SYMPOSIUM CC
Complex Fluids and Polymers
November 29 – December 3, 1999

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*Invited paper
8:30 AM *CC1.1 POLYELECTROLYTE ELECTROPHORESIS IN AQUEOUS SOLUTIONS CONTAINING ONLY SIMPLE ELECTROLYTE AND NEUTRAL POLYMER. David Honglad, Margaret Starkweather, C. Mathukumar, Cindy Welch, Univ of Massachusetts, Amherst, MA. 

The electrophoretic separation of polyelectrolytes, an analytical and preparative procedure that yields 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 these separations, we have investigated 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 weights, the dependence on chain length disappears, polyelectrolyte motion remains poorly predicted by any theory; hence, we have performed systematic experiments to better understand the nature of this dependence. 

9:00 AM *CC1.2 THERMO THICKENING POLYMERS AS NEW MAT RICES FOR HIGH THROUGHPUT DNA SEQUENCING. Jeong-Joon Yoo, Jun Seok Kim, Inserm U664, Paris, Paris, FRANCE, Dominique Heurteur, 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-hole capillaries. We developed a new family of separation matrices, based on the thermohaemolytic properties of specially designed and synthesized polymers. Thanks to this property, the separation method 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 materials 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; Dimitris Varkitsis, 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 a methylthiolane, which belongs to this class, has recently become the focus of systematic experimental studies. In equilibrium the molecular weight distribution (MWD) is the exponential Flory-Shultz distribution with mean $\bar{M}$, while the free monomer concentration reaches a value such that depolymerization and polymerization rates delicately balance. We find that any apparent small perturbation of the system, e.g., a small temperature jump $T'/T = e^{-\beta H}$, strongly disturbs this balance; there is no such thing as a linear perturbation. We find that this relaxation occurs in 3 stages: (1) Uniform transduction of the MWD on a timescale $\sim \bar{M}$ during which the monomer concentration and $\bar{M}$ relax; (2) Recovery of the depleted region of the MWD on a timescale $\sim \bar{M}^2$, (3) a true linear diffusive regime during which the width of the MWD and higher moments relax on a timescale $\sim \bar{M}^2$. We propose experiments in which free initiator concentration can 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 244 929 (1997).
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) 123-12 forms micelles which grow without any additional salt. Living polymers of 123-12 behave as polyelectrolytes and show a range of concentration where they do overlap but are not entangled. The temperature dependence of the onset concentration of entanglement determined by rheology provides a measure of the end cap energy. In trimer 133-13-12 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 dilute polymer solution. The end cap energy of the tetramer 133-12-13-12 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]

130 PM *CC2.1  
SCHLITLING OF GLAY 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 coaxing to flow to flocculants 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 associated with the aggregates which topology depends on 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. Heinz Kirkmeier, Jonathan Ensinger, Karen Wist, Univ of Pennsylvania, Dep of Materials Science, Philadelphia, PA.

Amphiphilic polymer microgels were produced by the suspension polymerization of polymerizable monomers with ammonium residues. These monomers had been prepared by the reaction of the corresponding diazonium salt with acrylamide. It has been shown that the associative properties of the ammonium groups in the polymeric microgels are retained in the hydrophobic core of the micelle. The aggregates grow in diameter as the temperature increases, leading to the formation of aggregates of an average size of 1-2 microns at 90°C.

2:15 PM CC2.3  
ASSOCIATION OF PERFLUORINATED IONOMERS INTO SUPERMOLECULAR STRUCTURES. Debra Perlini and Huiqiu Liu, 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 solutions 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 polymer 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 nanes at extremely low concentrations [C11 W0]. The micelle radius varies between 2 and 4 nm depending on temperature and concentration. The length was estimated to be around 1.520 nm. When these ionomers were allowed to self-assemble from solution onto a single crystal silicon wafer, clear layers were assembled. The temperature dependence of the aggregation behavior was studied by dynamic measurements in the linear regime. The branching point density is determined from the enhancement of elasticity as compared to the dilute polymer solution. The end cap energy of the tetramer 133-12-13-12 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.

