

SYMPOSIUM CC

Complex Fluids and Polymers

November 29 – December 3, 1999

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* Invited paper

SESSION CC1:

Chairs: David A. Hoagland and David J. Pine
Monday Morning, November 29, 1999
Salon J/K (M)

8:30 AM *CC1.1

POLYELECTROLYTE ELECTROPHORESIS IN AQUEOUS SOLUTIONS CONTAINING ONLY SIMPLE ELECTROLYTE AND NEUTRAL POLYMER. David Hoagland, Margaret Starkweather, M. Muthukumar, Cindy Welch, Univ of Massachusetts, Amherst, MA.

The electrophoretic separation of polyelectrolytes, an analytical and preparative procedure that plays a crucial role in modern molecular biology, has traditionally been performed in crosslinked gels. However, dilute and semidilute neutral polymer solutions, which lack a permanent pore structure, often separate polyelectrolytes by chain length as effectively as gels. To understand how these separations arise, we have been investigating the electrophoretic motion of polyelectrolytes in both free solution (i.e., in aqueous electrolyte only) and in dilute solutions of a monodisperse neutral polymer. In the free solution environment, we recently discovered an unexpected maximum of mobility with respect to chain length in the oligomer range for flexible polyelectrolytes. At higher molecular weight, where this dependence on chain length disappears, polyelectrolyte motion remains poorly predicted by any theory; here, we have performed systematic experiments to better understand how the mobility depends on ionic strength and charge density. Extending these experiments to environments containing a dilute concentration of neutral polymers, we have performed a systematic set of experiments varying polyelectrolyte and neutral polymer chain length. The best separations are noted with the two species possess nearly the same chain length. We believe the dominant mechanism behind the separation is transient formation of binary complexes between polyelectrolyte and neutral polymer; these entangled complexes relax in the electric field by pulley-like dynamics of the two chains.

9:00 AM CC1.2

THERMOTHICKENING POLYMERS AS NEW MATRICES FOR HIGH THROUGHPUT DNA SEQUENCING. Jean-Louis Viovy, Jan Sudor, Institut Curie, Paris, FRANCE; Dominique Hourdet, ESPCI, Paris, FRANCE.

The explosive development of large-scale genome projects puts a strong demand on DNA sequencing. The new generation of sequencers uses the electrophoretic separation of labeled DNA fragments inside large arrays of narrow-bore capillaries. We developed a new family of separation matrices, based on the thermothickening properties of specially designed and synthesized polymers. Thanks to this property, the separation medium can be easily replaced between each separation in the fluid state, and presents optimal sieving properties at the temperature at which separation occurs. Comparison with conventional matrices will be provided, and the correlation between structural, rheological and sieving properties will be discussed.

9:15 AM CC1.3

ULTRASENSITIVITY OF LIVING POLYMERS: THERE ARE NO LINEAR PERTURBATIONS. Ben O'Shaughnessy, Dept Chemical Engineering, Columbia University, New York, NY; Dimitrios Vavylonis, Dept Physics, Columbia University, New York, NY.

Living polymers grow by reversible addition of monomers to the ends of "live" chains. We study theoretically the dynamics of living polymers whose equilibrium is established within experimental timescales. The dynamical response of α -methylstyrene, which belongs to this class, has recently been the focus of systematic experimental studies¹. In equilibrium the molecular weight distribution (MWD) is the exponential Flory-Schultz distribution with mean \bar{N} , while the free monomer concentration reaches a value such that depolymerization and polymerization rates delicately balance. We find that any apparently small perturbation of the system, e.g. a small temperature jump $\delta T/T \approx \epsilon$ ($\delta T =$ few degrees for α -methylstyrene), strongly disturbs this balance; there is no such thing as a linear perturbation. We find that relaxation occurs in 3 stages: (1) Uniform translation of the MWD on a timescale $\sim \bar{N}$ during which the monomer concentration and \bar{N} relax. (2) Recovery of the depleted region of the MWD on a timescale $\sim \epsilon^2 \bar{N}^2$. (3) a truly linear diffusive regime during which the width of the MWD and higher moments relax on a timescale $\sim \bar{N}^2$. We propose experiments in which free initiator concentration be monitored (chains of length unity) as a non-invasive method to observe the above dynamical episodes which, unlike current methods avoid destroying the sample. 1. Zhuang et al. *Physica A* **244** 522 (1997).

9:30 AM CC1.4

AGGREGATION STATE OF LIVING POLYMERS.

Amalie Frischknecht, Scott T. Milner, Exxon Research and Engineering Co., Annandale, NJ.

Although living anionic polymerizations using organolithium compounds have long been established for synthesizing a great variety of polymers, the chain growth mechanism is still not well understood. Recent scattering experiments on living polymers with butadienyllithium and styryllithium head-groups have shown that these species self-assemble into various aggregation states, including both intermediate-sized oligomers and much larger scale aggregates with sizes of at least 100 nm. We investigate theoretically the equilibrium aggregation state of polystyrene chains with butadienyllithium headgroups. We have calculated binding energies of the headgroups for various proposed structures of the aggregates, using semi-empirical and density functional theory quantum chemistry packages. The aggregates are sufficiently dense for the polymer chains to follow polymer brush behavior, so that there is an increasing entropic penalty as the chain length increases. We calculate the stretching energies of the chains, including realistic parameters for polystyrene, using a numerical solution to the mean-field equations developed by Scheutjens and Fler. These elements allow us to explore the dependence of the equilibrium aggregation state on chain length and polymer concentration.

10:15 AM *CC1.5

Abstract Withdrawn.

10:45 AM *CC1.6

SHEAR THICKENING IN WORMLIKE MICELLAR SOLUTIONS. D.J. Pine, J. Politsch, Y.T. Hu, Dept of Chemical Engineering, Univ of California, Santa Barbara; J. Goveas, Dept of Chemical Engineering, Rice Univ.

Dilute and semidilute solutions of wormlike micelles become very viscous over a time period of minutes when subjected to shear flow above a certain critical stress. Light scattering microscopy measurements indicate that the shear thickening is associated with the formation of a dense viscous or gel-like phase which forms on the inner cylinder of a Couette cell, where the stress is greatest. Under constant applied stress, the system exhibits coexistence of the gel-like phase with the fluid phase for all flow conditions. By contrast, under constant applied shear rate, the system is unstable for a range of stresses just above the critical stress. The data compares favorably with a phenomenological model recently developed by Goveas and Pine.

11:15 AM CC1.7

A MODEL FOR SHEAR-THICKENING. Jacqueline L. Goveas, Rice Univ, Dept of Chem Engr, Houston, TX.

We present a simple phenomenological model which exhibits shear-thickening behavior. We consider a species in solution which undergoes reaction under an applied flow, to form an insoluble "gel". By writing an equation of motion for the height of this gel, as a competition between a stress-dependent reaction which creates gel, and a breaking reaction which destroys the gel, we are able to obtain a non-monotonic stress-shear rate curve under controlled stress conditions. Under controlled strain conditions, the stress-shear rate curve is monotonic and discontinuous. These results are in qualitative agreement with experimental data on worm-like micellar solutions by Pine et al.

11:30 AM CC1.8

PHASE SEPARATION OF MODEL FLUIDS IN COMPLEX GEOMETRIES. Peter D. Olmsted, Ovidiu Radulescu, Dept of Physics and Astronomy, University of Leeds, UNITED KINGDOM; C.-Y. David Lu, Dept of Physics, National Central University, TAIWAN.

Wormlike micelles under shear flow display behavior reminiscent of equilibrium phase transitions, including *phase coexistence*, *metastability* and *nucleation*. We present calculations for a cartoon model of wormlike micelles, the Johnson-Segalman (JS) model with an added diffusion term to resolve interfaces. Unlike the more realistic reptation-reaction equations of Cates *et al.*, the JS model allows for relatively efficient computation of qualitative results associated with complicated geometries, kinetics, and inhomogeneous behavior. We solve the model in the Couette geometry and find a variety of metastable states and kinetic signatures, and provide qualitative predictions as a function of cell curvature. We comment on the behavior in Poiseuille flow.

11:45 AM CC1.9

BRANCHED AND CLOSED-LOOPED WORMLIKE MICELLES OF SURFACTANT OLIGOMERS. Martin In, Complex Fluids Laboratory, CNRS-Rhodia, Cranbury, NJ.

Cationic surfactant oligomers (dimer, trimer and tetramer of DTAB) form wormlike micelles which endcap energy is determined by the oligomerization degree. While DTAB does not form wormlike micelles in aqueous solutions, its dimer (gemini) 12-3-12 forms micelles which grow without any additional salt. Living polymers of 12-3-12 behave as polyelectrolytes and show a range of concentration where they do overlap but are not yet entangled. The temperature dependence of the onset concentration of entanglement determined by rheology provides a measure of the end cap energy. In trimer 12-3-12-3-12 solutions, the end cap energy of the wormlike micelles is twice as high and very long but also branched micelles are observed by cryo-TEM. Their rheological behavior is studied by dynamic measurements in the linear regime. The branching point density is determined from the enhancement of elasticity as compared to the dimeric system. The end cap energy of the tetramer 12-3-12-4-12-3-12 micelles is high enough to allow the formation, at low concentration, of a dominant fraction of closed-looped wormlike micelles. Their contour length distribution, observed by cryo-TEM over a large population, is peaked and positively skewed, as expected from the ring closure probability for worm chains. From the length distribution the persistence length of the wormlike micelles is determined.

SESSION CC2:

Chairs: Andrey V. Dobrynin and Steve Granick
Monday Afternoon, November 29, 1999
Salon J/K (M)

1:30 PM *CC2.1

SCALING THEORY OF HYDROPHOBICALLY MODIFIED POLYELECTROLYTES. Andrey V. Dobrynin, Michael Rubinstein, Department of Chemistry, University of North Carolina, Chapel Hill, NC.

The existence of 'tunable' interactions in solutions of associative polymers provides a convenient control of their physical properties. This feature alone makes associative polymers extremely valuable for a number of industrial applications ranging from rheology modifiers for coating to flocculents for waste-water treatment. We have developed the scaling theory of the solution of charged associative polymers consisting of a polyelectrolyte backbone bearing the hydrophobic side chains. In the aqueous solutions the hydrophobic blocks associate forming the aggregates which topology changes with polymer concentration. At concentrations below the overlap concentration, these associations are predominantly intramolecular. At higher polymer concentrations, intermolecular associations become more probable. The change in the topology of aggregates is reflected in the unusually strong concentration dependence of the zero shear viscosity. The effects of the added salt on the rheological properties of the solutions are also discussed.

2:00 PM CC2.2

IONIC ASSOCIATIONS IN ACID-CONTAINING COPOLYMERS. Brian Kirkmeyer, Jonathan Laurer, Karen Winey, Univ of Pennsylvania, Dept of Materials Science, Philadelphia, PA.

Annular dark field scanning transmission electron microscopy has been used to directly determine the size, size dispersity, and shape of ionic aggregates in a variety of acid-containing copolymers. In a semi-crystalline system, the ionic aggregates are nearly spherical and monodisperse with diameters approximately 2nm. In amorphous copolymer systems, the ionic aggregates exhibit a variety of shapes, size, and spatial uniformity. In a latex system, the ionic concentration is non-uniform and changes substantially with heat treatment. Results will be discussed in terms of specific chemistries, processing conditions and results from complimentary techniques.

2:15 PM CC2.3

ASSOCIATION OF PERFLUORINATED IONOMERS INTO SUPERMOLECULAR STRUCTURES. Dvora Perahia and Xeusong Jiao, Department of Chemistry, Clemson University, Clemson, SC.

The aggregation of novel ionomers consisting of a hydrophobic perfluorinated backbone with hydrophilic short side chains was found to be a key issue in understanding the structure of the polymer both in solution and when cast as a thin film. This study introduces the correlation between the association of perfluoro-ionomers in dilute solution and the structure and wetting characteristics of the ionomer at the solid-air interface. Thin films of these polymers are of immense potential in the formation of new stable solid polymeric fuel cell membranes. We have previously shown that ionomers that were self assembled formed stable films while spin coated films, in which shear was applied, partially de-wetted upon annealing. In contrast to flexible non-charged polymers such as polystyrene, full de-wetting did not occur. This led to a conclusion that upon annealing, a more stable association of the polymer takes place. In the current work, small

angle neutron scattering revealed that these molecules in water-alcohol mixtures aggregate to form cylindrical micelles at extremely low concentrations (<0.1 Wt%). The micellar radius varies between 2 and 4 nm depending on temperature and concentration. The length was estimated to be around 15-20 nm. When these ionomers were allowed to self-assemble from solution onto a single crystal silicon wafer, clear images of these micelles were observed by both AFM and STM. Further x-ray reflectivity studies suggest that the dry film consists of stacks of cylindrical aggregates with a radius of 2 nm. The spin-coated films consist of much smaller stacks. The correlation between the stability of the film and the association of the polymer is currently under investigation.

2:30 PM CC2.4

MICROSPHERES LINKED BY TELECHELIC POLYMERS: PHASE BEHAVIOUR AND RHEOLOGY. Gregoire Porte, Mohammed Filali, Eric Michel, Jacqueline Appell, Francois Molino, GDPC, Universite Montpellier 2, Montpellier, FRANCE.

We consider dispersions of microspheres reversibly linked to one another by flexible chains bearing a sticker at each end. In practice, this is obtained with o/w droplet microemulsions into which we incorporate a hydrophobically end capped POE. Changing the concentration of the microemulsion one monitors the average distance between droplets: when it is larger than the size of the POE coil, sufficient addition of the polymer induces phase separation. We investigate in details the effective bridging interaction using neutron scattering: the corresponding free energy is of the order of few tenths of kT per chain. At sufficient concentrations in droplets and polymer, a reversible network is formed showing viscoelasticity characterized by a plateau modulus and a relaxation time related to the residence time of the hydrophobic sticker in the oil droplets. At high rates (non-linear regime), the stress response to steady shear shows a cusp like singularity associated with the formation of non-homogeneous flow. We compare this singularity with the well documented stress response of other complex fluids exhibiting banded flows. We conclude that it rather corresponds to the nucleation and fast propagation of a reversible fracture that anneals immediately after the cessation of shear.

2:45 PM CC2.5

EVIDENCE OF NONLINEAR STRETCHING OF THE ELASTICALLY ACTIVE CHAINS IN THE RHEOLOGY OF TRANSIENT NETWORK. Y. Serero and J.-F Berret, UMR CNRS 5581, Groupe de Dynamique des Phases Condensées, Montpellier, FRANCE.

Reversible crosslinked networks can be realized experimentally using telechelic polymers. A (water-soluble) telechelic polymer consists in a long middle chain that has been modified at each end by a small hydrophobic polar or ionic group. In water, the end-caps associate into an hydrophobic clusters comparable to surfactant micelles, the central chain forming then loops or bridges toward a neighboring cluster. We report on a novel telechelic associating polymers that self-assemble in solution into star-like flowers in the dilute regime and develop a fully connected network of flowers above some threshold concentration ϕ^* (~1% by weight). The peculiarity of these telechelics is that the end-caps are partially fluorinated. The resulting network has a low connectivity (or elastic modulus) but an extremely long residence time (or viscoelastic relaxation time). Small-angle neutron scattering has been used to investigate the form and structure factors of the star-like aggregates, whereas linear rheology was performed to identify the viscoelastic features of the physically cross-linked network (Y. Séréro et al., Phys. Rev. Let. 81, 5584 (1998)). Here we report on the nonlinear rheology of such networks of flowers. By applying a deformation of different amplitudes (within 10 ms) such as in step-strain experiments, we observe a strain hardening of the network. Under steady shear flow, shear-thickening is observed. These two results are representative of the flow behaviors of transient networks since they have been found by changing the temperature, the flower concentration, the length of the middle chain and the hydrophobic end-caps. We demonstrate that both phenomena, strain hardening and shear thickening are due to the nonlinear stretching of the elastically active strands (bridges), in agreement with the report by Marrucci et al. (Macromolecules 26, 6483 (1993)).

3:30 PM *CC2.6

SURFACE IONIZATION AND SURFACE DIFFUSION RATES OF WATER-SOLUBLE POLYMERS. Svetlana A. Sukhishvili, Feng Xie, Steve Granick, University of Illinois, Dept. of Materials Science, University of Illinois, Urbana, IL; Yan Chen, Joachim D. Muller, Enrico Gratton, Laboratory for Fluorescence Dynamics, University of Illinois, Urbana, IL.

In one study, we consider the ionization of a simple polypeptide, poly-L-glutamic acid, adsorbed in aqueous solution onto a polymer brush of opposite charge. We conclude that charge-charge repulsion

limits the extent of ionization; already present in bulk solution, this becomes particularly prominent near a surface when the average charge-charge spacing exceeds a critical level. Predictable consequences are tested in the field of multilayer deposition of ionizable polyelectrolytes. In a second study, we report the first direct measurement of the diffusion coefficient, D , at dilute surface coverage to ensure minimal chain-chain interaction. We find scaling with N to the power $3/2$ (N is degree of polymerization), a simple scaling that implies that the diffusion time scales and N to the power 3. In the absence of competing models of which we are aware, this suggests that surface diffusion of an isolated polymer chain is a reptation process not based on entanglement with other chains.

4:00 PM **CC2.7**

THE ADSORPTION OF POLYELECTROLYTES INTO MULTILAYER ASSEMBLIES AS STUDIED BY SECOND HARMONIC GENERATION. Richard McAloney, M.C. Goh, University of Toronto, Dept of Chemistry, Toronto, ON, CANADA.

Polyelectrolytes can assemble spontaneously onto charged surfaces to form well-ordered multilayer films. These films are prepared by sequential immersion of a charged surface, such as fused silica, into cationic and anionic polyelectrolyte solutions. Films of many bilayers can be prepared using a multitude of charged materials. We have investigated the formation of such films by Atomic Force Microscopy (AFM), UV-Vis spectroscopy, and Second Harmonic Generation (SHG). AFM measurements show that the polyelectrolytes adsorb in an unusually flat conformation with a thickness of about 1-2 nm. We used SHG to obtain real time information about the in-situ adsorption process of each layer within the multilayer film. This information can be used to examine the initial adsorption followed by the reorganization of the polyelectrolyte into its final conformation, and the factors that affect this process.

4:15 PM **CC2.8**

SHEAR AND NORMAL FORCES BETWEEN SMOOTH SOLID SURFACES IN SOLUTION OF ADSORBING PEO IN TOLUENE. Uri Raviv, Rafael Tadmor, Jacob Klein, Weizmann Institute of Science, Department of Material & Interfaces, Rehovot, ISRAEL.

