization, reptation, and the full dynamic confinement potential under quiescent