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limits the extent of ionization; already present in bulk solution, this becomes particularly prominent near a surface when the average change in surface potential 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 enable higher TMPC chains. At high TMPC concentration, 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 presence of competing models of which we are aware, this suggests that the model of an ion pair as a repetition 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 Maloney, M. C. Gilb, 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 a glass, onto a cationic or anionic polyelectrolyte solution. Films of many bilayers can be prepared using a multistage 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 unusual flat configuration with a thickness of about 1-2 nm. We used SHG to obtain real-time information about the surface adsorption of each layer within the multilayer film. This information could be interpreted by the chiral structure of the polyelectrolyte, 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 Racz, Rafael Tumas, Jacob Korn, 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 separation. Poly(ethylene oxide) (PEO) was covalently bonded to the mica surfaces (with a good solvent for PEO). Following full overnight adsorption of PEO (Mr=37,000) and 12,000) a force-distance law was indicated on rapid compression, the force-distance law was indicated on rapid compression, and the factors that affect this process.

SESSION CC3
Chairs: Maurice Klemm and Patrick Nowak Tuesday Morning, November 30, 1999

8:30 AM *CC3.1
DETECTORS’ STRUCTURE AND RHEOLOGY OF ANISOTROPIC FLUIDS. Maurice Klemm, Univ Pierre et Marie-Curie, LMCPP, 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 properties of liquid crystals and ordered colloidal systems, as they do in the plastic deformations of solids, for which a wealth of information. This talk will review our present knowledge of flows in lamellar systems in relation with various textures (of dislocations, focal conic domains, and multilayered vesicles), 2) in nematics (disclinations, band textures). Low shear-stress strain experiments in lamellar flows and their power-law behavior will be discussed in the light of high-temperature creep theories in metals.


9:00 AM CC3.2
NEMATIC LIQUID CRYSTALS VISCOELASTIC SOLIDS? Ralph C. Collyer, Materials Science and Engineering, The Pennsylvania State University, University Park, PA.

I review viscoelasticity data on a variety of layer-forming structured flows in bulk melts of dioxane polymers, aromatic thermotropic liquid crystalline (LC) polymer melts (both main chain and side chains, liquid crystalline LC 8CB and liquid crystalline LC 5CB). With the exception of the dioxane polymers, 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 lends 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. Lelidi, M. Klemm, and J.-L. Martin, Département de Physique, Institut de Gétologie Alpin, Polytechnique de Lausanne, Lausanne, SWITZERLAND.

As it is well known, a perfect Cauchy wedge with homoeotropic anchoring contains a tilt boundary of edge dislocations. These dislocations are easily made visible in a thermotatic sample at the vicinity of the SmA-Sc phase transition. Experimental results allow for a control in magnitude and in time of the displacement d normal to the layers, as well as a measurement of the stress σ... A controlled deformation velocity vσ...dσ.../dv is imposed. As the stress increases, four deformation regimes are observed: elastic, mechanic 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 Orowan equation (well known in solid crystal plasticity) which relates, in the present case, the density ρ... 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 (10^4-10^5 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 take the form of 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

In the present contribution the effects of shear flow on the orientation behavior of lamellar poly(styrene-b-isoprene) (PS-b-PI) diblock copolymer are discussed with emphasis on the observation of common behavior with other layered complex fluids like lyotropic lamellar phases. It is described that for large amplitude oscillatory shear (LAS) at temperatures close to the order-disorder-transition temperature, at which the microphasic 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 partially perpendicular 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. The 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 LAS experiments on a laboratory scale and technically relevant fast extrusion processes by showing 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, M. Moerth, Thomas Thurn-Albrecht, U. Wiesner, J. Chem. Phys. 110 (1999), 8295, [2] H. Leist, K. Goetter, U. Wiesner, Macromolecules 32 (1999), 1315

9:45 AM CC3.5
THE NATURE OF VISCOELASTICITY IN A LAMELLAR BLOCK COPOLYMERS: CONTRACTION CORRELATED TO STRAIN LOCALIZATION. Karen Winny, Daniel Pola, Univ. of Pennsylvania, Dept. of Materials Science, Philadelphia, PA; Anthony Ryan, Univ. of Sheffield, Sheffield, UNITED KINGDOM.