Direct measurements of the normal forces between two atomically smooth mica surfaces immersed in toluene have been carried out as a function of surface separation. Then poly(ethylene oxide) (PEO) was introduced into the toluene (which is a good solvent for PEO). Following full overnight adsorbance of PEO ($M_w=37,000$ and $112,000$) a force-distance law was indicated on rapid compression / decompression of the surfaces, with repulsion beginning at a distance of $\sim 8R_g$ (radius of gyration) and increasing monotonically at shorter distances. This behavior quantitatively resembles that of adsorbed PEO layers in toluene, as reported earlier. In addition, in this study, measurements of the shear response were carried out as a function of surface separation at the same conditions. The shear motion was applied in a series of separation distances from some tens of nanometers down to closest approach distance. The shear motion was at constant velocity in a zig-zag motion. A significant shear response was observed at a distance of $\sim 2R_g$ and increased monotonically at shorter distances. In the case of PEO ($M_w=37,000$) normal force measurements performed immediately after shear appeared very similar to those measured in pure toluene, but with stronger attraction. This shows that sliding of the two surfaces past each other can detach PEO from mica surfaces, in toluene. According to the force distance law after shear we estimated that about 10% of the polymers are still left on the surface. The attraction between the surfaces is due to bridging effect, which is known to take place at low surface coverage. In the case of PEO ($M_w=112,000$) normal force measurements performed immediately after shear appeared very similar to those measured just before shear (in the solution), i.e. the polymers remain on the surfaces. In the last case the friction coefficient was ~ 0.03 .

4:30 PM **CC2.9**

THICKNESS CONSTRAINTS ON MISCIBILITY IN COPOLYMER/HOMOPOLYMER THIN FILM MIXTURES. Peter F. Green, Michael D. Smith, The University of Texas at Austin, Department of Chemical Engineering and Texas Materials Institute, Austin TX.

We examined the effect of the addition of homopolymers of polystyrene (PS), tetramethyl-bisphenol-A-polycarbonate (TMPC) and poly(norbornene-methyl-d3-carboxylate) (NBMC) on the interlamellar spacing and on the phase stability of symmetric polystyrene-b-polymethacrylate (PS-b-PMMA) diblock copolymer thin films of thickness h on silicon substrates. h is on the order of the interlamellar thickness. The degrees of polymerization of the homopolymers, NPS, NTMPC and NNBMC, were comparable to one half of NC, the degree of polymerization of the copolymer. PS homopolymer chains segregated to the middle of the PS-rich domains

of the copolymer for PS homopolymer volume fractions of up to $j_{PS}=0.40$. The phase structure of the PS/PS-b-PMMA mixture remained in a lamellar state under these conditions. TMPC chains migrated to the middle of the PS domains for volume fractions of $j(TMPC) < 0.12$, whereas at higher $j(TMPC)$, the TMPC chains became more uniformly distributed throughout the domains. This mixture became more compatible at higher TMPC volume fractions. NBMC chains segregated to the middle of the PMMA domains for volume fractions of up to $j(NBMC)=0.04$. For $j(NBMC) > 0.04$, the NBMC homopolymer macrophase separated and formed a thin layer on the substrate. The copolymer formed an ordered microphase separated structure on this NBMC layer. These results are discussed in the context of the behavior of bulk copolymer/homopolymer mixtures and of mean field theory.

4:45 PM **CC2.10**

WETTING AND PHASE SEPARATION REGIMES IN THIN FILM POLYMER BLENDS. Howard Wang and R.J. Composto, Materials Science and Engineering, and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA.

We have investigated wetting and phase separation in thin films of deuterated poly(methyl methacrylate) (dPMMA) and poly(styrene-ran-acrylonitrile) (SAN) on silicon by forward recoil spectrometry and scanning force microscopy. By characterizing both the depth profile and lateral phase morphology, three regimes of evolution are identified for film thicknesses ranging from $10 R_g$ to $150 R_g$, where R_g is the dPMMA radius of gyration (ca. 8nm). Initially, wetting dominates resulting in a dPMMA/SAN/dPMMA layered structure. Hydrodynamic flow drives dPMMA wetting as supported by scaling of the surface layer growth as t^1 and direct observation of interconnected morphology just below the surface. During the intermediate stage, a bridging PMMA phase punctures the SAN interphase. The lateral correlation length crosses from t^{-1} to $t^{-1/3}$ as the lateral size approaches the initial film thickness. Capillary fluctuations at the dPMMA/SAN interface eventually rupture the middle layer by a spinodal decomposition mechanism resulting in isolated SAN-rich hills encapsulated by a thick dPMMA wetting layer. The surface and interphase roughnesses are measured and found to display growth regimes consistent with wetting, phase evolution, and dewetting, sequentially. In addition to providing a comprehensive understanding of wetting and phase separation, these studies reveal the complex interplay between wetting, phase coarsening, capillary fluctuations, and dewetting in thin film polymer blends.

SESSION CC3:

Chairs: Maurice Kleman and Patrick Navard
Tuesday Morning, November 30, 1999
Salon J/K (M)

8:30 AM ***CC3.1**

DEFECTS STRUCTURE AND RHEOLOGY OF ANISOTROPIC FLUIDS. Maurice Kleman, Univ Pierre-et-Marie-Curie, LMCP, Paris, FRANCE.

There are still few investigations on the rheology of anisotropic fluids which make specific references to topological defects. However there is no doubt that defects play a prominent role in the viscoelastic flow properties of liquid crystals and ordered colloidal systems, as they do in the plastic deformation properties of solids, for which there is a wealth of information. This talk will review our present knowledge of flows 1)-in lamellar systems, in relationship with various textures (of dislocations, focal conic domains, and multilamellar vesicles), 2)- in nematics (disclinations, band textures). Low shear-stress stationary experiments in lamellar flows* and their power-law behavior will be discussed in the light of high-temperature creep theories in metals. *C. Meyer, S. Asnacios, C. Bourgaux and M. Kleman, RheolActa, to appear

9:00 AM **CC3.2**

ARE NEMATIC LIQUID CRYSTALS VISCOELASTIC SOLIDS? Ralph H. Colby, Materials Science and Engineering, The Pennsylvania State University, University Park, PA.

I review viscoelasticity data on a variety of layer-forming structured fluids: lamellar melts of diblock copolymers, smectic thermotropic liquid crystalline (LC) polymer melts (both main chain and side chain), low molar mass thermotropic LC SCB and lyotropic lamellar organic dye salts in water. With the exception of the diblock copolymer melts, all of these materials are clearly viscoelastic solids that flow like viscoelastic liquids, when subjected to stresses above their yield stress. I present new torsional creep data on a main-chain LC polymer melt in its nematic phase. At a low stress level (37 dynes/cm²) the long-time creep becomes time-independent and all deformation is recoverable, indicating that this material is a

viscoelastic solid as well. This leads me to suggest that all structured fluids are viscoelastic solids, but some simply have yield stress values that are lower than I can apply with my present instrumentation. The solid-like character is presumably due to the supermolecular defect texture present in structured fluids.

9:15 AM CC3.3

ROLE OF DISLOCATIONS AND OTHER DEFECTS IN THE FLOW OF A SMECTIC-A PHASE. I. Lelidis, M. Kleman*, and J.-L. Martin, Département de Physique, Institut de Génie Atomique, Ecole Polytechnique Fédérale de Lausanne, Lausanne, SWITZERLAND; *Laboratoire de Minéralogie-Cristallographie (CNRS-UMR 7590, Université de Paris-6) Paris, FRANCE.

As it is well-known, a perfect Cano wedge with homeotropic anchoring contains a tilt boundary of edge dislocations. These dislocations are easily made visible in a thermotropic sample at the vicinity of the SmA-SmC transition. Our experimental setting allows for a careful control in magnitude and in time of the displacement Δz normal to the layers, as well as a measurement of the stress σ_{zz} . A controlled deformation velocity $\epsilon = \Delta \epsilon_{zz} / \Delta t$ is imposed. As the stress increases, four deformation regimes are observed: elastic, anelastic with a reversible bowing of the edges, plastic with a jerky climb motion of the edges cutting through a forest of screw dislocations, then a viscous climb motion. In this latter regime, we are able to check the validity of the Rowan equation (well known in solid crystal plasticity) which relates, in the present case, the density ρ_e of edge dislocations in the tilt-boundary, their Burgers vector b , and their climb velocity v . These events are clearly visible under the polarizing microscope and allow for an estimation of the screw dislocation density (10^9 - $10^{12}/m^2$). This quantity is of the same order of magnitude as the density of hill-shaped surface irregularities on the glass plates, which we have studied by atomic force microscopy observations. These dislocations transform to an helical geometry under compression, as it was foreseen. These helical lines are also visible in confocal microscopy. Other types of defects than dislocations, which appear under shear or compression, will also be discussed.

9:30 AM CC3.4

COMPLEX POLYMER FLUIDS UNDER SHEAR FLOW: ORDER AND DYNAMICS. Ulrich Wiesner, Cornell Univ, Dept of Materials Science and Engineering, Ithaca, NY.

In the present contribution the effects of shear flow on the orientation behavior of lamellar poly(styrene-block-isoprene) (PS-b-PI) diblock copolymers are discussed with emphasis on the elucidation of common behavior with other layered complex fluids like lyotropic lamellar phases. It is described that for large amplitude oscillatory shear (LAOS) at temperatures close to the order-disorder-transition temperature, at which the microphase separated polymer melt transforms into an isotropic melt, three orientation regimes related to the dynamic shear viscosity of the block copolymers are observed: parallel orientation at high, perpendicular orientation at intermediate, and parallel orientation again at very low shear frequencies. It is demonstrated that one of the key issues to understand these non-equilibrium type experiments is the behavior of instabilities leading to flips of orientation from parallel to perpendicular alignment and vice versa. An orientation diagram showing the position of these instabilities in the amplitude-frequency space as well as their temperature dependence is derived experimentally (1) suggesting a consistent phenomenological picture of orientation phenomena of layered systems under shear. In the last part the gap is bridged between long LAOS experiments on a laboratory scale and technically relevant fast extrusion processes by studying the lamellar orientation of PS-b-PI diblock copolymers after extrusion from a miniaturized high pressure capillary rheometer. It is shown that under extrusion conditions rapid macroscopic parallel and, after annealing, perpendicular orientations of the lamellae can be obtained which may open an avenue to applications (2). (1) H. Leist, D. Maring, Thomas Thurn-Albrecht, U. Wiesner, J. Chem. Phys 110 (1999), 8225 (2) H. Leist, K. Geiger, U. Wiesner, Macromolecules 32 (1999), 1315

9:45 AM CC3.5

THE NATURE OF VISCOELASTICITY IN LAMELLAR BLOCK COPOLYMERS: CONTRACTION CORRELATED TO STRAIN LOCALIZATION. Karen Winey, Daniel Polis, Univ of Pennsylvania, Dept of Materials Science, Philadelphia, PA; Anthony Ryan, Univ of Sheffield, Dept of Chemistry, Sheffield, UNITED KINGDOM.

We determined the local strain profile in sheared lamellar block copolymers. A trilayer model, based on elastic brushes separated by viscous interpenetration zones, captures the rheological response of these materials and provides a measure of the relative contributions of elastic versus viscous strain. Elastic chain distortions are evident from a reversible lamellar contraction, as measured from in situ small angle x-ray scattering. The contraction directly correlates to the elastic

strain, as determined from our trilayer model, and shows universal behavior for three block copolymers.

10:30 AM CC3.6

Abstract Withdrawn.

10:45 AM CC3.7

FIBRILLATION AND SHEAR THINNING BEHAVIOR IN PC/LCP BLENDS. Tan Lay Poh, Yue Chee Yoon, Tam Kam Chiu, Nanyang Technological Univ, SINGAPORE.

The effect of LCP content on the morphological and rheological properties of polycarbonate (PC) and LC5000, a thermotropic liquid crystalline polymer consisting of 80/20 of hydroxybenzoic acid and poly(terephthalate) were studied. As the shear rate increased, the fibrillation of the dispersed LCP phase in the blend enhanced as expected. However, for blends with LCP contents greater than 10wt%, shear thinning was observed at shear rates below that for which fibrillation occurred. Hence, the shear thinning behavior is not governed entirely by fibrillation of the dispersed phase but by the LCP content as well. The shear thinning behavior of LCP at low shear rates is caused by the tumbling of the LCP domain and the behavior confers to that predicted by the rule of mixtures. At higher shear rates, fibrillation of LCP acts in concert with the shear thinning behavior resulting in greater deviation in the rheological response to that predicted by rule of mixtures. At a LCP loading of 1wt%, no significant changes in the rheological and morphological properties were observed throughout the shear rate tested. The LCP content has a significant influence on the coalescence of the dispersed phase and subsequent shear thinning behavior of the PC/LCP blend studied.

11:00 AM CC3.8

NEMATO-CAPILLARITY THEORY AND MARANGONI FLOWS IN LIQUID CRYSTAL INTERFACES. Alejandro Daniel Rey, Dept of Chemical Engineering, McGill University, Montreal, CANADA.

The macroscopic equations of nemato-capillarity, including the interfacial linear momentum balance equation and the interfacial torque balance equation are derived, analyzed, and characterized. The surface stress tensor for nematic interfaces contains normal and bending stresses, nonexistent in isotropic interfaces. In addition it is found that the anisotropic surface tension also gives rise to tangential Marangoni forces, whenever surface gradients of the nematic ordering exist. The strength of the nematic Marangoni flow is proportional to the anchoring energy of the nematic interface. Finally, it is shown that interfacial nematic normal forces may exist even under zero curvature. Examples of applications of nematic Marangoni and normal forces are given.

11:15 AM CC3.9

SYSTEMATIC STUDIES OF THE EFFECTS OF SURFACE CHEMISTRY, TOPOGRAPHY, DIPOLE INTERACTION AND MOBILITY ON LIQUID CRYSTAL ALIGNMENT.

Christiane Cramer, Mei-Wei Tsao, John F. Rabolt, Department of Materials Science and Engineering, University of Delaware, Newark, DE.

With the prediction that Liquid Crystal Displays will share the market with the traditional CRT-based displays by the year 2003, it is surprising that little is known or understood about the underlying mechanisms for liquid crystal alignment. In this study, we have assessed the roles played by surface chemistry, topography, dipolar interaction and mobility in determining the liquid crystal orientation induced by different surfaces. Using both polymer and self-assembled monolayers, surfaces have been engineered with specific topographies, domain structure and dipolar architectures and investigated by FTIR, XPS, ToF-SIMS, contact angle and ellipsometry. Following this characterization, the LC alignment properties were determined by polarized microscopy and conoscopy. Based on our experimental results, we conclude that a combination of topography and dipolar interaction between the liquid crystal molecules and the aligning layers is responsible for the different tilt geometries observed.

11:30 AM CC3.10

DIFFUSING-WAVE SPECTROSCOPY OF A LIQUID CRYSTAL CONFINED IN RANDOM POROUS MATRIX. T.V. Krouglov and F.M. Alev, Department of Physics, University of Puerto Rico, San Juan, PR.

Diffusing-wave spectroscopy (DWS) is an effective method for investigations of dynamic properties of opaque media exhibiting high multiple scattering. This technique extends the analytic power of conventional dynamic light scattering and was applied earlier successfully [1] for studies of liquid like systems such as suspensions polystyrene spheres in water or foams. We have performed DWS investigations of quasi-solid media based on liquid crystal and solid porous matrix. Porous glass with randomly oriented, interconnected

pores with average pore size of 1000 Å and volume fraction 40% has been used as host random porous matrix. The matrix was impregnated with liquid crystal - 8CB. The sample was completely opaque with $\sim 10^2$ -fold scattering. Confinement has a strong influence on the dynamics of director fluctuations in liquid crystal. Two slow relaxation processes which do not exist in the bulk phase were observed. We assign the appearance of the first slow process, with the relaxation time $\tau \sim 10^{-3}$ s, to the presence of surface layer at the solid pore wall-liquid crystal interface in which the dynamics of director fluctuations is different from that in the bulk. The slowest process ($\tau \sim 1$ s) is probably due to the dynamics of reorientational motion of domains formed in random porous media. These slow processes are highly non-exponential. Modified bulk-like relaxation process due to director fluctuations was also observed in confined geometry. The investigations of the temperature dependence of relaxation process lead to the conclusion that the smectic phase is still present in pores, however, the smectic-A to nematic phase transition is considerably broadened. [1] D.J. Pine, D.A. Weitz, J.X. Zhu and E. Herbolzheimer, *J. Phys. (France)*, **51**, 2101 (1990). This work is supported by DoD grant N00014-99-1-0558.

11:45 AM CC3.11

ON THE DIRECTOR REORIENTATION DYNAMICS IN ELONGATED BIPOLAR NEMATIC DROPLETS. Philip K. Chan, Ryerson Polytechnic Univ, School of Chemical Engineering, Toronto, Ontario, CANADA.

Polymer dispersed liquid crystal (PDLC) films are used in a vast array of practical applications such as switchable windows and flat panel displays. A PDLC film scatters light and appears opaque in its natural state. However, the film transmits light and appears transparent when an external electric or magnetic field is applied normally to it. These electro-optical and magneto-optical properties depend on the nematic liquid crystal director field confined within the slightly elongated droplets that are dispersed uniformly in the film. Therefore, to properly design and control PDLC films, it is important to have a fundamental understanding of the transient director reorientation dynamics in confined elongated geometries. This paper presents results from the computer simulation of the director reorientation dynamics in elongated bipolar droplets, which are typically found in PDLC films. The numerical results replicate frequently reported experimental observations on the application of PDLC films. In addition, this paper presents new fundamental results not known previously but are important to the optimal application of PDLC films.

SESSION CC4:

Chairs: Ralph H. Colby and Joachim O. Radler
Tuesday Afternoon, November 30, 1999
Salon J/K (M)

1:30 PM *CC4.1

LINEAR VISCOELASTICITY OF NEMATIC LIQUID CRYSTALLINE POLYMER MELTS, TUMBLING AND MAGNETIC COMPLIANCE. Didier Long, David C. Morse, Univ. of Minnesota, Dept of Chemical Engineering and Materials Science, Minneapolis, MN.