We determined the local strain profile in sheared lamell block copolymers. An atom probe 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 reverse homogenization reaction in situ small x-ray scattering. The contraction directly correlates to the elastic strain, as determined from our atom probe models, 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/LC BLENDS. Tan Lay Poli, Yue Yue Yoon, Tuan Kim Chai, Nanyang Technological Univ., SINGAPORE.

The effect of LCP content on the morphological and rheological properties of poly(ethylene (PE)-LC) and LC1000, 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 1 wt%, shear thinning was observed at shear rates below that for 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 transfers 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 1 wt%, no significant changes in 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 Roy, Dept. of Chemical Engineering, McGill University, Montreal, CANADA.

The macroscopic equations of nemato-capillarity, including the interface linear momentum balance equation and the interfacial surface tension balance equation, are derived. 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 the surface gradients of the nematic ordering exist. The strength of the nemato-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. Christopher David Mu-Wai Fung, John F. Rokos, Department of Materials Science and Engineering, University of Delaware, Newark, DE.

With the prediction that Liquid Crystal Display will share the market with the traditional CRT-based displays by the year 2000, it is surprising that little is known or understood about the underlying mechanisms for liquid crystal alignment. In this study, we have measured the roles played by surface chemistry, topography, dipole 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 dipole 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 conoscopic. Based on our experimental results, we conclude that a combination of topography and dipole 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. Kreskov and F. M. Aliev, 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 polyurethane spheres in water or foams. We have performed DWS investigations of quasi-solid media based on lamellar liquid crystal confined in solid porous matrix. Porous glass with randomly interconnected
poles 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 ~ 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. The assignment of the appearance of these processes 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 $\tau \sim 10^3$ s is probably due to the dynamics of orientational motion of domains formed in random porous media. These slow processes are highly non-exponential. Modified bulk-like relaxation processes due to director fluctuations are 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 not observed. D.A. Weiss, J. N. Zhu and E. Herbolzheimer, J. Phys. (France), 51, 2101 (1990). This work is supported by DoD grant N00014-94-1-0558.
Deflection and relaxation behavior of these polymers under extensional deformation have revealed the origin of elasticity at a molecular level.

3:30 P.M. **CC4.6**
FROM TWO-DIMENSIONAL SMECTIC TO DNA-CATIONIC LIQUID CRYSTAL 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, Kolover, and Safinya. Shortly after the discovery, the phase has been elucidated by theorists in 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 crystal fluctuations, and the so-called decoupled phases, concluding with the sliding columnar phase of the DNA-Membrane complexes.

4:00 P.M. **CC4.7**
INVESTIGATIONS OF THE SMECTIC PHASE IN A HOMOLOGOUS SERIES OF GENETICALLY ENGINEERED VIRUSES. Zvonimir Dagic, Marie Adams, Seth Fraden, Complex Fluids Group, Department of Physics, Brandeis University, Wellesley, MA.

Smeics phase characterized by one dimensional order is ubiquitously predicted by various theories and computer simulations of hard rods. However, the smectic phase is seldom observed in experimental hard rods systems. An important unification 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 Sm and TAP and biaxial liquid crystals. We confirm this assumption. Using methods of molecular biology we prepare artificially polydisperse and bidisperse suspensions of rod-like virus particles and study the stability of the smectic phase in these mixtures. We also study the influence of rod flexibility, interaction strength, and addition of non-absorbing polymer on the smectic phase. Finally we argue that additional of hard spheres with specific dimensions dramatically increases the stability of the smectic phase.

4:15 P.M. **CC4.8**
PHASE BEHAVIOR AND MICROSTRUCTURE OF CATANIONIC SURFACTANT MIXTURES WITH ADDED POLYMER. Jonathan V. Selinger¹, Jinglie Xu², Robin L. N. Selinger², B.R. Rutan³ and R. Shashikumar¹. ¹Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, DC, ²Catholic University, 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 liquid crystal 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 this 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 begins to decay. The theory also predicts that the chiral modulations 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 experiments 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 the model at finite temperature show chiral fluctuations including both tilt modulation and localized chiral vortices.