We describe the linear viscoelastic response of monodomains of unentangled nematic liquid crystalline polymers, using a generalized Rouse model. We calculate the dynamic relaxation functions analogous to the Leslie viscosities. As a consequence of the coupling of the macroscopic director orientation \mathbf{n} to relaxation of the chain conformations, we predict 1) a non-monotonous evolution of the director orientation after a step deformation and predict continuous tumbling of extended chains (with no hairpins) in shear flow and steady alignment of anisotropic Gaussian chains and 2) we introduce a new phenomena of 'magnetic compliance', related to the evolution of \mathbf{n} as a function of the duration of the application of a strong magnetic field.

2:00 PM CC4.2

INFLUENCE OF THE NEMATIC ORDER ON THE FORMATION OF STRETCHED COMB-LIKE LIQUID CRYSTALLINE POLYMERS. A. Brûlet, V. Fourmaux-Demange, F. Boué, J.P. Cotton, LLB, Saclay, France; P. Davidson, LPS, Univ. Paris XI, Orsay, FRANCE.

Thermotropic liquid-crystalline polymers combine the long-range orientation order with the mechanical properties of polymers. We study melts of comb-like liquid-crystalline polymers in which the mesogenic part is linked as a side-chain on each unit of a flexible polymer. The understanding of the dynamics of these materials in the nematic phase raises fundamental questions: what is the influence of the comb-like structure? And what is the specific effect of the nematic interaction on the dynamics? For this purpose, we have synthesized

two isomers of a comb-like polymetacrylate polymer (one nematic, one isotropic). Even with high degrees of polymerization N (40-1000), the polymer chains are not entangled. Small angle neutron scattering has been used in order to determine the evolution of the chain conformation, after stretching, as a function of the relaxation time t . The chain conformation is totally determined with two parameters: λ , the global deformation of the polymer and p , the number of monomers locally relaxed. For a linear polymer chain, without entanglements, λ has the value λ_S (the deformation ratio of the whole sample) while p varies as $t^{1/2}$. For the comb-like polymer, the chain deformation is pseudo-affine λ always smaller than λ_S . In the isotropic phase, λ has a constant value while p increases with t . In the nematic phase, on the contrary, λ decreases as a stretched exponential while p remains constant.

The dynamics of the comb-like polymers is discussed in term of living clusters of which junctions are produced by interactions between side chains. The nematic interaction increases the time of life of these junctions and, strikingly, the relaxation times of the chain remain the same for all scales of the whole polymer chain (no longer scale dependant).

2:15 PM CC4.3

MICROPHASE AND MESOPHASE ORDERING IN SIDE-CHAIN LIQUID CRYSTALLINE DIBLOCK COPOLYMERS.

Paula T. Hammond, Mitchell Anthamatten, Massachusetts Institute of Technology, Dept. of Chemical Engineering, Cambridge, MA.

The thermotropic behavior in a series of side-chain smectic C* liquid crystalline (LC) diblock copolymers has been investigated to determine how mesophase ordering within the LC domain affects microphase segregation between the two blocks. A combination of temperature-dependent SAXS, optical microscopy, calorimetry, and TEM analysis enabled mesogenic order transitions to be correlated with block copolymer ODT's and OOT's. Efforts are being made to explain these ordering phenomena using a combination of Maier-Saupe and chain-stretching free energy expressions. Other issues to be discussed include the preferred orientation of smectic layers relative to block copolymer morphology and the importance of mesogenic structure on ordering behavior. These results lead us closer to understanding the ordering behavior of LC groups constrained by a polymer chain and confined within microphase segregated domains.

2:30 PM CC4.4

THE ASSEMBLY OF LINEAR-DENDRITIC ROD DIBLOCK COPOLYMERS AT INTERFACES AND IN THE BULK.

Catherine M. Santini², T. Alan Hatton¹, Paula T. Hammond¹, Massachusetts Institute of Technology; ¹Department of Chemical Engineering, ²Department of Materials Science and Engineering, Cambridge, MA.

A series of linear-dendritic rod diblock copolymers has been synthesized by divergently adding dendrons to a linear diblock copolymer backbone. These diblock copolymers, consisting of a dendritic rod block and a linear block, represent a new type of diblock copolymer architecture. Specifically, these copolymers are composed of polyamidoamine (PAMAM) dendrons which were attached to the linear polyethylene imine block of a polyethylene imine-polyethylene oxide diblock copolymer backbone. To increase the hydrophobicity of the dendritic block, n-alkyl amines were added to various generations of the ester terminated dendritic block, resulting in alkyl terminated dendritic ends. A series of n-alkyl amines, including n-butyl, n-hexyl, and n-octyl were studied. Since polyethylene oxide is hydrophilic and the dendritic block was made hydrophobic, the resulting linear-dendritic diblock copolymers were found to be amphiphilic. These diblock copolymers are surface active and have been assembled into Langmuir films. Not surprisingly, of the n-alkyl chains which we have studied thus far, the n-octyl terminated polymers have resulted in the most stable films. Our current efforts include transfer of these Langmuir films to solid substrates. In addition, we are in the process of studying the bulk morphology of these diblock copolymers. Since the chemistries of the blocks were found to be dissimilar enough to be surface active at the air-water interface, we expect these systems will lead to phase segregation in the bulk.

2:45 PM CC4.5

STRUCTURE AND DYNAMICS OF ELASTOMERIC POLY-PROPYLENE. Zhong-Ren Chen, Robert M. Waymouth, John Pople, Alice Gast, Departments of Chemistry and Chemical Engineering, Stanford, CA.

Stereo-block polypropylene (ePP) is a new class of elastomer synthesized by unbridged 2-phenylindene metallocene catalysts. The thermoplastic elastomeric behavior is proposed to arise from stereo-block nature of isotactic and atactic stereosequences. We have investigated the structure and dynamics of these microstructurally heterogeneous polymers with a wide range of techniques (NMR/IR, DSC/DMA, WAXD/SAXS, SANS, microscopy, and mechanical tests).

Deformation and relaxation behaviors of these polymers under extensional deformation have revealed the origin of elasticity at molecular-level.

3:30 PM *CC4.6

FROM TWO-DIMENSIONAL SMECTICS TO DNA-CATIONIC LIPID MEMBRANE COMPLEXES. Leonardo Golubovic, West Virginia University, Morgantown, WV.

There is a strong recent interest in DNA-Lipid membrane complexes since the discovery of a novel liquid crystalline phase in these systems, in the experiments of Radler, Salditt, Koltover, and Safinya. Shortly after the discovery, the phase has been elucidated by theorists as an unusual state of matter having properties that are somewhere between those of conventional two-dimensional and three-dimensional liquid crystals. In this talk, we review the statistical physics novelties emerging in this area of soft condensed matter systems. We discuss two dimensional and quasi-two-dimensional liquid crystalline systems, and the so-called decoupled phases, concluding with the sliding columnar phase of the DNA-Membrane complexes.

4:00 PM CC4.7

INVESTIGATIONS OF THE SMECTIC PHASE IN A HOMOLOGOUS SERIES OF GENETICALLY ENGINEERED VIRUSES. Zvonimir Dogic, Marie Adams, Seth Fraden, Complex Fluids Group, Department of Physics, Brandeis University, Waltham, MA.

Smectic phase characterized by one dimensional order is ubiquitously predicted by various theories and computer simulations of hard rods. However, the smectic phase is seldomly observed in experimental hard rods systems. A common assumption is that most of these systems are too polydisperse to form a stable smectic phase. The fact that the smectic phase has only been observed in very monodisperse suspensions of fd and TMV and biosynthesized PBLG seems to confirm this assumption. Using methods of molecular biology we prepare artificially polydisperse and bidisperse suspension of rod-like virus fd and look at the stability of the smectic phase in these mixtures. We also study the influence of rod flexibility, ionic strength, and addition of non-absorbing polymer on the smectic phase. Finally we show that additions of hard spheres with specific dimensions dramatically increases the stability of the smectic phase.

4:15 PM CC4.8

PHASE BEHAVIOR AND MICROSTRUCTURE OF CATIONIC SURFACTANT MIXTURES WITH ADDED POLYMER-SURFACTANT. Bret A. Coldren, Hee-Tae Jung, Joseph A. Zasadzinski, Dept of Chemical Engineering, University of California, Santa Barbara, CA.

Highly swollen bilayers of dimyristoylphosphatidylcholine, pentanol and polyethylene glycol polymer-lipid (PEG-lipid) form gel-like phases with up to 90% water. Freeze-fracture electron microscopy directly shows that these gels are induced by the proliferation of interconnected, high curvature liquid crystalline defects which are stabilized by the steric requirements of the wedge-shaped PEG-lipid. This novel behavior is being generalized to create similar hydrogels using dilute lamellar phases of simple surfactant mixtures. Cationic-anionic mixtures can have interesting phase behaviors, forming lamellar phases or multilamellar vesicle phases with up to 80% water, in addition to spontaneous vesicles at even lower surfactant concentrations. Adding PEG-lipid to a swollen cationic lamellar phase greatly enhances its viscoelasticity and potential water content. Additionally, we find it possible to replace the PEG-lipid molecules with simple block copolymers or polymer-surfactants of comparable molecular weights. The lower cost and enhanced chemical stability of the cationic surfactants and block copolymers makes these novel gel-like materials potentially useful as thickening agents, personal care products, detergents, etc., where viscosity control at high water fractions is desirable.

4:30 PM CC4.9

INTENSITY FLUCTUATION MICROSCOPY AT THE NEMATIC-SMECTIC-A INTERFACE: A REAL-SPACE OPTICAL PROBE OF A WEAKLY FIRST-ORDER PHASE TRANSITION. Anand Yethiraj*, John Bechhoefer, Physics Dept, Simon Fraser University, Burnaby, CANADA. *Present Address: Van 't Hoff Laboratory, Debye Institute, Utrecht University, Utrecht, and FOM-Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS.

An important development in the theory of phase transitions was the understanding of how thermal fluctuations can alter the analytical properties of the free energy, modifying the critical exponents of a second-order phase transition. A second consequence, equally fundamental but less widely explored, is that thermal fluctuations can also change the order of the transition. In one such fluctuation mechanism, proposed by Halperin, Lubensky and Ma (HLM), the

coupling between the fluctuations of a gauge field and the order parameter can convert a second-order transition to one that is always at least weakly first order. Such an effect is expected in two systems: in type-1 superconductors and the nematic-smectic-A (NA) transition. This effect is immeasurably small in superconductors; at the NA transition it is weak but detectable. Moreover, adding an external field to the HLM theory, Mukhopadhyay et al. have found that a modest (magnetic) field of 10 T can drive the weakly-first order transition in a small-nematic-range liquid crystal, 8CB, back to second order. Moreover, the theory predicts a linear suppression of t_0 for small fields, with a non-analytic cusp at $H = 0$. Using a new high-resolution, real-space optical technique that we have developed, we explore the HLM effect at the NA transition experimentally in pure 8CB, and in 8CB-10CB mixtures. We find, surprisingly, no evidence for the predicted field effect at magnetic fields up to $\approx 1.5T$, implying a critical field of $> 30 T$. Moreover, we find in zero-field measurements in 8CB-10CB mixtures on the "second-order" side of the LTP that the discontinuity observed is substantially larger than that predicted by HLM, not smaller as one might expect! These non-trivial fluctuation effects lend credence to past observations of non-monotonic crossover behaviour of critical exponents, and underline the importance, theoretically, of considering smectic fluctuations.

4:45 PM CC4.10

THEORY OF CHIRAL MODULATIONS AND FLUCTUATIONS IN SMECTIC-A LIQUID CRYSTALS UNDER AN ELECTRIC FIELD. Jonathan V. Selinger*, Jianling Xu†, Robin L. B. Selinger†, B.R. Ratna* and R. Shashidhar* ; *Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, DC, †Catholic Univ., Physics Dept., Washington, DC.

Chiral liquid crystals often exhibit periodic modulations in the molecular director; in particular, thin films of the smectic-C* phase show a chiral striped texture. Here, we investigate whether similar chiral modulations can occur in the *induced* molecular tilt of the smectic-A phase under an applied electric field. A continuum elastic theory shows that the state of uniform induced tilt can become unstable when the system approaches the smectic-A-smectic-C* transition, or when a high electric field is applied. Beyond that instability point, the system develops a chiral striped modulation in the tilt, which induces a corresponding modulation in the smectic layers; the modulation persists up to an upper critical electric field and then again disappears. The theory also predicts chiral fluctuations in the uniform state. We compare these predictions with observed chiral modulations and fluctuations in smectic-A liquid crystals. To study the details of the tilt modulation, we perform simulations on a two-dimensional lattice, using a free energy functional based on continuum elastic theory. We observe the onset of tilt modulation at a lower critical field and its disappearance at an upper critical field as predicted, though the phase boundaries are shifted slightly due to lattice effects. Simulations of this model at finite temperature show chiral fluctuations including both tilt modulation and localized chiral vortices.

SESSION CC5:

Chairs: Frank S. Bates and Dennis E. Discher
Wednesday Morning, December 1, 1999
Salon J/K (M)

8:30 AM *CC5.1

COMPLEX FLUIDS WITH A YIELD STRESS VALUE. H. Hoffmann, University of Bayreuth, Physical Chemistry I, Bayreuth, GERMANY.

It is shown that vesicle phases from single chain surfactants can be highly viscoelastic and can have a yield stress value. These phases can be prepared from cat-anionic surfactants, from surfactants and cosurfactants, from ionic surfactants with hydrophobic counter-ions and from mixtures of zwitterionic surfactants with Ca-salts of ionic surfactants. The viscoelastic properties and the yield stress values of these phases are particularly strong if the bilayers of the vesicles are ionically charged and the charge is not shielded by excess salt. For dilute solutions with 2% surfactant the yield stress value can be large enough to suspend small particles from sedimentation and air bubbles from up-creaming but low enough to allow the fluids to flow. The yield stress value in these systems is a result of the dense packing of the uni- and multilamellar vesicles (SUV/MLV). The behavior of the systems is similar as the behavior of concentrated emulsions and polyhedral foams. The viscoelastic properties of the phases was determined by oscillating rheological measurements and will be discussed as a function of various parameters like charge density, surfactant concentration and ionic strength. The viscoelastic vesicle phases are formed when ionically charged La-phases with stacked bilayers are sheared. We studied the mechanism of this transformation. At low shear rates the transition time decreases linearly with the shear rate while at higher shear small unilamellar vesicles (SUV) are formed. All three phases (the stacked bilayers, the

MLV - and the SUV - phase) are stable for long times and no spontaneous transition from one phase into the other takes place at rest.

9:00 AM **CC5.2**

VESICLE-TO-MICELLE TRANSITION INDUCED BY GRAFTED DIBLOCK COPOLYMERS. Aude Schalchli-Plaszczynski, Loic Auvray, Laboratoire Leon Brillouin, CEA Saclay, Gif sur Yvette, FRANCE.

We study by small angle neutron scattering a vesicle-to-micelle transition induced by anchoring diblock copolymers on the surfactant membranes. The ternary system SDS (sodium dodecyl sulfate)/ octanol/PS-POE (polystyrene-polyoxyethylene) is chosen as a model of more complex biological systems. We investigate, in particular, the influence of the polymer mass on this vesicle-to-micelle transition. It appears that longer polymer chains destabilize membranes less than the smaller ones. We interpret this experimental result in terms of membrane curvature effects due to the grafted polymers. We find a good agreement with theoretical predictions concerning the spontaneous mean curvature of polymer-grafted membranes.

9:15 AM **CC5.3**

THE ORIGINS OF STABILITY OF EQUILIBRIUM VESICLES. Hee-Tae Jung, Bret Coldren, Joseph A. Zasadzinski, Department of Chemical Engineering and Materials, University of California, Santa Barbara, CA.

Spontaneous equilibrium vesicles can be prepared from aqueous mixtures of single tailed cationic and anionic surfactants. We present measurements of the bilayer elastic constant, K , for equilibrium vesicles by an analysis of the vesicle size distribution determined by cryo-transmission electron microscopy (TEM). We find that there are large differences in elastic modulus with changes in the hydrophobic portion of the surfactant. The bending constant of the hydrogenated surfactant mixture (CTAB/SOS) is of order $\sim kBT$, confirming that equilibrium unilamellar vesicles are stabilized against formation of lamellar phases or dispersed multilamellar liposomes by thermal membrane fluctuations that lead to a net repulsive interaction between bilayers. However, the bending constant of CTAB/ FC8 vesicles is of order $\sim 6 kBT$, suggesting that these vesicles are stabilized by the high energy cost of deviation from the spontaneous curvature. Adding electrolyte to the CTAB/ FC8 vesicles eliminates electrostatic repulsion and leads to stable vesicles with two bilayers, consistent with a competition between attractive bilayer interactions and deviations from the spontaneous curvature. The replacement of long chain fluorinated molecules by short ones dramatically reduce bending modulus from $\sim 10 kBT$ to $\sim kBT$. The microstructure and morphology of the mixed surfactant systems are also discussed.

9:30 AM ***CC5.4**

POLYMERSOMES: TOUGH VESICLES ASSEMBLED FROM DIBLOCK COPOLYMERS. D.E. Discher, J.C.-M. Lee, B.M. Discher, Y.-Y. Won*, D.S. Ege, F.S. Bates*, D.A. Hammer, University of Pennsylvania, *University of Minnesota.

Vesicles were made in aqueous solutions from amphiphilic diblock copolymers and characterized by micromanipulation. The average molecular weight of the polymer primarily studied, polyethyleneoxide-polyethylene (EO40-EE37), is several-fold greater than that of typical phospholipids in natural membranes. Both the membrane bending and area expansion moduli of polymersomes (polymer-based liposomes) fell within the range of lipid membrane measurements, but the giant polymersomes proved to be almost an order of magnitude tougher in sustaining far greater areal strain before rupture. The polymersome membrane was also at least tenfold less permeable to water than common phospholipid bilayers. The results are explained primarily on the basis of an increased thickness to the membrane and suggest a new class of synthetic thin-shelled capsules based on block copolymer chemistry.

10:30 AM **CC5.5**

STABILITY OF TWO-DIMENSIONAL FOAMS IN LANGMUIR MONOLAYERS. E.K. Mann, S.V. Primak, Kent State University, Dept of Physics, Kent, OH.