SESSION CC5: 8:30 A.M. **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 catanionic surfactants, from surfactants and copolymers from ionic surfactants with hydrophobic counterions and from mixtures of zwitterionic surfactants with Cs-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 spreading 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 multimembranes vehicles (SUV/MIL). The behavior of the system is almost identical to that of concentrated emulsions and polymeric solutions. The viscoelastic properties of the phases was determined by oscillating rheological measurements and will be discussed in relation to various parameters like charge density, surfactant concentration and ionic strength. The viscoelastic vesicle phases are formed when ionically charged liposomes with stacked bilayers are sheared. It was also shown that the transformation at low shear rates the transition times can be increased linearly with the shear rate while at higher shear small unilamellar vesicles (SUV) are formed. All three phases (the stacked bilayers, the
VESICLE-TO-CELLULE TRANSITION INDUCED BY GRAFTED DIBLOCK COPOLYMERS. Aude Schlicht-Chmieszynski, Leic Auvray, Laboratoire Leon Brillouin, CEA Saclay, Gifsur Yvette, FRANCE.

We study 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-P20E (polystyrene-polyethylene) is chosen as a model of more complex 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 equilibrium and dynamic light scattering data to find a good agreement with theoretical predictions concerning the spontaneous mean curvature of polymer-grafted membranes.

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 [CTEM]. We find that there are large differences in elastic modulus with changes in the hydrophobic character of the surfactants. The bending constant of the hydrogenated surfactant mixture [CTEM/SOS] is of order ~4kBT, confirming that equilibrium unilamellar vesicles are stabilized against formation of lamellar phases or dispersed multilamellar liposomes by thermal membrane fluctuations that lead to net repulsive interaction between bilayers. However, the bending constant of CTAB/FC8 vesicles is of order ~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 vesicle eliminates the 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 reduces bending modulus from ~10 kBT to ~5 kBT. The microstructure and morphology of the mixed surfactant systems are also discussed.


Vesicles were made in aqueous solutions from amphiphilic diblock copolymer micelles as used in many applications. The average molecular weight of the polymer primarily studied, polyethylene oxide-polyethylene (EO45E57), is several thousand greater than that of typical phospholipids in natural membranes. Both the membrane bending and area expansion moduli of polymeromes [polymer-based liposomes] fell within the range of lipid membrane parameters, but the giant polymeromes proved to be almost an order of magnitude tougher in sustaining far greater strain before rupture. The polymerome membrane was also at least tenfold less permeable to water than common phospholipid bilayers. The results are explored primarily on the basis of an increased thickness to the membrane and suggest a new class of synthetic thin-shell capsules based on block copolymer chemistry.

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

Stable three-dimensional foams are observed only in the presence of surfactant, micelle, or particular 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 lamellae acts even in the absence of a boundary layer, due to alignment of dipole moments within the Langmuir monolayer. Two-dimensional Langmuir monolayer films of poly(dimethylsiloxane) show markedly different stability on two different substrates. These forms will be used to explore the roots of Langmuir monolayer foam stability. Measurements of line tension in the two cases were performed by optical microscopy, which 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, correlated with foam stability.

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

Experiments show that the permeability of aqueous foams is $K = C^2$, where $K$ is a constant, $C$ is the liquid volume fraction, and the exponent $a = 1/2$ [Koehler et al., PRL 81, pp. 4323-4325 (1998)]. This behavior is sensitive to the type of surfactant and liquid viscosity. We also explore this relationship as the forms ages (coarsens).

STRUCTURE AND FLUCTUATIONS OF MICROEMULSION NETWORKS. T. Tkatch, S.S. Salitra, The Weizmann Institute of Science, Department of Materials and Interfaces, Rehovot, ISRAEL, R. Srey, Institut für Physikalische Chemie, Köl, GERMANY, A. Bernebein, R. 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, sponge-like structures. The predicted energetic and dynamic light scattering data to network the structures and thermodynamics is presented by both phase behavior measurements (and their agreement with the theoretical scaling laws) and cryo-transmission electron microscopy. The microemulsion models also indicate that similar mechanisms govern the networks that exist in binary, micellar systems.

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 allows 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 vicinities of the bicontinuous microemulsions at $c_{0}$, focused between the lamellar two/three phase regions in the phase prism. A combination of experimental measurements, including small-angle x-ray and neutron scattering, has revealed universal phase behavior for this class of mixtures for block copolymers with molecular weights ranging from 2 x 10$^5$ to 10$^6$ g/mol. These results will be discussed in the context of conventional surfactant science. This research was conducted in collaboration with Terry Markov, Wayne Mauer, Tim Lodge, Newell Warnburn, Marc Hillmyer, and Kristoffer Almdal.