Stable three-dimensional foams are observed only in the presence of surfactant, macromolecular, or particulate layers at the gas/liquid interfaces. Stability may be governed by decreased surface energies, by long-range electrostatic repulsion between the surfactant layers sandwiching the film, by viscosity within the film, and by the viscoelastic response of the monolayer. In the two-dimensional case, within a partial Langmuir monolayer, long-range electrostatic repulsion across foam lamella acts even in the absence of a boundary layer, due to alignment of dipole moments within the Langmuir monolayer. Two-dimensional foams within a Langmuir monolayer of poly(dimethylsiloxane) show markedly different stability on two

different substrates. These foams will be used to explore the roots of Langmuir monolayer foam stability. Measurements of line tension in the two cases were performed by optical micro-rheology, which also demonstrated that substrate viscosity was the dominant source of viscous friction, at the foam scale. Surface potential measurements gave access to the long-range electrostatic forces. The only significant difference between the two systems was found in the surface potential difference between gas and liquid domains, correlating with foam stability.

10:45 AM **CC5.6**

PERMEABILITY OF AQUEOUS FOAMS. Stephan A. Koehler, Sascha Hilgenfeldt, Howard A. Stone, Harvard University, Division of Engineering and Applied Science, Cambridge, MA.

Experiments show that the permeability of aqueous foams is $K\epsilon^\alpha$, where K is a constant, ϵ is the liquid volume fraction, and the exponent $\alpha \approx 1/2$ (Koehler et al., PRL **82**, pp. 4232-4235 (1999)). The prefactor K depends on the bubble size distribution, as well as material parameters such as the type of surfactant and liquid viscosity. We also explore this relationship as the foams ages (coarsens).

11:00 AM ***CC5.7**

STRUCTURE AND FLUCTUATIONS OF MICROEMULSION NETWORKS. T. Plusty, S.A. Safran, The Weizmann Institute of Science, Department of Materials and Interfaces, Rehovot, ISRAEL; R. Strey, Institut für Physikalische Chemie, Köln, GERMANY; A. Bernheim-Grosswasser, Y. Talmon, Technion, Dept. of Chemical Engineering, ISRAEL.

We present a fluctuating network model for microemulsions that describes their evolution from globular to bicontinuous, spongelike structures. The predicted entropic attractions between the network junctions provide a natural explanation of the observed re-entrant phase separation regions and critical points. Experimental confirmation of the link between the network structure and thermodynamics is presented by both phase behavior measurements (and their agreement with the theoretical scaling laws) and cryo-transmission electron microscopy. The microscopy experiments also indicate that similar mechanisms govern the networks that exist in binary, micellar systems.

11:30 AM ***CC5.8**

BLOCK COPOLYMERS AS MACROMOLECULAR SURFACTANTS. Frank S. Bates, Dept of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN.

Block copolymers belong to a broad class of amphiphilic compounds that includes lipids, soaps, and nonionic surfactants. A macromolecular architecture affords certain advantages over conventional low molecular weight amphiphiles in constructing nanoscale composites with prescribed morphologies and physical properties. This presentation will focus on ternary mixtures of A-B diblock copolymers blended with A and B homopolymers in the vicinity of the bicontinuous microemulsions state, located between the lamellar and two/three phase regions in the phase prism. A combination of experimental measurements, including small-angle x-ray and neutron scattering, and dynamic light scattering, has revealed universal phase behavior for this class of mixtures for block copolymers with molecular weights ranging from 2×10^3 to 10^5 g/mol. These results will be discussed in the context of conventional surfactancy.

This research was conducted in collaboration with Terry Morkved, Wayne Maurer, Tim Lodge, Newell Washburn, Marc Hillmyer, and Kristoffer Almdal.

SESSION CC6/G7: JOINT SESSION:

NONLITHOGRAPHIC APPROACHES

Chairs: Richard A. Register and Thomas P. Russell

Wednesday Afternoon, December 1, 1999

Salon J/K (M)

1:30 PM ***CC6.1/G7.1**

NANOSCALE ASSEMBLY OF RECHARGEABLE BATTERY COMPONENTS. A.M. Mayes, P.P. Soo, B. Huang, P.E. Trapa, D.R. Sadoway, M.I.T., Dept. of Materials Science and Engineering, Cambridge, MA.

Rechargeable lithium polymer batteries, with the highest energy density of all rechargeable technologies now under development, are of interest in applications ranging from microbatteries to wireless communications to automotive traction. We have developed a class of self-organizing block copolymer electrolytes (BCEs) that exhibit nanoscale periodic domains formed from mutually immiscible, covalently joined polymer chains. The nanoscale morphology confers

mechanical properties similar to a crosslinked rubber and creates continuous Li ion-conducting pathways through the material. The BCEs are also being exploited as ion-conducting binders for electrodes that incorporate nanoscale active components, e.g., metal nanoclusters or carbon nanotubes. The high specific interface inherent in these nanocomposite materials facilitates ion/electron transport, translating into increased battery current and capacity.

2:00 PM CC6.2/G7.2

SURFACE MORPHOLOGIES OF SMECTIC LIQUID CRYSTALLINE DIBLOCK COPOLYMER ULTRATHIN FILMS.

Jung-Sheng Wu, Michael. J. Fasolka and Paula. T. Hammond, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

New terraced surface morphologies of side chain liquid crystalline (LC)-amorphous PS diblock copolymers are examined. Ultrathin films exhibit terracing on two length scales corresponding to the block copolymer lamellar period, L_0 , and the smectic LC layer period, s_0 . We use AFM, TEM, XPS, and ellipsometry data to construct the complicated morphologies and explain in a proposed model. The vertical profile is also proved by the cross-section TEM. A complex surface morphology is observed within the holes and upon the islands of these films, which present a free surface composed of LC columnar perforations in a continuous PS top layer. Unlike earlier reports of LC block copolymers, the homeotropic LC layer in the air surface may be parallel to the block copolymer interface. Thin films with different bulk morphologies, like lamellae (41% LC content), predominately lamellae (50%), and cylinder (79%, 80%) are also investigated by varying the LC contents of this series of diblock copolymers. These self-oriented LC ultrathin films can be used to approach nano-patterning and potential advantages in electrical and optical applications.

2:15 PM CC6.3/G7.3

ORGANIZATION OF TWO- AND THREE-DIMENSIONAL ELECTRICALLY SWITCHABLE LC NANOCOMPOSITES.

T.J. Bunning, Air Force Research Laboratory, Materials and Manufacturing Directorate/MLPJ, WPAFB, OH; V.P. Tondiglia, L.V. Natarajan, R.L. Sutherland, Science Applications International Corp., Dayton, OH.

Holography is a standard tool to impart information in thick and thin polymeric films. The information is typically induced via anisotropic polymerization and diffusion processes. Conventional holographic information, once written, remains indefinitely. The use of holography to induce periodic phase separation of nanosized domains of liquid crystal molecules is described here. The use of liquid crystalline media as one of the components allows for structured elements with switchable optical properties to be generated. The ability to fabricate two- and three-dimensional arrays (periodicities of 100 nm to microns) of switchable nanocomposites will be demonstrated. We report here on the real-time monitoring of the optical properties as a function of Bragg spacing, LC concentration, and light intensity for films in a reflective geometry. These studies are being used to shed insight into the kinetics of the phase separation process.

2:30 PM CC6.4/G7.4

POLYELECTROLYTE-SURFACTANT COMPLEXES AS TEMPLATES FOR NANOPOROUS BIOPOLYMER MATERIALS.

Helmut H. Strey, Michael Leonard, Univ. of Massachusetts Amherst, Polymer Science and Eng., Amherst, MA.

When polyelectrolytes are mixed with oppositely charged surfactant at 1:1 charge ratio, they form water-insoluble complexes possessing long-range order. The surfactant molecules assemble into micelles, cylinders or membranes, with the polyelectrolyte filling the intervening space. Little is known about the polyelectrolyte-mediated attraction between surfactant moieties. We present the phase diagram of polyelectrolyte-surfactant complexes as a function of polyelectrolyte charge density, osmotic pressure, salt concentration and type, and surfactant chain length. We utilize ordered polyelectrolyte-surfactant complexes as templates for preparing materials with uniform pore sizes in the nanometer range. By crosslinking the polyelectrolyte matrix by either chemical or physical means, and then washing out the surfactant, we are preparing materials ideally suited for applications, such as filtration, electrophoresis, or controlled drug release.

2:45 PM CC6.5/G7.5

COLLOIDAL CORE-SHELL PARTICLES FOR PHOTONIC APPLICATIONS. K.P. Velikov^a, A. van Blaaderen^{a,b}, ^aVan 't Hoff Laboratory, Debye Institute, Utrecht Univ, THE NETHERLANDS, ^bFOM-Institute for Atomic and Molecular Physics, Amsterdam, THE NETHERLANDS.

A new kind of composite particles with a ZnS core and a SiO₂ shell

has been developed. ZnS cores up to a micron in size are coated by a silica layer of well-defined thickness in a seeded growth procedure to produce a core-shell particle. Due to the high refractive index of ZnS (~2.35) these particles strongly interact with light. In addition they can be made with low polydispersity which makes these particles ideal building blocks for photonic applications; either on a single particle level (e.g. as optical resonator) or in self-organised 2D and 3D photonic crystals. Both the optical properties and interaction potential between the particles can be tuned by changing shell thickness with respect to the core. Moreover, the ZnS can be doped with manganese to induce fluorescence or a fluorescent dye can be incorporated into the silica layer at a well-defined radial position. In this way the local density of photonic states can be probed. The location of the dye inside the particle is guided by theoretical calculation of local radiation rate enhancement. The structure and optical properties of a single particle are studied by means of static light scattering and absorption measurements and compared to Mie scattering theory. Transmission measurements on 2D and thin 3D colloid crystals on a glass substrate will be discussed.

3:30 PM *CC6.6/G7.6

NANOARRAYS: THE EASY WAY USING BLOCK COPOLYMERS.

Lee Rockford, Thomas Thurn-Albrecht, Jason DeRouchey, Mark Tuominen and Thomas Russell, Univ of Mass, Depts of Polymer Science and Engineering and Physics and Astronomy, Amherst, MA.

Using controlled interfacial interactions and electric fields, thin films having high ordered and aligned arrays of block copolymers were prepared. Standard lithographic processes were used to generate well-ordered arrays of cylindrical pores and channels having dimensions of several nanometers with aspect ratios ranging from unity to in excess of one hundred. Reactive ion etching with CF₄ was found to be an effective means by which the nanoscopic pattern could be transferred to a silicon substrate. Applications of these porous films and patterns transferred into the silicon will be discussed.

4:00 PM CC6.7/G7.7

SELF-ORGANIZING POLYMER MEMBRANES FOR WATER

FILTRATION. J.F. Hester, P. Banerjee, A. Akthakul, A.M. Mayes, M.I.T., Department of Materials Science and Engineering, Cambridge, MA.

Filtration of oil- and protein-containing solutions using polymer membranes is strongly limited by fouling of the membrane surface and pores, which results in decreased permeate flux over time. In this work, self-organizing blends of amphiphilic comb polymers and poly(vinylidene fluoride) are investigated as a means to impart fouling resistance to PVDF filtration membranes. Surface segregation of the comb component is shown by XPS analysis to occur during the coagulation step of phase inversion casting. Ultrafiltration studies indicate substantial reduction of protein adsorption on the surface-modified membranes. The development of self-healing membrane surfaces is described, as well as strategies to impart pH-tunable pore sizes.

4:15 PM CC6.8/G7.8

THIN FILM PHASE SEPARATION ON A NANOSCOPICALLY PATTERNED SUBSTRATE. Kenji Fukunaga, Hubert Elbs, Robert Magerle, Georg Krausch, Lehrstuhl fuer Physikalische Chemie II, Universitaet Bayreuth, Bayreuth, GERMANY.

We investigate phase separation in a thin film of a binary polymer blend A/C in the presence of a solid substrate covered with immobilized nanoscopic domains of the respective polymers. The patterned substrate is realized by physisorbing a microphase separated brush of an ABC triblock copolymer. We observe a marked suppression of phase separation in the blend on the pattern as compared to a laterally homogenous substrate. The effect is studied as a function of blend film thickness. The results are compared to a simple estimate of the interfacial energies.

4:30 PM CC6.9/G7.9

MICRODOMAIN STRUCTURE OF ULTRATHIN SBS AND SBM COPOLYMER FILMS. Robert Magerle, Matthias Konrad, Armin Knoll, Georg Krausch, Lehrstuhl fuer Physikalische Chemie II, Universitaet Bayreuth, Bayreuth, GERMANY.

Block copolymers composed of two or more blocks of immiscible polymers tend to phase separate into regular structures with translational symmetry resembling crystalline materials with characteristic lengths given by the size of the blocks. The particular morphology characteristic of a given block copolymer is determined by both volume filling arguments and by the degree of incompatibility between the blocks. In thin films the interfacial energies at the film boundaries constitute an additional factor for the resulting film structure. In the present contribution we study the morphology of

ultrathin films of SBS and SBM tri-block copolymer films with scanning force and optical microscopy. The samples have been spin cast and subsequently exposed to the vapours of different solvents. Details of the microdomain structure (observed on the micron and nanometer scale) resemble phenomena like island formation, surface reconstruction, and dislocations, which are generally observed in crystalline material on the atomic scale. We present a new method for 3D imaging of block copolymer microdomain structures with nanometer resolution.

4:45 PM CC6.10/G7.10

PERM-SELECTIVE ELASTOMERIC MEMBRANES FROM SELF-ASSEMBLED BLOCK COPOLYMER IONOMERS.

N. Beck Tan, D. Crawford, E. Napadensky, Weapons and Materials Research Directorate, U.S. Army Research Laboratory, Aberdeen Proving Grounds, MD; K. Laverdure, S. Gido, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA; D. Reuschle, D. Mountz, K. Mauritz, Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS; W. Liu and B. Hsiao, Department of Chemistry, State University of New York, Stony Brook, NY.

Current technology in protective clothing materials utilizes high barrier elastomers to prohibit the penetration of toxins. This method, though effective, imposes a tremendous physiological heat stress on the wearer. New technologies being explored for protective materials include perm-selective membranes. These membranes are designed to allow the passage of water vapor thereby providing for heat transfer without sacrificing the resistance to toxin penetration. Ideally, these materials should have fast water vapor transport, flexibility, ready processability, and low cost. One potential candidate material for perm-selective clothing is based on a self-assembled triblock copolymer. The copolymer, Poly(styrene-*b*-isobutylene-*b*-styrene) has a morphology composed of a high barrier elastomer matrix (isobutylene) with glassy, cylindrical polystyrene channels. The styrenic component is sulfonated to encourage water vapor transport. Initial studies, reported here, show that the sulfonation does not change the morphological pattern in the system (cylinders), but greatly disrupts the long range order. Mechanical properties are also significantly modified by sulfonation. Sorption and permeation studies indicate that water transport is greatly enhanced by sulfonation. Effects of processing conditions, choice of sulfonic acid counter-ion and sulfonation level in the styrene block are presented.

SESSION CC7:

Chairs: Christoph F. Schmidt and Helmut H. Strey
Thursday Morning, December 2, 1999
Salon J/K (M)

8:30 AM *CC7.1

MICRO-RHEOLOGY OF SEMIFLEXIBLE POLYMERS. W. Moehler¹, M.W. Allersma², R.M. Fondacave², L.M. Clarke², F. Gittes², F.C. MacKintosh², C.F. Schmidt¹; ¹ Vrije Universiteit, Div. Physics & Astronomy, Department of Biophysics, Amsterdam, THE NETHERLANDS; ² Univ. Michigan, Dept. Physics & Biophys. Res. Div., Ann Arbor, MI.

Several techniques have been developed in recent years for viscoelastic measurements on microscopic scales. Such methods provide new prospects for high frequency rheology, for characterization of inhomogeneities in soft materials, as well as for studies of material properties in small samples, including living biological cells. Many of the diverse material properties of soft materials stem from their complex structures and dynamics with multiple length and time scales. Examples of such materials are polymer solutions, gels, or the filamentous protein networks forming the cytoskeleton of cells. Such materials are usually viscoelastic, exhibiting both viscous- and elastic-like response. One of the most frequently studied material properties of such systems is the shear modulus. In contrast to ordinary solids, the shear modulus of polymeric materials can exhibit significant time or frequency dependence in the range of milliseconds to seconds or even minutes. Semiflexible polymers and networks or solutions made of such polymers behave quite differently from flexible polymers, and have received recent experimental and theoretical attention. Most biological polymers fall in this class. I will give an overview of recent developments in the field and will report on our dynamic experiments with F-actin gels and with single filaments of F-actin and with microtubules.

9:00 AM CC7.2

RHEOLOGICAL PROPERTIES OF SEMIFLEXIBLE FILAMENTOUS BACTERIOPHAGE FD. Frank G. Schmidt, Bernhard Hinner, Erich Sackmann, Technische Universität München, Institut für Biophysik München; Jay X. Tang, Physics Department, Indiana University, Bloomington, IN.

In order to test recent theoretical advance in understanding viscoelastic properties of semiflexible filaments, we performed both macroscopic and microscopic rheological measurements with solutions of filamentous bacteriophage fd. The fd viruses are semiflexible filaments of length 0.9 μm , diameter 6.6 nm, and persistence length 2.2 μm . The viscoelastic storage and loss moduli, $G'(f)$ and $G''(f)$ were measured in a frequency-range of $f=0.01$ to 4 Hz. The onset of a narrow and slanted plateau-like region of $G'(f)$ can be located at around 2 Hz. The dependence of the plateau-modulus on concentration approximates a power law with an exponent of 1.4 ± 0.3 , similar to what has been found for solutions of F-actin without crosslinks. In the low-frequency regime, the frequency-dependence of the viscoelastic moduli can be described by power laws of $G'(f) \propto f^{1.0-1.2}$ and $G''(f) \propto f^{0.7-0.9}$, respectively. Although the exponent for $G'(f)$ increases slightly with decreasing concentration, the significant deviation from the simple theoretical predictions of $G'(f) \propto f^2$ at the low frequency limit indicates interesting filament dynamics of fd in solutions of several mg/ml concentrations. At the low shear limit, the concentration-dependence of dynamic viscosity fits a power law of $\eta(f) \propto f^{2.6}$. This exponent is close to 3.0, as expected for a suspension of hardrods at the low frequency limit. The overall experimental results suggest rich dynamic properties of short semiflexible filaments at both low and high frequency ranges, which require further studies.

9:15 AM CC7.3

THEORY OF THE TUBE DIAMETER IN TIGHTLY-ENTANGLED SOLUTIONS OF SEMI-FLEXIBLE POLYMERS. David Morse, Univ. Minnesota, Dept. of Chemical Engineering and Materials Science, Minneapolis, MN.