SESSION C6S/G7. JOINT SESSION: NONLINEAR PHOTOGRAPHIC APPROACHES. Chairs: Richard A. Register and Thomas P. Russell Wednesday Afternoon, December 1, 1999

1:30 PM C6S/G7.1 NONLINEAR ASSEMBLY OF RECHARGEABLE BATTERY COMPONENTS. A. M. Mays, P.P. Soo, B. Huang, P.E. Trapa, D.R. Sidoway, 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 automobile traction. We have developed a class of self-organizing block copolymer electrodes (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-transporting pathways through the material. The BCPs can be used as an ionic liquid 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, transducing into increased battery current and capacity.

2:00 PM CCG6.2/G7.2
SURFACE MORPHOLOGIES OF SPUMIC LIQUID CRYSTAL-LIKE DIBLOCK COPOLYMERS ON ULTRATHIN FILMS
Jung-Sheng Wu, Michael J. Fancilu and Paula T. Hammond, Massachusetts Institute of Technology, Dept of Chemical Engineering, Cambridge, MA.

New teraced 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, Lc, and the smectic LC layer period, L. We use AFM, TEM, XPS, and ellipsometry 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 inlets 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 bulk copolymer plane position. The films differ in bulk morphologies, like lamellae (41% Lc content), predominantly lamellae (51%), and cylinder (79%, 80%) are also investigated by varying the LC contents of this series of diblock copolymers. These self-organized LC ultrathin films can be used to approach nanopatterning and potential advantages in electrical and optical applications.

2:15 PM CCG6.3/G7.3
ORGANIZATION OF TWO- AND THREE-DIMENSIONAL ELECTRICALLY SWITCHABLE LC NANO COMPOSITES

Holography is a standard tool to import information in thick and thin polymer films. The information is typically induced via photo 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 crystal mesogens 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 micrometers) of LC is 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 light into the kinetics of the phase separation process.

2:30 PM CCG6.4/G7.4
POLYELECTROLYTE SURFACTANT COMPLEXES AS TEM- PLATES FOR POLARIZATION BIOPOLYMER MATERIALS
Helmut H. Stre, Michael Leonard, Univ. of Massachusetts Amherst, Polymer Science and Eng., Amherst, MA.

When polyelectrolytes are mixed with oppositely charged surfactant at a 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 self-assembly behavior beyond the phase diagram of polyelectrolyte-surfactant complexes as a function of polyelectrolyte charge density, cmc, 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 CCG6.5/G7.5
COLLOIDAL CORE-SHELL PARTICLES FOR PHOTONIC APPLICATIONS: K.P. Velicka, A. van Buulleen 6, 7, 8 T. Hoff Laboratory, Delft Institute, Utrecht UN, THE NETHERLANDS. 6FOM 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 silicon layer of well-defined thickness in a seeded growth procedure to produce a core-shell structure. 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. optical resonator) or in selforganised 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 phosphorescent dyes to induce fluorescence or biocides. Due to the high fluorescence dyes can be incorporated into the silicon 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 field enhancement. The structure and optical properties of a single particle are studied by means of static light scattering and absorption measurements and compared to micromechanics theory. Transmission measurements on 2D and thin 3D colloidal crystals on a glass substrate will be discussed.

3:30 PM CCG6.6/G7.6
NANOARRAYS: THE EASY WAY USING BLOCK COPOLYMERS
Lee Rockoff, Thomas Thorn-Albrecht, Jason DeRouchey, Mark Tuominen and Thomas Russell, Univ. of Mass., Dept 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 micrometers 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 CCG6.7/G7.7
SELF-ORGANIZING POLYMER MEMBRANES FOR WATER FILTRATION

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) were 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 concomitant 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 CCG6.8/G7.8
THIN FILM PHASE SEPARATION ON A NANOSOPCICALLY PATTERNED SUBSTRATE
Kenji Fukumig, Hubert Elbs, Robert Magerle, Georg Krausch, Lehrstuhl fuer Physikalische Chemie II, Universitats 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 nanosopic domains of the respective polymers. The patterned substrate is realized by microcontact printing 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 homogenoous 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 CCG6.9/G7.9
MICRODOMAIN STRUCTURE OF ULTRATHIN SBS AND SBS COPOLYMERS. Robert Magerle, Matthias Konrad, Armin Knoll, Georg Krausch, Lehrstuhl fuer Physikalische Chemie II, Universitats Bayreuth, Bayreuth, GERMANY.

Block copolymers composed of two or more blocks of immiscible polymers tend to phase separate into regular structures with transversal symmetry resembling, for example, a cylindrical, lamellar or spherical structure. 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
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 0.9μm, diameter 0.6 nm, and persistence length 2.8 nm. The viscoelastic storage and loss moduli, G* and G″, were measured in a frequency range of f = 0.01 Hz. The onset of a narrow and shifted plateau-peak of G(f) can be located at around 30 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 polynomials of G(f) ≈ f^n. The exponent n increases slightly with decreasing concentration, the significant deviation from the simple theoretical predictions of G(f) ≈ f^n in the low frequency limit indicates interesting filament dynamics of fd in solutions of several mg/ml. At concentrations above 1 mg/ml, the low frequency limit the concentration-dependence of dynamic viscosity fits a power law of η(f)^α, as expected for a suspension of hard rods 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 semiflexible 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 it by the network to the test chain 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 Vaylonis, 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 is hydrolyzed with each free actin monomer to a hydrolyzed state. The hydrolysis process then continues, leading toactin 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 polymerization rates, free monomer concentration, nucleation, and filament capping through a series of specialized proteins. We examine the dynamics of these perturbations and discussed 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. Welsch, 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
elasticiy at low Reynolds number. Examples include DNA transcription and replication and bacterial flagellar motion. In order to elucidate fluid flow processes in these systems, consider the model problem of a rotationally forced filament with twist and bend elasticity. Competition between twist injection, twist diffusion, and writhe 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 twisting, and (ii) steady-state crankshaking motion, or writhe.

Electrostatic interactions play an important role in a variety of biophysical phenomena. For example, the condensation of run-long DNA into microparticle scale micelles and viral capsids requires electrostatic organization. This is achieved in spite of the very high monovalent charge density of DNA arising from the base pairs (approximately one negative charge per 1.7 A), we now understand that the overall driving force for DNA condensation is attractive either by either multi-valent cations or higher order assembly engendered by cationic proteins, histones, into nucleosomes and ultimately into supercoiled chromosomes. This presentation will focus on the Coulombic interactions between highly charged surfaces in an aqueous environment. In particular, we shall discuss how correlated fluctuating ions, enhanced by multi-valent counterions, lead to short-range attractive forces between such charged surfaces. The relationship 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 Chaimi-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.

1:30 PM #CC8.1

SAFETY SURFACES. P. Pincus, Meierink and Physics Deps., Univ. of California, Santa Barbara, CA.

Electrostatic interactions play an important role in a variety of biophysical phenomena. For example, the condensation of run-long DNA into microparticle scale micelles and viral capsids requires electrostatic organization. This is achieved in spite of the very high monovalent charge density of DNA arising from the base pairs (approximately one negative charge per 1.7 A), we now understand that the overall driving force for DNA condensation is attractive either by either multi-valent cations or higher order assembly engendered by cationic proteins, histones, into nucleosomes and ultimately into supercoiled chromosomes. This presentation will focus on the Coulombic interactions between highly charged surfaces in an aqueous environment. In particular, we shall discuss how correlated fluctuating ions, enhanced by multi-valent counterions, lead to short-range attractive forces between such charged surfaces. The relationship 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 Chaimi-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 INVERSE OF CHARGE. B.I. Sklodowski, 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 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 DNA 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 BIOPOLYEOLECTROLYTE SYSTEMS STUDIED BY COUNTERION NMR. L. Neumann, Depts. of Chemistry, Applied Chemistry, and Nuclear Science, University of California, Berkeley, CA.