An approximate statistical mechanical theory is presented for the tube diameter and corresponding plateau modulus of very tightly-entangled solutions of semi-flexible polymers, such as F-actin, in which the tube diameter is much less than the polymer persistence length. An effective confinement potential for a randomly chosen test chain in such a solution is defined by considering the average increase in the free energy of the surrounding network that results if the test chain is displaced sideways while maintaining the topology of the network. It is assumed that each of the surrounding chains is also confined to a tube by a confinement potential whose magnitude must be chosen so as to be consistent with that calculated for the test chain. Many-chain correlations are introduced via an effective medium approximation, in which it is assumed that the tube contour of each surrounding chain is displaced by forces exerted on the network by the test chain as if it were embedded in an elastic continuum with a shear modulus equal to the self-consistently determined plateau modulus of the solution. Predictions are compared to measurements of the tube diameter (by fluorescence microscopy) and the plateau modulus in F-actin solutions.

9:30 AM CC7.4

HOW DOES ACTIN FILAMENT TREADMILLING GENERATE MOTION? Ben O'Shaughnessy, Dept Chemical Engineering, Columbia University, New York, NY; Dimitrios Vavylonis, Dept Physics, Columbia University, New York, NY.

The dynamics of assembly and disassembly of the actin cytoskeleton are central to cell locomotion. In vitro studies have shown that shortly after incorporation into a polymerizing filament, the ATP nucleotide associated with each free actin monomer is hydrolyzed. This leads to "treadmilling" of monomers; attaching at the "barbed" end, they traverse the length of the filament and are released at the "pointed" end. The filament translates spatially in the process. In this way ATP hydrolysis is the suggested driving force for cell motion. Here we study theoretically the dynamics of actin treadmilling in vitro and the approach to steady state of the filament length, free monomer pool, and ATP hydrolysis rate. Fluctuations in the length distribution are important at high treadmilling rates and sufficiently long times. Living cells are believed to control actin dynamics by tuning depolymerization rates, free monomer concentration, nucleation, and filament capping through a series of specialized proteins. We examine the dynamics of these perturbations and discuss the time-dependent motion they would imply for an oriented filament array moving against an external load.

9:45 AM CC7.5

TWIRLING AND WHIRLING: VISCOUS DYNAMICS OF ROTATING ELASTICA. Charles W. Wolgemuth, University of Arizona, Dept of Physics, Tucson, AZ; Thomas R. Powers, Harvard University, Division of Engineering and Applied Sciences, Cambridge, MA; Raymond E. Goldstein, University of Arizona, Dept of Physics and Program in Applied Mathematics, Tucson, AZ.

The stability and dynamics of rotationally forced elastic filaments arise in several important biological settings involving bend and twist

elasticity at low Reynolds number. Examples include DNA transcription and replication and bacterial flagellar motion. In order to elucidate fundamental processes common to these systems, we consider the model problem of a rotationally forced filament with twist and bend elasticity. Competition between twist injection, twist diffusion, and writhing instabilities is described by a novel pair of coupled PDEs for twist and bend evolution. Analytical and numerical methods elucidate the twist/bend coupling and reveal two dynamical regimes separated by a Hopf bifurcation: (i) diffusion-dominated axial rotation, or twirling, and (ii) steady-state cranksafting motion, or whirling. Experiments are proposed to examine these phenomena and the consequences for swimming investigated.

10:30 AM *CC7.6

SINGLE MOLECULES ON CATIONIC SUPPORTED MEMBRANES. Joachim O. Rädler, Institut für Biophysik, Physik Department, Technische Universität München, Garching, GERMANY.

We report on the dynamic conformation of single double-stranded DNA molecules on fluid supported membranes. Using fluorescence microscopy and image processing the radius of gyration, self-diffusion and rotational relaxation is measured.

The scaling behavior is found to be in good agreement with predicted scaling laws for a self-avoiding random walk in two dimensions.

Cationic membranes saturated with DNA exhibit chain segregation and reduced self-diffusion due to crowding. The excluded area is estimated from the electrostatic rod-rod interaction on mixed lipid membranes. We will furthermore discuss the wetting behavior of phospholipid membranes on solid substrates, which turns out to be a fundamental aspect in the preparation of supported membranes. Experiments on microstructured solid surfaces visualize the role of pinning centers. Ultimately fluid supported membranes have prospective applications for molecule manipulation in microdevices.

11:00 AM *CC7.7

MICROSCOPIC THEORY OF CONVECTIVE CONSTRAINT RELEASE. S.T. Milner, Exxon Research and Engineering, Annandale, NJ.

We develop a microscopic description of the contribution to stress relaxation in entangled polymer melts of convective constraint release, which is the release of entanglement constraints due to the effects of convective flow on chains entangling a given chain. Our theory resolves two of the main shortcomings of the Doi-Edwards model in nonlinear rheology, in that it predicts 1) a monotonically increasing shear stress as a function of shear rate, and 2) shear stress independent of molecular weight at sufficiently high shear rates, in agreement with experiment.

11:30 AM CC7.8

Abstract Withdrawn.

11:45 AM CC7.9

SHRINKING PATTERNS OF POLYMER GELS DURING VOLUME PHASE TRANSITION. Gang Bai, Atsushi Suzuki, Yokohama National University, Dept of Materials Science, Yokohama, JAPAN.

We report the shrinking patterns of the neutral and the slightly ionized poly(N-isopropylacrylamide) (NIPA) gels during the volume phase transition. The gel was synthesized in a cylindrical shape with submillimeter diameter. The macroscopic conformation change was observed on heating process in two different methods. One is a continuous heating process with a constant temperature drift rate, and the other is an isothermal process after a step-like temperature increase beyond the transition point. In the neutral gel, two types of surface pattern as well as the growth of a collapsed surface skin layer appeared, which depends on the temperature drift rate as well as the degree of super-heating (how far the final temperature is from the transition point). On the other hand, the macroscopic behavior of the slightly ionized gels can be characterized by several different conformation changes, including the phase coexistence (or linked-dumplings), the grain-like pattern, the bubble-like pattern, and the opaque phase. It was found that the shrinking patterns have correlation with the phase transition velocity. The results will be discussed qualitatively on the basis of the classical phase separation model of nucleation and spinodal decomposition, as well as the phase diagram of the present gel system. We will present a simple model to describe the stability of the phase coexistence and the relation to the transition mechanisms on the basis of the diffusion not only of the polymers but also of the ions in the solvent.

SESSION CC8:

Chairs: David G. Grier and V. Adrian Parsegian
Thursday Afternoon, December 2, 1999
Salon J/K (M)

1:30 PM *CC8.1

SALTY SURFACES. P. Pincus, Materials and Physics Depts., Univ of California, Santa Barbara, CA.

Electrostatic interactions play an important role in a variety of biomolecular phenomena. For example, the condensation of mm long DNA into micron scale cell nuclei and viral capsids requires exquisite organization. This is achieved in spite of the very high anionic charge density of DNA arising from the base pairs (approximately one negative charge per 1.7 Å). We now understand that the overall driving force for DNA condensation is attractive interactions induced by either multi-valent cations or higher order assembly engendered by cationic proteins, histones, into nucleosomes and ultimately into supercoiled chromatin. This presentation will focus on the Coulombic interactions between highly charged surfaces in an aqueous environment. In particular, we shall discuss how correlated fluctuations, enhanced by multi-valent counterions, lead to short range attractive forces between like charges. The relation between the fluctuation forces and two dimensional Wigner crystals will also be considered. Quantum fluctuations of the 2D wigner crystal are shown to yield a long-range Casimir-like attractive interaction with an unusual power law behavior. If time permits, additional mechanisms leading to attractive forces associated with dielectric contrast and depletion interactions will be mentioned.

2:00 PM *CC8.2

SCREENING OF A MACROION BY MULTIVALENT IONS: CORRELATION INDUCED INVERSION OF CHARGE.

B.I. Shklovskii, Theoretical Physics Institute, Univ. of Minnesota, Minneapolis, MN.

Screening of a strongly charged macroion by multivalent counterions is considered. It is shown that counterions form a strongly correlated liquid at the surface of the macroion. The cohesive energy of this liquid leads to an additional attraction of counterions to the macroion surface which is absent in conventional solutions of the Poisson-Boltzmann equation. Away from the surface this attraction can be taken into account by a new boundary condition for the concentration of counterions near the surface. The Poisson-Boltzmann equation is solved with this boundary condition for a charged flat surface, a cylinder and a sphere. In all three cases, screening is much stronger than in the conventional approach. At some critical exponentially small concentration of multivalent counterions in the solution they totally neutralize the surface charge at small distances from the surface. At larger concentrations they invert the sign of the net macroion charge. The absolute value of the inverted charge density can be as large as 20% of the bare one. In particular, for a cylindrical macroion, it is shown that for screening by multivalent counterions predictions of the Onsager-Manning theory are quantitatively incorrect. The net charge of the cylinder is smaller than their theory predicts and inverts sign with growing concentration of counterions. Moreover the condensation loses its universality and the net charge linear density depends upon the bare one. Applications of this theory to the modification of the bending rigidity of membranes or polyelectrolytes and to the reentrant condensation of DNA induced by multivalent ions are discussed.

2:30 PM CC8.3

ELECTROSTATIC INTERACTIONS IN CLOSELY PACKED ORDERED BIOPOLYELECTROLYTE SYSTEMS STUDIED BY COUNTERION NMR AND COMPUTER SIMULATIONS.

Lars Nordenskiöld, Lorens van Dam, Alexander Lyubartsev, Nikolay Korolev and Aatto Laaksonen, Physical Chemistry, Arrhenius Laboratory, Stockholm University, Stockholm, SWEDEN.

Biopolyelectrolytes such as DNA, F-actin and filamentary virus particles form aggregated ordered structures upon addition of multivalent ions. The polyelectrolyte properties of condensed ordered biopolyelectrolytes have recently received considerable attention and it is of importance to obtain experimental data on the ionic interactions that can be compared with theoretical predictions based on polyelectrolyte theories. We have studied the interaction between Cs and Li counterions in oriented DNA fibres of varying water contents, by means of NMR self-diffusion measurements on the counterions. Data from MD simulations on the corresponding systems have been used to calculate self-diffusion coefficients and orientational distribution functions for the counterions. The Li ion diffusion is considerably slower than that of the Cs ion which is found to be due to loss of water of hydration for the Li-ions, giving strong and long lived interactions with the DNA phosphate groups with one shared hydration shell around the Li-phosphate complex. In another set of experiments, results of self-diffusion of water and the following polyamines in oriented DNA have been obtained: spermidine (three-valent), putrescine and diaminopropane (both divalent). The results show that the diffusion of the three-valent spermidine ligand is considerably slower than that of the divalent polyamines. At high water content where DNA is in the B-form, the divalent polyamines

have identical diffusion coefficients. We have also studied the competitive interaction of mono- and divalent counterions with condensed, bundled forms of such biopolyelectrolytes as DNA and the filamentous virus particles fd and M13 by means of Monte Carlo simulations.

2:45 PM **CC8.4**

DOES SALINITY AFFECT ELECTROPORATION?

H. Aranda-Espinoza and N. Dan, Dept. of Chemical Engineering, Drexel University, Philadelphia, PA.

High voltage electric pulses are known to increase membrane permeability through electroporation, namely, the creation of temporary pores. Determining the minimal pulse strength and duration required for pore formation is essential for minimization of cell damage. Using a mean field model we calculate the free energy of a permeable membrane vs. an impermeable one, as a function of the applied electrostatic potential and system parameters. When this difference exceeds a critical value, a pore would form. Surprisingly, we find that over a wide range of parameters the free energy difference is independent of the salt concentration in the system. This prediction is in excellent agreement with the recent experiments of Diederich, et al. (PRE vol. 58, p. 4883, 1998).

3:30 PM ***CC8.5**

THE ELECTROSTATIC DOUBLE LAYER RE-VIEWED.

V. Adrian Parsegian, LPSB/NICHD/NIH, Bethesda, MD.

Formulation and computation of electrostatic double layers has become a cottage industry. The majority of practitioners comfortably forget the fragility of the usual simplifying assumptions of continuum dielectrics, metallic-sphere ions, and ideal interfaces. In two directions this talk with look away from common practice. These departures were forced on us by experiments in our lab as well as in many others. * Macroscopically, the properties of electrostatic double layers are often better described by spatial averages. There is profit in treating the simultaneous push and pull on co- and counter-ions from the viewpoint of Gibbs adsorption isotherms. Count the number of ions perturbed a charged surface and estimate the extent to which that surface perturbs its surroundings. * Microscopically, ions interact with each other and with surfaces far more instructively than if they were spherical metal bits floating in infinitesimally smooth waters. Examples will be drawn from: Computer simulations, of double layers and of ion-reactive proteins, which can be far more useful than usually realized in predicting experiments. Interacting charged bilayers where charge can come or go from non-coulombic ion-bilayer binding Ionic channels ensconced in charged membranes when conductance reflects the influence of membrane charge on the surrounding salt solution DNA over its assembly phase diagrams where measured free energies of formation provide rigorous tests of theories than are usually applied. Neutral polymers, polysaccharides, whose intermolecular forces are measured in salt solutions. Single molecule mechanics, such as DNA stretching sensitive to bathing ions.

4:00 PM **CC8.6**

POSITIVELY CHARGED VESICLES CAN REPEL NEGATIVE OBJECTS.

H. Aranda-Espinoza and N. Dan, Drexel Univ; Y. Chen, T. Lubensky, P. Nelson, Univ of Pennsylvania; L. Ramos, Univ de Montpellier; D. Weitz, Harvard Univ.

Charged bilayer vesicles can direct the formation of a surprising new class of colloidal aggregates. Mixed vesicles of neutral and cationic surfactant, when combined with anionic colloidal spheres, spontaneously self-assemble into complexes with close-packed, self-limiting, rafts of spheres floating on tense round vesicles. To understand the phenomenon we show how a positively-charged, mixed bilayer vesicle in the presence of negative surfaces can spontaneously partition into an adhesion zone of definite area, and another zone which repels additional negative objects. Though the membrane itself has nonnegative charge, negative counterions on the interior of the vesicle spontaneously aggregate to the nonadhering zone and present a net negative charge to the exterior.

4:15 PM **CC8.7**

DIRECT-FORCE MEASUREMENTS BETWEEN COLLOIDAL PARTICLES BY SOME SIMPLE NEW METHODS.

S. Olugebefola, P. Banerjee, C.J. Barrett, A.M. Mayes, Massachusetts Inst. of Technology, Dept. of Materials Science and Engineering, Cambridge, MA; J. Iyer, P.T. Hammond, Massachusetts Inst. of Technology, Dept of Chemical Engineering, Cambridge, MA; T.G.M. van de Ven, McGill Univ., Pulp & Paper Res CTR, Dept of Chemistry, Montreal, CANADA.

Polymer chains that are chemically attached to solid surfaces have important commercial uses in colloidal stabilization. In this investigation, recently developed force measurement methods (micro-collision dynamic light scattering, force microscopy, and

Langmuir trough compression) have been employed to observe the interactions between colloidal particles stabilized by tethered polymer chains. Monodisperse latexes stabilized by hydrophilic side chains of surface-attached comb polymers are analyzed by the above methods in a water environment. By modifying the comb architecture to incorporate both hydrophilic and hydrophobic side chains, attractive wells are introduced into the force-distance profiles, in agreement with recent self-consistent mean field predictions.

4:30 PM ***CC8.8**

UNSOLVED PROBLEMS IN SCATTERING OF CONCENTRATED CHARGED COLLOIDAL SYSTEMS. Thomas Zemb, Service de Chimie Moléculaire, Gif sur Yvette, FRANCE.

When the Debye length exceeds the average distance between bilayers or globular colloids and when the area per charge is of the order of 1 structural charge/nm², one is in high surface potential regime. In this physical situation of "strongly coupled" charged colloids, some counter-intuitive scattering results that are difficult to reconcile with current electrostatic interaction theories will be described: 1 - Radial versus azimuthal broadening of Bragg peaks of strongly fluctuating charged bilayer stacks. During dilution, Bragg peaks quickly disappear while smectic bilayers stacks are still observed by electron microscopy. 2 - Orstein-Zernike behavior of small angle light scattering on asymmetric sponge phases (disordered connected lamellar) can be fitted but produces unrealistic correlation lengths.

SESSION CC9: POSTER SESSION
Thursday Evening, December 2, 1999
8:00 P.M.

Exhibition Hall D (H)

CC9.1

VISCOSITY AND MORPHOLOGY OF SYNTHETIC LUNG SURFACTANT MONOLAYER. Junqi Ding¹, Heidi E. Warriner¹,

Anja von Nahmen¹, Joseph A. Zasadzinski¹, Alan J. Waring²; ¹Department of Chemical Engineering, University of California, Santa Barbara, CA, ²Department of Pediatrics, MLK/Drew University Medical Center and Perinatal Labs, Harbor-UCLA, CA.

The primary function of lung surfactant (LS) is to form a monolayer at the alveolar air/water interface capable of lowering the surface tension to near zero values. An important corollary to this is that the monolayer must also be able to resist collapse upon the compression that accompanies expiration. One role of the lung surfactant specific proteins SP-B and SP-C is to stabilize the monolayer against collapse; the collapse structure of monolayers with SP-B or SP-C are dramatically different from that without lung surfactant proteins. These novel collapse structures are likely due to changes in the mechanical properties of the monolayer induced by the proteins. We use a magnetic needle viscometer along with optical and probe microscopy to study synthetic lung surfactant systems to determine the relationship between lung surfactant components and monolayer mechanical properties. Systematic measurements of monolayer viscosity as function of protein concentration, temperature, and phase behavior are reported and their relations with the mechanism of a novel buckling mechanism found in lung surfactant mixtures are discussed.

CC9.2

DETECTION OF SHAPE FLUCTUATIONS IN LARGE LIPID VESICLES USING DIFFUSING-WAVE SPECTROSCOPY.

Michael Lamont and Barbara Frisken, Simon Fraser Univ, Dept of Physics, Burnaby, BC, CANADA.

Diffusing-wave spectroscopy (DWS) is a light scattering technique which uses highly scattering samples that randomize the path of photons as they pass through the sample. Thus the photon paths can be modelled using the diffusing equation. Because a photon is scattered many times before it exits, the small change in path length due to a single scattering event can be amplified to detectable levels. Thus DWS allows for the resolution of small amplitude signals and has previously been used successfully in detecting thermal fluctuations in emulsion droplets [1]. Because a vesicle is a spherical shell made of a thin lipid bilayer, it does not scatter light strongly enough to use DWS directly. However, when a dense sample of vesicles is combined with polystyrene spheres, the spheres effectively increase the path length of the photons in the sample cell and increase the number of scattering events from the vesicles. By studying the DWS intensity correlation for temperatures above and below the bilayer's transition temperature, the existence of shape fluctuations in 300nm vesicles has been confirmed. [1] Hu Gang, A.H. Krall and D.A. Weitz, Phys. Rev. E 52, pp6289-6302 (1995)

CC9.3

X-RAY SCATTERING FROM HOMOPOLYMER-BLOCK COPOLYMER BLENDS: PART II, DYNAMICS. P. Falus, M.A. Borthwick, D. Lumma, L.B. Lurio and S.G.J. Mochrie, Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Dynamic X-ray Scattering measurements are presented of the dynamics of cylindrical polymeric micelles, self-assembled in homopolymer-block copolymer blends. The emerging technique of Dynamic X-ray Scattering was used at the 8-ID beam line of the Advanced Photon Source to characterize the low-energy diffusive micellar dynamics in the limit of high wavevectors (Q) *i.e.* for $2\pi/R > Q > 2\pi/L$, where L = micellar length. Our Dynamic X-ray Scattering results will be compared to what may be expected for the dynamics of hard cylinders.

CC9.4

LARGE SCALE ALIGNMENT OF ABC BLOCK COPOLYMER MICRO DOMAINS VIA SOLVENT VAPOR TREATMENT. Kenji Fukunaga, Hubert Elbs, Robert Magerle, Georg Krausch, Universitaet Bayreuth, Lehrstuhl fuer Physikalische Chemie II, Bayreuth, GERMANY.

We have studied the micro domain morphology of thin ABC triblock copolymer films supported by a solid substrate. The films were exposed to various solvent vapors and the effect of the solvent removal speed on the resulting morphologies is investigated. Slow solvent extraction rates lead to a parallel alignment of lamellar micro phases within the plane of the film. On fast drying, a perpendicular orientation of the lamellae is found. In the case of block copolymer samples with a highly anisotropic macroscopic shape the micro domains can be aligned over large lateral areas. The results are discussed in view of the mechanical strain fields present during the drying process.

CC9.5

THE EFFECT OF SALT VALENCY ON THE SHEAR THICKENING OF DILUTE WORM-LIKE MICELLAR SOLUTIONS. Jennifer M. Politsch, Department of Chemical Engineering, University of California, Santa Barbara, CA; David J. Pine, Departments of Chemical Engineering and Materials, University of California, Santa Barbara, CA.

We investigate the shear thickening of dilute worm-like micellar solutions at concentrations ranging from the CMC to the micelle overlap concentration. The systems studied consist of a cationic surfactant, cetyltrimethylammonium bromide (CTAB) and a complex salt, the salicylate ion (Sal^-) salted with either a monovalent counterion, sodium (Na^+), or a divalent counterion, magnesium (Mg^{+2}). Comparisons between the two salts are made by maintaining a constant CTAB: Sal^- ratio. While significant shear thickening is observed in solutions containing either salt, the shear-thickening is much stronger in those samples containing the divalent counterion. The divalent salt solutions are more viscous in the shear-thickened state and exhibit lower critical strain rates. This suggests that Coulombic interactions and polyelectrolyte effects play a crucial role in controlling shear thickening in these systems. This work was supported by the MRL Program of the National Science Foundation under Award No. DMR96-32716.

CC9.6

MOLECULAR DYNAMICS SIMULATION OF SUBSURFACE DEFORMATIONS IN NEMATIC LIQUID CRYSTALS. J.J. Castro, A. Calles, R.M. Valladares, Facultad de Ciencias, UNAM, Mexico City, MEXICO.

Using molecular dynamics simulation, we study the existence of subsurface deformations in the orientational ordering of a nematic liquid crystal of finite volume. Our model consists of a nematic medium confined to a space between two planar substrates. The molecular interaction in the nematic phase is describe by the superposition of the anisotropic induce dipole-induced dipole and isotropic Maier-Saupe interaction, and the external anchoring (nematic-substrate) is describe by the Rapini-Papoular interaction. We compare our results with calculations based on lattice models and also with some other molecular dynamics simulations using different interparticle potential.

CC9.7

SALT EFFECTS ON THE PRE-AGGREGATION OF NANOPARTICLES. T. Zemb, S. Lyonnard, O. Spalla, L. Belloni, J. Bartlett, K. Finnie, J. Woolfrey, CEA Seaclay, Gif sur Yvette, FRANCE.

Advanced ceramics formulation requires a controlled step of adiabatic compression of concentrated inorganic nanoparticles. During this step,

engineering recipes require that the addition of a particular amount of divalent or trivalent salt to the inorganic nanoparticle solution. Excess salt leads to flocculation, while too little salt in the formulation induces fragmentation of the droplets during drying, hence producing fine aerosols instead of porous powder of controllable granulometry. We have correlated the SANS produced by the initial sols, which gives the interparticle potential with the USAXS spectra of the final powder produced. The "right engineering amount" corresponds to the case of "soft repulsion" between nanoparticles which is the physical requirement to control the production of porous powder from a dense titania/zirconia colloidal solution.

CC9.8

EFFECT OF THE DIPOLAR INTERACTIONS ON THE PHASE BEHAVIOR OF POLAR LIQUIDS: A SIMULATION STUDY. Godfrey Gumbs and Girija S. Dubey, Department of Physics and Astronomy, Hunter College of CUNY, New York, NY.

We will present computer simulation results for the structural behavior of polar fluid. To have a better insight of this complex problem, we have done a detailed simulation study of polar fluids to investigate the structural behavior of chain formation based on an electrostatic interaction potential and its dependence on the dipolar strength. We have used the Ewald summation method with suitable boundary conditions for the long-range interaction. Our simulation results clearly show that chain formation is certainly not just temperature-dependent but it also depends on the dipolar strength.

CC9.9

SWELLING PROPERTIES OF POLYMER GELS UNDER BIAxIAL MECHANICAL CONSTRAINT. Xi Rong Wu, Atsushi Suzuki, Yokohama National University, Dept of Materials Science, Yokohama, JAPAN.

We report the volume phase transition of poly(N-isopropylacrylamide) (NIPA) gels under biaxial mechanical constraint. The film-like gels were prepared by a free radical polymerization reactions between two glass plates with a thin spacer (thickness is submillimeter) in pure water under nitrogen atmosphere at 0°C . One of the gel surfaces was chemically adhered on a glass plate by using Bind Silane (Pharmacia). After the gelation, one glass plate was carefully removed from the gel, thus forming a clamped film gel on the other glass plate. By the same method, we synthesized the gel both surfaces of which are chemically adhered on glass plates. The sample was set in a small thermostat bath with water, and the temperature was regulated within $\pm 0.05^\circ\text{C}$. The thickness of each system was measured as a function of temperature by an optical microscopy. When one surface of the gel was chemically adhered onto a glass plate, the phase transition becomes continuous, and the swollen (collapsed) thickness becomes larger (smaller) than the linear swelling ratio of the free gel. On the other hand, the transition temperature is evidently increased and the transition becomes more discontinuous, when both surfaces were chemically adhered onto the glass plates. These observations were discussed by the equation of states of gels on the basis of the extended Flory-type free energy taken into account the uniaxial and biaxial mechanical constraint.

CC9.10

PARTICLE INTERACTIONS AND RHEOLOGICAL PROPERTIES OF POLYVINYL ACETATE SUSPENSIONS STABILIZED BY POLYVINYL ALCOHOL. Stefano Carra, Vinavil Spa, Villadossola (VB), ITALY; Leonardo Malcovati, Sergio Carra, Dept. Chimica Fisica Applicata, Politecnico di Milano, Milano, ITALY.

Polyvinyl acetate emulsions are commodity raw-materials for the coating industry, widely applied in the production of water-borne adhesives and coatings. Since conventional anionic surfactants are quite ineffective in the stabilization of polyvinyl acetate-based emulsions, they are often replaced by nonionic polymer molecules, generically referred to as steric stabilizers. A variety of polymeric stabilizers is used industrially, polyvinyl alcohol being the most common, particularly in the case of latices for the formulation of adhesives. The effects of polyvinyl alcohol on the final properties of the emulsion are important but scarcely understood. Furthermore the use of polyvinyl alcohol has been identified as a major source of irreproducibilities in final latex properties. An attribute particularly important in applications is the latex viscosity. Viscosity control in industrial practice is usually delegated to empirical correlations, but a quantitative treatment of the problem would definitely pave the way to the development of effective strategies for product optimization. In particular, it is important to appreciate the influence of stabilization mechanisms on the nature and strength of interparticle forces, since these directly affect the rheological properties of the latex. The relative viscosity of a dispersion can be expressed in the form of a virial expansion, as a function of the total solids volume fraction. The virial coefficients depend upon the form of interparticle potentials. In the course of this work several polyvinyl acetate emulsion poly-

merization reactions were performed, with different amounts and types of polyvinyl alcohol. Final viscosity values were demonstrated to be consistent with a sticky hard sphere potential. In this paper the attention is focused onto the low-solids regime, with the intention of extending the approach to high solids content in future work. A particular attention here has been devoted to the problem of the estimation of the adsorption parameters of polyvinyl alcohol: the total amount adsorbed onto the polymer particles and the thickness of the adsorbed layer.

CC9.11

FIRST-PRINCIPLES MOLECULAR DYNAMICS OF A KNOT IN A POLYMER STRAND. Antonino Marco Saitta, Michael L. Klein, Univ of Pennsylvania, Center for Molecular Modeling, Philadelphia, PA.

The mechanical resistance of a rope subject to tension and the way its properties are affected by the presence of knots are, and have always been, subjects of widespread interest in everyday life. We model this very general situation by studying the strain-induced breaking of the simplest polymer, i.e. polyethylene (A.M.Saitta *et al.*, Nature **399**, 46-48 (1999)). Those *ab-initio* molecular dynamics calculations show that the chain resistance is significantly weakened by the presence of a knot, which also affects the location of the rupture along the chain, which invariably breaks just outside the entrance to the knot. Further dynamical evolution of the chain fragments gives rise to a series of fast and unexpected chemical reactions falling in the range of "femtochemistry".

CC9.12

INSERTION PROCESS OF A PROTEIN SINGLE LAYER IN A FREE STANDING BILAYER FILM OF LIPIDS. J.J. Benattar, M. Nedyalkov, Service de Physique de l'Etat Condense, Gif sur Yvette, FRANCE; J. Prost, Institut Curie, Paris, FRANCE; A. Tiss, R. Verger, CNRS, Marseille, FRANCE.

We report a new process which inserts a dense monolayer of proteins within the core of a Newton Black Film (NBF). We present the first results of the investigation of this new system by X-ray reflectivity. Black films are the ultimate stages of the thinning of soap films (more generally surfactant films), after water drainage. They are stable, free standing bilayers with lateral sizes of a few centimetres. The described method leads to a two dimensional layer of water-soluble proteins, protected against denaturation by two surfactant monolayers. Very high packing fractions can be obtained in a controlled manner, simply by adjusting the protein chemical potential in the solution connected to the film. This new method opens the possibility for further studies, including the investigation of interfacial processes under perfectly controlled conditions, or the two dimensional crystallisation of such proteins over very large areas. We apply this method here to the confinement of a model protein (BSA) associated to a non-anionic surfactant (C12E6). We observed a time dependent insertion of the protein within the NBF, leading to a close packed single layer. This process is explained in terms of chemical potential gradients. We have shown that this process is also working with phospholipids and other proteins thus leading to a new approach of the biological membranes.

CC9.13

MONTE CARLO SIMULATION OF SMECTIC LIQUID CRYSTALS AND THE ELECTROCLINIC EFFECT. Jianling Xu, Robin L.B. Selinger, Catholic Univ., Physics Dept., Washington, DC; Jonathan V. Selinger, B.R. Ratna and R. Shashidhar, Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, DC.

Using Monte Carlo simulation methods, we explore the role of molecular shape in the phase behavior of liquid crystals and the electroclinic effect. We study a "bent-rod" mesogen shaped like the letter Z, composed of seven soft spheres bonded rigidly together with no intra-molecular degrees of freedom. For strongly angled molecules, we find that steric repulsion alone provides the driving force for a smectic-C phase, even without intermolecular dipole-dipole interactions. For weakly angled (nearly rod-like) molecules, we find a stable smectic-A (SmA) phase and a strong electroclinic effect with a saturation tilt angle of about 19 degrees. In the SmA phase we find evidence of vortex-like point defects. We also observe a field-induced nematic-smectic phase transition.

CC9.14

INTERACTION OF POLYMER WITH CLAYS. Jyotsana Lal, IPNS, ANL, Argonne, IL; Loic Auvray, LLB, CE-SACLAY, Gif-Sur-Yvette, FRANCE.

Normally synthetic well defined monodisperse discotic laponite clays are known to form a gel phase at mass concentrations as low as a few percent in distilled water. Hydrosoluble polymer polyethylene oxide was added to this intriguing clay system, it was observed that it either prevents gelation or slows it down extremely depending on the

polymer weight, concentration or the laponite concentration. Small Angle Neutron scattering (SANS) was used to study these systems because only by isotopic labelling can the structure of the adsorbed polymer layers be determined. The contrast variation technique is specifically used to determine separately the different partial structure factors of the clay and polymer. In this way the signal of the adsorbed chains is separated from the signal of the free chains.

CC9.15

SOLUTION PROPERTIES AND ASSOCIATION OF POLY (BENZOYL P-PHENYLENES): NOVEL HIGH PERFORMANCE POLYMERS. Richard Niro, Amit Sehgal, Thomas A.P. Seery, Univ. of Connecticut, Polymer Science Program, Storrs, CT; Richard Vaia, Air Force Research Center, Wright-Patterson AFB, OH.

Poly(benzoyl p-phenylene) (PBP) is a novel polymer that offers possibilities for use in high temperature composites. Fundamental study of polymers with paraphenylene backbones has not been performed previously due to the insoluble and infusible nature of these polymers. The polar benzoyl group in PBP's provides the means to dissolve the paraphenylene backbone in organic solvents such as dichloromethane, tetrachloroethane, and m-cresol. A series of PBP's were studied using static and dynamic light scattering in order to determine the solution properties of this system. Various molecular weight fractions were obtained by preparatory GPC and analyzed. Specific observations of the rodlike nature of the polymer, the conditions of its known aggregation in solution, and its behavior in various organic solvents were made. Correlations were drawn between this data and an existing set of viscosity measurements along with results from molecular simulations. Knowledge of these solution characteristics can provide information about the conditions under which these high performance polymers can be processed.

CC9.16

NON-DEBYE DIELECTRIC RELAXATION IN LIQUID CRYSTALS CONFINED TO RANDOM POROUS MEDIA. G.P. Sinha and F.M. Aliev, Department of Physics, University of Puerto Rico, San Juan, PR.

Application of broadband dielectric spectroscopy to confined liquid crystals has shown [1] that even relaxation due to the rotation of molecules around short axis, which is of a purely Debye type process in bulk, is broadened when liquid crystal is confined in random porous media. We present results of dielectric investigations on alkylcyanobiphenyls (5CB and 8CB) confined in random porous matrices of two pore sizes (100 Å and 1000 Å) in very broad frequency (10^{-3} Hz - 10^9 Hz) and temperature (140 K to 330 K) range. The dielectric behavior of 5CB and 8CB confined in random porous matrices is very different from their bulk behavior. New properties observed in confined LCs are the appearance of two low frequency non-Debye relaxation processes absent in bulk LCs. The first low frequency process is probably a collective mode due to the relaxation of the surface induced polarization. The second low frequency process is due to the molecular relaxation in the surface layers at liquid crystal-solid pore wall interface. This mode probably is also collective because there could be coupling in molecular motion via surface and coupling of molecules with surface as well. Two bulk-like modes due to the rotation of molecules around short axes and the tumbling motion were present but found to be modified. Additionally the confinement in narrow pores of liquid crystals, which are non-glass formers in bulk, is resulted in the appearance of glass transition absent in the bulk. Anomalous broadening of the dielectric spectrum of the mode due to molecular reorientation motion is observed in deeply supercooled state. Dielectric modes were active in smaller pores at much lower temperatures than in large pores. [1] G.P. Sinha and F.M. Aliev, Phys. Rev. E **58**, 2001 (1998). This work is supported by DoD grant N00014-99-1-0558.

CC9.17

NMR SPECTRA FROM MONTE CARLO SIMULATIONS OF POLYMER DISPERSED LIQUID CRYSTALS: EFFECTS OF MOLECULAR MOTION. C. Chiccoli, P. Pasini, Istituto Nazionale di Fisica Nucleare, Sezione di Bologna, Bologna, ITALY; G. Skačej, S. Žumer, Physics Department, University of Ljubljana, Ljubljana, SLOVENIA; C. Zannoni, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Bologna, ITALY.

Polymer dispersed liquid crystals (PDLC) are materials consisting of nematic droplets embedded in a polymer matrix. In such droplets various nematic structures can occur, depending on the surface molecular alignment imposed by the surrounding polymer. In our analysis the nematic liquid crystal within a PDLC droplet was modeled by the Lebwohl-Lasher lattice spin model. We have applied the Monte Carlo (MC) simulation technique to this model and calculated a sequence of equilibrium molecular configurations inside the droplet for radial, bipolar, and random boundary conditions. Since the deuterium NMR is an appropriate experimental tool widely

used to investigate PDLC, we decided to interpret the output from MC simulations in terms of NMR spectra. Calculating the spectra, two types of dynamic effects have been included: fluctuations of molecular long axes (the corresponding data provided from the sequence of MC-generated configurations) and translational diffusion (simulated by a molecular random walk on the lattice). The results show that molecular fluctuations lead to a narrowing of the NMR spectrum, maintaining the spectral shape, while the diffusive motions result in an averaged spectrum, which in the fast diffusion limit consists of one or two rather narrow lines, depending on the type of boundary conditions considered. In presence of non-negligible molecular motion, a possibility of identifying the nematic structure type from an inspection of the spectra has been discussed. Finally, we considered also cases where an external magnetic field was applied.

CC9.18
CELL MORPHOGENESIS INDUCED BY DISRUPTION OF CYTOSKELETAL ELASTICITY. Roy Bar-Ziv¹, Tsvi Tlusty², Elisha Moses¹, Samuel A. Safran² and Alexander Bershadsky³, Weizmann Institute of Science, Departments of ¹Physics of Complex Systems, ²Materials and Interfaces and ³Molecular Cell Biology, Rehovot, ISRAEL.

Gradual disruption of the elasticity of the actin cytoskeleton by a drug induces a series of structural shape changes in cells that adhere to substrates, leading to a transformation of cylindrical cell extensions into a periodic chain of "pearls". Quantitative measurements of the pearling instability give a square root behavior for the wavelength as a function of drug concentration. We present a theory that explains these observations in terms of the interplay between rigidity of the sub-membranous actin shell and tension that is induced by boundary conditions set by adhesion points where the cell is forced to stick to the substrate. The theory allows an estimation of the rigidity and thickness of this supporting shell. The same considerations explain the shape of non-adherent edges in the general case of untreated cells.

CC9.19
EFFECT OF LONG RANGE ORDER AND MIXED BOUNDARY CONDITIONS ON MICROSTRUCTURE PHENOMENA IN CARBONACEOUS MESOPHASES UNDER SHEAR. Arvinder P. Singh and Alejandro D. Rey, Department of Chemical Engineering, McGill University, Montreal, QC, CANADA.

Carbonaceous mesophases (CMs) or discotic mesophases are an important class of low cost precursor materials that are used to manufacture high performance mesophase pitch-based carbon fibers which possess excellent mechanical and thermal transport properties. These fibers are used to produce a new generation of composite materials that are revolutionizing the aircraft, electronics and automotive industries. The superior properties of mesophase carbon fibers depend on the texture that evolves during the spinning process, and which is a function of the operating conditions, geometry, and material properties. There has been a great interest in understanding the texture evolution during the fiber formation melt spinning process in which the CMs are subjected to non-homogeneous mixed shear and extensional flows. In this work flow modeling of model CMs is performed using a complete phenomenological theory that takes into account short range and long range order elasticity, and viscous flow effects. The present theory is fully compatible with the well-known Leslie-Ericksen and Doi theories, and thus fills the parametric gap where these classical theories are inapplicable. The microstructural response of model CMs under rectilinear shear flows is simulated, and the numerical results are used to identify and characterize the novel relations among rheology, microstructure and processing conditions. A novel mode of continuous generation of defect-like structures in the bulk has been discovered. The defect-like structures emerge due to asynchronous rotational orientation kinematics. The numerical results are characterized mathematically as well as in terms of the basic physical mechanisms. The simulations are further used to put forth the fundamental principles that govern carbon fiber texture generation under shear.

CC9.20
LIQUID CRYSTALLINE ASPECTS OF STARCH GRANULE STRUCTURE. Thomas A. Waigh, Paul A. Perry, Athene M. Donald, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

The native starch granule contains two main polysaccharides: highly branched amylopectin and linear amylose. By treating the amylopectin as a side chain liquid crystalline polymer, in which the mesogens are double helices formed between neighbouring side chain branches, we can rationalise many aspects of self-assembly within the native granule. In particular, we can understand how appropriate combinations of temperature and plasticisation (involving water or organic solvents) are required to permit long range smectic correlations to develop which give rise to the characteristic SAXS peak

at 9nm. These results are important in understanding the granule breakdown which occurs during processing (eg in thermoplastic starch) and consequences of the variation between species.

CC9.21
POLYMER BLENDS SYNTHESIS BY PHASE SEPARATION METHOD IN AN ACRYLIC SYSTEM. R. Velezquez, J. Reyes, A. Cabrera and V.M. Castao, Instituto de Física, UNAM, Queretaro, MEXICO.

A polymer system consisting of one casting syrup and triethylene glycol dimethacrylate (TEGDMA) monomer was prepared to obtain polymer blends. The casting syrup were made of methyl methacrylate monomer (MMA) and polymethyl methacrylate (PMMA) in concentrations of 10, 20 and 30% by weight of the polymer; each of the casting syrup was mixed with TEGDMA in different proportion from 0% to 100% by weight of the monomer. The combination of both components originated 36 reacting mixtures with different chemical compositions. The reacting mixtures were polymerized separately by bulk polymerization using N,N dimethyl p-toluidine as an accelerator. The use of this amine produces a phase separation in the polymer, which has a microstructure of microdomains. The influence of the chemical composition on the density, microstructure and morphology of the polymer was studied. The monomer conversion as a function of time and the specific volumes of all materials were determined by volume dilatometry using a dilatometer specially constructed for these purposes. The tensile properties were also determined and the microstructure and morphology were observed by scanning electron microscopy. It is possible to control the elastic modulus, the size and shape of the microdomains and the shrinkage of the polymer through the variation of chemical composition.

CC9.22
SELF-ASSEMBLY OF CARBON BLACK IN POLYMERS. Vaclav Bouda, Jiri Chladek, Jiri Rajman, Czech Technical University, Dept of Electrical Engineering, Prague, CZECH REPUBLIC.

In polymer compounds with carbon black (CB) content, the CB-volume fraction at which a CB-network of touching CB-particles (percolation threshold) is formed is not a constant but depends on the manufacturing process. It was found that the resistivity of a plastic that has a lower CB-concentration than the percolation threshold shows a percolation-like transition. This can be observed when the samples are held at a temperature higher than the glass transition temperature T_g or melt temperature T_m of the polymer matrix for a certain period or percolation time. At this characteristic time, a sharp step decrease in resistivity occurs. It is shown that by applying the theory of colloids, the results of the experimentally found percolation times can be explained. The coulombic force can cause a potential energy barrier to hinder the CB-particles from coming into close enough contact with each other to form a conductive carbon network. The barrier can be surmounted either by external shear forces or by reduction of the repulsive coulombic force by increasing the ionic concentration. The critical ionic concentration can be reached either above a critical salt concentration or after a certain time (percolation time) of special heat treatment of the composite melt in electrical field.

CC9.23
SIMULATIONS OF BINARY LENNARD-JONES FLUIDS CONFINED IN A SLIT-PORE. Margarita Rivera and Hector Dominguez, University of North Carolina, Dept. of Chemistry, NC; and G. Ramirez-Santiago, Instituto de Física, UNAM, MEXICO.

We have carried out extensive NPT Monte Carlo simulations of liquid binary mixtures confined within a slit-pore. To keep the pressure constant we allow the simulational box to fluctuate in the $x - y$ direction, where periodic boundary conditions are imposed, while the separation between plates of the pore remains fixed. Particles of the same and different kind interact through a 12-6 Lennard-Jones potential while the wall particle interaction is via a 10-4-3 potential. Several values of the potential strength between particles of different species have been considered in order to simulate different mixtures. We use attractive as well as repulsive walls. In the former case the particles of both species distribute uniformly through the pore, while in the latter, the mixture tends to separate at the middle of the pore. These results suggest that in confined mixtures the liquid-liquid separation is not only affected by the system thermodynamic properties, but also by the fluid-wall interaction. In addition, there appears that the separation of the confined mixture occurs at different thermodynamic conditions as to those at which the bulk mixture separation happens. Work supported by CONACYT-MEXICO under grant No. 25298-E.

CC9.24
NEUTRON SPIN ECHO SPECTROSCOPY STUDIES OF SOFT CONDENSED MATTER AT THE NIST CENTER FOR NEUTRON

RESEARCH. N. Rosov¹, S. Rathgeber^{2,1}, M. Monkenbusch³; ¹NIST Center for Neutron Research, Gaithersburg, MD, ²University of Maryland, College Park, MD, ³Institut für Festkörperforschung, Forschungszentrum Jülich, GERMANY.

The NIST Neutron Spin Echo (NSE), Disk Chopper Time-of-Flight, and Backscattering spectrometers comprise a trio of high-resolution inelastic instruments that have recently come on-line at the NIST Center for Neutron Research. These instruments are able to study dynamic processes with time scales that range from 10^{-13} s to 10^{-7} s. In particular, the NIST NSE spectrometer, based on the NSE spectrometer at the Forschungszentrum-Jülich [1], can probe the intermediate scattering function $I(Q, \tau)$ (the cosine transform of $S(Q, \omega)$) over the range $0.01 \text{ \AA}^{-1} < Q < 2 \text{ \AA}^{-1}$ with Fourier times extending to 10^{-7} s. Access to these long Fourier times has been accomplished without sacrificing intensity by keeping the neutron path length short. Further gains in intensity have been realized by the use of correction elements that allow the use of off-axis and divergent neutrons onto a $20 \times 20 \text{ cm}^2$ area detector. A carefully implemented coil-winding and compensation scheme assures that the large fields required for the long Fourier times do not affect the echo condition at high scattering angles, allowing the study of large samples at high- Q without loss of resolution.

NSE is especially suited for the investigation of relaxation-type motions, which are of interest in polymer and glass studies, among others. The availability of an area detector is particularly useful for SANS-regime studies of polymer systems. In addition, the study of the dynamics of biological systems in the nanosecond and longer time regime are possible. Results demonstrating the capabilities of the instrument will be presented.

[1] M. Monkenbusch *et al.*, Nucl. Instr. Meth. Phys. Res. A **399**, 301 (1997).

CC9.25

MECHANISM OF STRESS PRODUCTION AND THE ENTROPIC NATURE OF STRESS IN MODEL POLYMERIC MELTS.

Catalin R. Picu, Rensselaer Polytechnic Institute, Department of Mechanical Engineering, Aeronautical Engineering and Mechanics, Troy, NY.

A new atomic-level physical picture of stress production and relaxation in polymeric melts is presented. The mechanisms of atomic-level stress production and the relationship between stress and structural changes during deformation of the melt are analyzed by equilibrium and non-equilibrium molecular dynamics simulations of model systems. A structural invariant to deformation is introduced and it is shown that it corresponds to an intrinsic stress tensor, which has a non-zero deviatoric component in equilibrium. This tensor is defined in an intrinsic coordinate system tied to the representative covalent bond of the macromolecule. The global stress is obtained by the summation of intrinsic stress tensors over all intrinsic frames. The relevance of this finding to stress relaxation is discussed. Based on this new description of stress, the entropic vs. energetic nature of global stress is analyzed. It is shown that both entropic and energetic components are naturally captured in the intrinsic description, with the entropic one becoming dominant at higher temperatures and later times of the stress relaxation history.

CC9.26

THERMALLY STIMULATED DESORPTION OF SELF-ASSEMBLED FILMS.

Maria Raposo, Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Departamento de Física, Monte Caparica, PORTUGAL; Oswaldo N. Oliveira Jr., Universidade de Sao Paulo, Instituto de Física de Sao Carlos, Sao Carlos, SP, BRAZIL.

The thermally stimulated desorption method, normally used for studying desorption of gases adsorbed on solids, was adapted to study desorption of macromolecules adsorbed onto solid substrates in self-assembled films, by placing the film in an aqueous solution and increasing the solution temperature at a constant rate. It was used here to investigate the interactions between poly(*o*-methoxyaniline) (POMA) and poly(vinylsulfonic acid) (PVS), in self-assembled POMA/PVS films prepared from aqueous solutions with pH=3. For the desorption experiments, the films were placed in pH=3 HCl aqueous solutions and the solution+film temperature was increased at a rate of $0.5^\circ\text{C}/\text{min}$, with the film UV-vis. spectra being measured for several temperatures. From these spectra one can estimate the amount of polymer in the film and consequently determine the desorbed amount, which was differentiated in relation to time and plotted as a function of temperature. Considering an Arrhenius process, one can estimate the activation energies of desorption, from which three types of interaction are associated with POMA/PVS self-assembled films: van der Waals forces, hydrogen bonding and ionic forces.

CC9.27

STUDY OF THE (PEG/PPG/PEG) TRIBLOCK COPOLYMER

COMPLEXED WITH LITHIUM TRIFLATE. R.A. Silva, Universidade Federal de Minas Gerais, Department of Physics, Belo Horizonte MG, BRAZIL; C.A. Furtado, Centro de Desenvolvimento da Tecnologia Nuclear-CDTN/CNEN, Belo Horizonte MG, BRAZIL; G. Goulart Silva, Universidade Federal de Minas Gerais, Department of Chemistry, Belo Horizonte MG, BRAZIL; R.L. Moreira, M.A. Pimenta, Universidade Federal de Minas Gerais, Department of Physics, Belo Horizonte MG, BRAZIL.

Non-aqueous electrolytes systems, either typical solvents or dry polymers are being used with alkali metal salts to high-energy density batteries and for other electrochemical applications. The changes in the matrix structure related to the presence of the ions, the matrix-ion interaction and the ionic associations are determinant factors for the conductivity behavior. This work presents a study of the (Triblock - poly (ethylene glycol) PEG/poly (propylene glycol) PPG/poly (ethylene glycol) PEG) copolymer complexed with lithium triflate (LiTf) using Thermal Analyses (TG and DSC), Micro-Raman spectroscopy and Ionic Conductivity measurements. The parameters studied are salt concentration from 12 to 58 % w/w and temperature. The Thermogravimetry (TG) measurements indicates that the Triblock/LiTf system is thermally stable below $T = 350^\circ\text{C}$. The glass transition temperature (T_g) obtained by the DSC results increases with salt concentration due to the decrease of the segmental flexibility in the polymer chain. The ionic conductivity first increases and then decreases with increasing salt concentration and the maximum in the conductivity occurs for the polymeric electrolyte with 30% w/w of salt concentration. Besides, the conductivity increases with increasing temperature, even for the highly concentrated samples. The micro-Raman technique allows the determination of different ionic association as ion pairs and higher associate species, whose concentration increases with increasing salt concentration. Ours results indicate the precipitation of salt micro-crystals in the polymeric electrolytes for salt concentration above 30% w/w. Besides, the ionic association increases with increasing temperature. Despite the fact that the ionic association is a limiting factor for the conductivity, the increases of the conductivity with temperature is ascribed to the enhancement of the polymer chain flexibility for higher temperatures.

CC9.28

ION FLOTATION USING SURFACTANT CAGE MOLECULES.

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Ion flotation experiments, using nitrogen bubbles foaming, have been conducted in surfactant solutions. The specially synthesised nonionic surfactant used combine three elements: a cage molecule, a large sugar based headgroup and two to four hydrocarbon chains. These surfactants show selectivity towards some cations, called target ions. The selectivity and affinity is controlled via pH. When salt including the target ion is added to the micellar solution, the aggregation number as well as the cmc vary only slightly. Precise measurement of the effective charge of the micelle also prove that effective charge of the micelle varies less than number of adsorbed target cations. Thus anions are also bound to the micelle charged by cation recognition. Ion flotation can be quantified when foam as well as remaining surfactant solution are analysed for surfactant, target ion and counter-ion. We show that quantitative selectivity coefficients, to be compared with theoretical expectation from surface force theory, can be obtained when a target and a non-target ions are present as mixed salt competing for the selective surfactant air-water monolayer.

CC9.29

PLASTIC POLYMER BATTERY WITH GELLED POLYMER ELECTROLYTE.

Myung D. Cho, Electrochemistry Lab, Samsung Advanced Institute of Technology, Suwon, KOREA.

For a growing number of production and applications new powerful batteries with improved process and handling in manufacturing was requested. In gelled polymer electrolyte is one of key factors for successful of lithium polymer battery manufacturing. The selection right polymer with right electrolyte is the key factors the lithium polymer battery system. A new method for the preparation of the lithium polymer battery with crosslinked gelled polymer electrolyte was developed. The gelled polymer electrolyte was prepared with crosslinking agent, polymer and liquid electrolytes. With the conventional liquid electrolyte such as ethylene carbonate/propylene carbonate (EC/PC) with 1M, LiPF_6 , the gelled polymer electrolyte was showed wide ranges of electrochemical stability windows, and high ionic conductivity at elevated temperature. In this research, the properties of gelled polymer electrolyte were investigated as a roll of lithium polymer battery system. Each of battery components, such as cathode, anode and SPE were studied with SEM measurements for distributions of crosslinking agent inside the matrix. This distribution of crosslinking agent may important effects on lithium polymer

battery system. In a high distribution of crosslinking agent in cathode or anode electrode, it can be results in reducing charge and discharge efficiency and as well as long-term cyclability. In oppositely, when less crosslinking agent in SPE, this will not be available to hold enough liquid electrolyte, nor free standing film and results in electrical short in battery. Therefore, it is very important to choose right concentration and control the distribution of crosslinking agent in electrode and SPE. In our research, we have found the distribution of this crosslinking agent and depend on this distribution we tested the lithium polymer battery.

CC9.30

TYPE I COLLAGEN CRYSTALLITE FORMATION.

Matthew F. Paige, M.Cynthia Goh, University of Toronto, Dept of Chemistry, Toronto, ON., CANADA.

The solution-phase association of biological molecules to form aggregates has been studied from a variety of perspectives, such as the flocculation of polymers, association of colloids and the aggregation of proteins. The latter subject has been the target of particular attention, mainly because of its importance in biomedical applications as well as its implication in diseases such as spongiform encephalopathies and Alzheimer's disease. Investigating protein aggregation at a fundamental level, however, is often complicated by the poorly-defined structures of the aggregation products formed. In these experiments, we have studied Type I collagen, a rod-like protein which can be made to aggregate in a lateral fashion, forming a highly-ordered protein 'crystallite'. The relative simplicity of the final aggregate structure makes this system an ideal model for the controlled study of protein aggregation. We have investigated the growth mechanism of this crystallite using turbidity, isothermal titration calorimetry and atomic force microscopy (AFM) to collect kinetic, thermodynamic and morphological information, respectively. In particular, we focus upon an apparent contradiction between the AFM and turbidity data. While our turbidity curves are sigmoidal in shape, suggesting growth occurs via a classical nucleation-and-growth mechanism, the AFM data reveals the formation of stable intermediates, indicating a step-wise or hierarchical assembly. We discuss the difference in these results and comment upon the importance of applying a variety of analytical techniques to problems of this complexity. Additionally, a comparison between the results obtained in this investigation are made with those obtained for structural variants of collagen aggregation products, including several different types of highly-ordered fibrous aggregates.

CC9.31

DISORDER IN HIGHLY CHARGED BILAYERS IN THE ABSENCE OF SALT. Monique Dubois, CEA, Saclay, FRANCE; Thomas Zemb, CEA, Saclay, FRANCE; Bruno Deme, ILL, Grenoble, FRANCE; Thadeusz Gulik-Krzywicki, Gif-sur-Yvette, CGM-CNRS, FRANCE.

By diluting highly charged bilayers such as DOPS in the absence of added salt or counter-ions, swelling of a lamellar phase exceeding more than hundred of nanometers is observed. The same situation is obtained with mixed anionic and cationic single chain surfactant, who associate as ion pairs. The set of Bragg peaks associated with the lamellar phase (SAXS and SANS) progressively widen and finally transform in an inflexion point only in the decaying scattering curve. Samples are characterized by SAXS, SAXS and cryofracture experiments, as well as osmotic pressure control. The different physical origins of this dispartition of Bragg peak during swelling of an electrostatic lamellar phase, i.e. fluctuation of spacing, correlated bending and dissociation in nanodiscs will be discussed.

CC9.32

DYNAMICS OF DNA FRAGMENTS IN PORES AND IN SOLUTION. Udayan Mohanty, Boston College, Dept of Chemistry, Newton, MA.

Ogstron and "tube" reptation models are generalized to describe the mobility of ss oligomeric DNA in polyacrylamide gel. The model predicts that significant anomalous migration exists with sequences about six residues such that the electrophoretic mobility of a 3-residue fragment is comparable to a 14-residue fragment. Experimental measurement of gel mobility for DNA fragments of form $N(pN)_n$, where $n=1-11,14$ and 19 have substantiated this phenomenon. A model for the free solution electrophoresis mobility of oligo ds DNA relevant to capillary electrophoresis is described that explicitly takes into account screening of the hydrodynamic interactions, counterion condensation, Coulombic end-effects, ionic strength and pH of the buffer solution. We find, in agreement with experiments that the free solution mobility of ds DNA increases as the molecular weight increases up to a few hundred bp. We have developed a model of gel retardation of intrinsically curved DNA molecule, such as the A-tracs, that takes into account in an approximate way the low and the high frequency viscoelastic response of the polyacrylamide gel matrix and the transverse frictional drag forces. Dynamical motions of the

"probe" chain are accompanied by viscoelastic response of the "vicinal" matrix chains by reptation. In agreement with Crothers and coworkers, analysis shows that the gel mobility of DNA with a bend at the center is slower than that of the same molecule with a bend at its end. Finally, generalization of the above model to the determination of binding parameters via gel-shift assay of protein-DNA complexes in polyacrylamide gel will be described.

CC9.33

MICROSCOPIC STUDY OF ORGANIC GEL STRUCTURE BY TAPPING MODE AFM. Rong Wang, Cristina Geiger, Liaohai Chen, Basil I. Swanson, David G. Whitten, Los Alamos National Laboratory, Chemical Science and Technology Division, Los Alamos, NM; University of Rochester, Center for Photoinduced Charge Transfer, Department of Chemistry, Rochester, NY.

The structure of organic gels formed from cholesterol-stilbene derivatives in octanol or acetonitrile has been investigated by atomic force microscope (AFM) using the tapping mode. It was found that the organic gels consist of fibrous structures with distinct helical characteristics. Large bundle of fibers, consisting of tens of twisted individual fibers, were observed. The finest fiber that can be resolved is as thin as 14 nm. It is estimated that this fiber may contain 7-8 basic fiber units from molecular modeling. Effects of UV irradiation as well as the aging or annealing process, which involves multi heating and cooling cycles (through the gel-liquid transition), were also studied by AFM. Even though macroscopically the gel melts upon UV irradiation due to the conformational distortion that occurs during the photoisomerization of stilbene, it still keeps the fibrous structures microscopically. However, the helical twisting characters disappeared in most of the fibers, replaced by ribbon-like features. Interestingly, all the untied fiber bundles seemed cracked from the center, with two parallel fibers forming boundaries to keep the fiber bundles in shape. When the gel was carried through the aging process, the relatively rigid fiber bundles from the fresh gel were replaced by more flexible ones.

SESSION CC10:

Chairs: Anna C. Balazs and Jacqueline L. Goveas
Friday Morning, December 3, 1999
Salon J/K (M)

8:30 AM CC10.1

SMALL ANGLE SCATTERING STUDY OF THE STRUCTURE AND ORDERING OF MICELLES IN TRIBLOCK COPOLYMER SOLUTIONS. Yong Li, Rama Bansil, Guangdong Liao, Karl Ludwig, Boston University, Dept. of Physics, Boston, MA; Cestmir Konak, Institute of Macromolecular Chemistry, Prague, CZECH REPUBLIC; Jyotsana Lal, Argonne National Lab., Argonne, IL.

We have used small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) to study the micelle structure of a polystyrene(PS)-*block*-poly(hydrogenated butadiene)(PHB)-*block*-polystyrene triblock copolymer in dilute - semidilute solutions in solvents selective for either the outer PS block (dioxane) or for the middle PHB block (heptane or decane). Equilibrium structure factors were measured over the temperature range of 20 - 90 C for different concentrations of the copolymer, ranging from 4% -15%. Our results showed that micelles were formed in both types of selective solvents. In the case of dioxane the micelles are isolated, whereas in the case of heptane/decane a bridged micellar structure may be formed at higher copolymer concentrations. In either case we observed an ordered cubic structure of insoluble domains (micellar cores) at high concentrations. The micellar scattering function can be fit by the Percus-Yevick interacting hard sphere model. The core radius, the hard sphere interaction radius and the volume fraction of hard spheres increase and then saturate as the temperature decreases. For the case where ordering occurs Gaussians were used to describe the ordered Bragg peaks and Lorentzians for the liquid-like peaks.

8:45 AM CC10.2

X-RAY SCATTERING FROM HOMOPOLYMER-BLOCK COPOLYMER BLENDS: PART I, STATICS. M.A. Borthwick, P. Falus, D. Lumma, L.B. Lurio and S.G.J. Mochrie, Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Static X-ray Scattering measurements are presented of the structure of polymeric micelles, self-assembled in homopolymer-block copolymer blends. Analysis of the scattering lineshape reveals cylindrical morphology at low block copolymer volume fractions. Interestingly, there is a transition to a different morphology as the copolymer concentration is increased beyond about 10%. These results will be compared to theoretical predictions of homopolymer-block copolymer phase behavior.

9:00 AM CC10.3

MOLECULAR DESIGN OF MISCIBILITY INTO BLOCK COPOLYMERS. A.-V. G. Ruzette, P. Banerjee, A. M. Mayes, Dept of Materials Science and Engineering, Massachusetts Inst of Technology, Cambridge, MA; M. Pollard, T.P. Russell, Polymer Science and Engineering Dept, Univ of Massachusetts, Amherst, MA.

The tendency of block copolymers to self-assemble at the molecular level, producing a wide array of highly ordered nanostructures, is of particular interest from an engineering standpoint due to the unique resistance to flow and mechanical, optical or electrical properties which ensue from this self-assembly. The recent development of more versatile and industrially amenable synthetic routes for the preparation of block copolymers has unveiled new opportunities for optimizing the resulting properties of these molecules via a judicious choice of both chemistry and architecture. One limitation arises, however, from the lack of control over bulk thermodynamics in most block copolymers of reasonably large molecular weight. Although highly beneficial from an application standpoint, the strong incompatibility between the different blocks of most block copolymers results in stable microphase separated morphologies even at the elevated temperatures typically used for melt processing and where flow is desirable. In this work, the ability to control the appearance of order/disorder (solid like/liquid like) transitions by the molecular design of weakly interacting block copolymer melts is demonstrated. Marginally compatible diblock copolymers exhibiting both pressure- and temperature-tunable thermodynamic and rheological properties are discussed, along with the molecular origin of their phase behavior.

9:15 AM CC10.4

BIOACTIVE AMPHIPHILIC DENDRIMERS. Chris Z. Chen, Stuart L. Cooper, University of Delaware, Dept of Chemical Engineering, Newark, DE.

Dendrimers are well defined, highly branched macromolecules that emanate from a central core. The novel architecture of dendrimers provides a very high number of functional groups in a compact space. Thus, it is reasonable to expect that these novel molecules will play a major role in materials whose performance depends on high local concentration, such as drugs or antimicrobial agents. In this study, a series of amphiphilic dendrimers based on commercial poly (propylene imine) dendrimers have been synthesized. Different generations of dendrimers with primary amine surface groups are coupled with 4-(dimethylalkyl ammonium chloride) benzoic acid using 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide as the catalyst. The alkyl chain that contributes to the hydrophobic character can be varied from C8 to C18. The dendrimer core is hydrophilic while the shell is hydrophobic, which leads these dendrimers to associate into micelle-like structures in water. The antimicrobial properties of these novel compounds have been illustrated using recombinant *E. coli* bioluminescence techniques. Because of the high density of functional groups, the polycationic structure and the associative behavior of these dendrimers, they are more potent than their small molecule counterparts. Preliminary results on the mode of action of these biocidal dendrimers will also be discussed.

9:30 AM CC10.5

PHYSICAL PROPERTIES OF POLY(BENZYL ETHER) DENDRIMERS. Michael E. Mackay, Dept. of Chem., Biochem. and Materials Eng., Stevens Institute of Tech., Hoboken, NJ; Grant Hay, Peter Farrington, Dept. Chem. Eng., Univ. of Queensland, Brisbane, AUSTRALIA; Craig, J. Hawker, IBM Research, San Jose, CA; Jean M.J. Fréchet, Dept. Chemistry, Univ. of California, Berkeley, CA.

The rheological properties of dendrimers have been studied via torsional, melt rheometry to reveal that dendrimers do not form entanglements. In other words, they follow the Rouse and simple free volume models even up to relatively large molecular masses. However, our re-examination of glass transition data shows that it is not clear how the free volume causes a change in the glass transition temperature with molecular mass. Thus, some complexity in the physical properties is probably present and the free volume model is too simplistic. Further, we have measured the density of the neat dendrimers as a function of temperature and pressure (up to 200 MPa). We find the dendrimers are less compressible than linear polymers and perhaps more importantly, the thermodynamics can not be modeled by considering each dendrimer acting as an individual entity. Heat capacity data confirms this conclusion. All the above physical properties will be presented to show that dendrimers seem to be much more complicated than simple, individually acting spheres.

9:45 AM CC10.6

SELF-ASSEMBLY OF ARBORESCENT GRAFT POLYSTYRENE. T.M. Chou, R. Briber*, M. Gauthier** and M. Libera, Stevens Institute of Technology, Hoboken, NJ; * University of Maryland,

Arborescent polymers are highly branched materials synthesized by grafting multiple generations of macromolecular precursors on a central core. They can have characteristic length scales on the order of tens of nanometers or more depending on the molecular weight of the precursor chain used in the grafting reaction. They possess many of the unique and attractive structural, thermodynamic, and rheological properties characteristic of dendrimers and hyperbranched polymers but do so on a length scale roughly one order of magnitude higher. This research studies the structure and self-assembling behavior of thin films of second (G2) and third (G3) generation arborescent graft polystyrene synthesized from 5k and 30k Mw anionic polystyrene precursor chains. Small-angle neutron scattering from solutions and blends indicate that these polymers are essentially noninterpenetrating with sizes that depend on the quality of the solvent. These polymers self assemble to form self-supporting micron-sized monolayer films during solvent evaporation when cast on holey-carbon TEM grids. Real-space imaging of the projected structure by TEM and of the surface structure by SEM show round contrast features with characteristic length scales consistent with those measured by neutron scattering. These contrast features are attributed to individual arborescent polymer molecules. Within monolayer films the arborescent polymers assemble with varying degrees of order. At one extreme they form an essentially 2-D array with only short range liquid-like order while at the other they form hexagonal arrays which remain coherent over lateral distances of several hundred nanometers. The nature and degree of order is quantified by digital Fourier methods.

10:30 AM CC10.7

RHEOLOGICAL CHARACTERISTICS OF SOLDER PASTES. Donghun Lee, William J. Walker, Jr., William M. Carty; New York State College of Ceramics at Alfred University, Alfred, NY; Peter Borgesen, Universal Instruments, Binghamton, NY.

The solder pastes used for electronic assembly processes are viscoelastic in nature; their response to applied stress has a liquid-like (viscous) component and a solid-like (elastic) component. A set of five solder pastes were prepared from a single flux medium with different metal contents (88 to 92 wt %), and characterized over a range of temperatures to systematically vary rheological behavior. Steady-state rheology measurements were performed to characterize the shear-thinning flow behavior in terms of apparent viscosity. Influences on steady-state rheology were dominated by particle crowding effects of the suspended metal powder and temperature dependent changes to the shear thinning flux medium. Temperature dependence of paste rheology showed three distinct regions distinguished by the onset and completion of solvent evaporation. Using a dynamic strain rheometer the viscoelastic behavior was characterized and described in terms of a relaxation modulus and a spectrum of relaxation times. The linear viscoelastic region of solder pastes was found to be very narrow (below 0.1% strain). Relaxation modulus was nearly independent of temperature, but highly dependent on metal content, while relaxation time (defined for a shear rate of 10^3 s^{-1}) was a function of both variables, with a maximum at low temperature and low metal content.

10:45 AM CC10.8

VISCOELASTIC PROPERTIES OF A COLLOIDAL SUSPENSION. Raul Esquivel-Sirvent, Cecilia Noguez, and Guillermo Ramirez-Santiago, Instituto de Física, Universidad Nacional Autónoma de México, México DF, MEXICO.

By means of extensive non-equilibrium molecular dynamics simulations we study the viscoelastic properties of a colloidal suspension. We model the colloids using a Lennard-Jones potential and we subject the system to an oscillatory shear. The hydrodynamic interactions are taken into account introducing a Stokes-like damping force. We measure the shear viscosity and the attenuation as a function of shear amplitude, volume fraction and frequency. We find a shear thinning effect at a frequency of 300 Hz as the shear amplitude is varied. The viscosity as a function of volume fraction increases linearly at low frequencies and shows a non-linear behavior for higher frequencies. Our results are compared with the case where hydrodynamic interactions are absent.

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11:00 AM CC10.9

PHASE SEPARATION UNDER SHEAR OF BINARY MIXTURES CONTAIN HARD PARTICLE S. Feng Qiu, Valeriy Ginzburg, Gongwen Peng, Anna C. Balazs, Chemical Engineering Department; David Jasnow, Physics Department, University of Pittsburgh, Pittsburgh, PA.

We simulate the motion of spherical particles in a phase-separating binary mixture. By combining cell dynamical equations with Langevin dynamics for particles, we show that the addition of hard particles significantly changes both the speed and the morphology of the phase separation. At the late stage of the spinodal decomposition process, particles significantly slow down the domain growth, in qualitative agreement earlier experimental findings. Using this model, we then determine the behavior of the mixture under shear. In the initial stages of the evolution of the microstructure, the morphology of the domains is isotropic. At later times, the domains grow faster in the shear direction than in the perpendicular direction. For sufficiently large particle densities, however, this anisotropic growth is destroyed by the randomly moving particles, and the domains are isotropic in shape even for large shear strains. Thus, solid additives can be used to tailor the morphology of the mixture, and thereby control the mechanical integrity of the composite.

11:15 AM CC10.10

QUANTIFYING DYNAMICAL HETEROGENEITY IN MODEL GLASS-FORMING LIQUIDS VIA FOUR-POINT DENSITY CORRELATIONS. Thomas B. Schroeder, Sharon C. Glotzer.

Polymers Division and Center for Theoretical and Computational Materials Science, National Institute of Standards and Technology, Gaithersburg, MD.

Glass-forming liquids represent one class of complex fluids where subtle details of the local structure dramatically influence dynamics. In these fluids, approach to the glass transition causes the local dynamics to become spatially correlated over a range that grows with decreasing temperature [1,2]. To quantify this "dynamical heterogeneity", it is necessary to define higher order correlation functions. In this talk, we define a time-dependent fourth order density correlation function, and the corresponding generalized susceptibility [3]. By calculating these quantities in molecular dynamics simulations of model glass-forming liquids, we identify various contributions arising from spatial correlations between temporarily localized particles, and between cooperatively moving particles. As the temperature is lowered these correlations are found to increase, signaling a growing degree of dynamical heterogeneity. We demonstrate that the decoupling of diffusion and structural relaxation observed in glass-forming liquids follows naturally from dynamical heterogeneity. Results from molecular dynamics simulations of a polymer melt are presented [4], and compared to results from a model atomic glass-former [3]. We discuss the possible implications of our results for T_g shifts under confinement, and the possibilities of new experimental measurements.

[1] C. Bennemann, C. Donati, J. Baschnagel and S.C. Glotzer, *Nature* **399** 246 (1999)

[2] C. Donati, S.C. Glotzer, and P.H. Poole, *Phys. Rev. Lett.* **82** 5064 (1999)

[3] S.C. Glotzer, V.N. Novikov, and T.B. Schröder, preprint

[4] T.B. Schröder and S.C. Glotzer, preprint

11:30 AM CC10.11

MAGNETO- AND ELECTORRHEOLOGY IN UNIAXIAL AND BIAXIAL FIELDS. James E. Martin, Sandia National Laboratories, Albuquerque, NM.

We have conducted large scale 3-D simulations of magneto- and electrorheology in steady and oscillatory shear. These simulations are both for the standard case - that of a uniaxial field applied normal to the shear - and for a biaxial, or rotating, field applied in the plane normal to shear, and include Brownian motion. In the uniaxial case, hexagonal sheets form normal to the axis of vorticity, even in oscillatory shear at low strain amplitude. The formation of these sheets is apparently a kinetic phenomenon, and they reduce the stress significantly from that expected based on chain calculations. The formation of sheets normal to the axis of vorticity can be frustrated by the application of a rotating field in the plane normal to the direction of shear flow. The rotating field causes the formation of hexagonal sheets in the plane of the field, successfully preventing sheet formation orthogonal to the axis of vorticity, and results in stresses that are much larger than the uniaxial case, and in much better agreement with the simple chain model of field-induced rheology. In addition to the simulation results we will show structures formed in shear and in a biaxial field. Finally, we will describe the surprising effects of Brownian motion on stress and structure formation. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-94AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy.

11:45 AM CC10.12

CONFOCAL MICROSCOPY STUDIES OF ELECTRO-RHEOLOGICAL FLUIDS. Ujitha Dassanayake, Seth Fraden Dept. of Physics, Brandeis University; Alfons van Blaaderen FOM Institute, AMSTERDAM.

Specially synthesized, fluorescently labelled core-shell silica particles were used as a model electrorheological fluid to experimentally explore structure formation under conditions of no shear. Using confocal microscopy, we measured the location of each colloidal particle in three dimensions. We observed the equilibrium body centered tetragonal phase, and non-equilibrium structures such as sheets and isolated chains of colloidal particles. The formation of structures was studied at different volume fractions and starting configurations of the colloid. Results compare favorably with recent computer simulations.