Biopolyelectrolytes such as DNA, F-actin and filamentous 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 theory. We have studied the interaction between Cys and Li counterions in the DNA fibrs of varied ionic compositions, 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 Cys 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 Liophosphate complex. In another set of experiments, results of self-diffusion of water and the following polynucleotides in oriented DNA have been obtained: thymidine (three-valent), purine and dideoxythymidine (both divalent). The results show that the diffusion of the three-valent spermine is considerably slower than that of the divalent polynucleotides. At high water content where DNA is in the B-form, the divalent polynucleotides...
have identical diffusion coefficients. We have also studied the competitive interaction of mono- and divalent cations with condensed, bundled forms of such polyelectrolytes as DNA and the filamentous virus particles fd and M13 by means of Monte Carlo simulations.

2:45 P.M. C88.4
DOES SALINITY AFFECT ELECTROPORATION?
H. Arandia-Espinosa 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, pores 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. (PFE vol. 58, p. 3883, 1998).

3:30 P.M. C88.5
THE ELECTROSTATIC DOUBLE LAYER RE-VIEWED.
V. Adrian Parsegian, LSIB/NCID/NIMH, 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, metal-sphere ions, and ideal interfaces. In two directions this talk will look away from common practice. These departures were forced on us by experiments in our lab as well as in many others.

Microscopic properties of the electrostatic double layers are often better described by spatial averages. There is profit in treating the simultaneous push and pull on co- and counterions from the viewpoint of Gibbs adsorption theories. Count the number of ions perturbed a charged surface and estimate the extent to which that surfaces perturbs its surroundings. * Microscopically, ions interact with each other and with surfaces far more inductively than if they were spherical metal balls floating in infinitely 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-covalent ionic-bilayer binding Ionic channel 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, polyelectrolytes, whose intermolecular forces are measured in salt solutions. Single molecule mechanics, such as DNA stretching sensitive to buffering ions.

4:00 P.M. C88.6
POSITIVELY CHARGED VESICLES CAN REPEL NEGATIVE OBJECTS.
H. Arandia-Espinosa and N. Dan, Drexel Univ.; Y. Chen, T. Laibinis, P. Nathan, Univ. of Pennsylvania, L. Barons, Univ de Montpellier; D. Weitz, Harvard Univ.

Charged bilayer vesicles can direct the formation of a surprising new class of colloidal particles. Mixed vesicles of neutral and cationic surfactants, when combined with anionic colloidal spheres, spontaneously self-assemble into complexes with closed-packed, self-limiting, rafts of spheres floating on tense round vesicles. To understand the mechanism we show how a positively-charged, mixed bilayer vesicle in the presence of negative charges can spontaneously partition into an adsorption zone of definite area, and another zone which repels additional negative objects. Through the membrane itself, the area in sequence is one of the 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 P.M. C88.7
DIRECT-FORCE MEASUREMENTS BETWEEN COLLOIDAL PARTICLES BY SOME SIMPLIFIED METHODS.
S. Olguin, E. J. Pincus, University of California at Berkeley, CA.

Polymer chains that are chemically attached to solid surfaces have important commercial uses in colloidal stabilization. In this investigation, we provide a new method for mapping the forces, in microcolloid dynamic light scatting, force microscopy, and Langmuir trough compression, to have been employed to observe the interactions between colloidal particles stabilized by tethered polymer chains. Monolayer-assembled Ag @ Au liposomes by hydrophobic side chains of surface-attached charged 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 P.M. C88.8
UNCONTROLLED 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/m², one is in high surface potential regime. In this physical situation of 'strongly 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 smeared bilayers stacks are still observed by electron microscopy. 2. Ossein-Zemik behavior of small angle light scattering on asymmetric sponge phases (disordered connected lamellae) can be fitted but produces unrealistic correlation lengths.

SESSION C89: POSTER SESSION
Thursday Evening, December 2, 1999
8:00 P.M.
Exhibition Hall D (I)

C89.1
VISCOITY AND MORPHOLOGY OF SYNTHETIC LUNG SURFACANT MONOLAYER.
Jung Dong, Heidi E. Warriner, Anja van Nahmen, Joseph A. Zawadzki, Alan J. Waring.

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 is to stabilize the monolayer against collapse, the collapse structure of montan and 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.

C89.2
DETECTION OF SHAPE FLUCTUATIONS IN LARGE LIPID VESICLES USING DIFFUSING-WAVE SPECTROSCOPY.
Michael Lemont and Barbara Frisen, 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 diffusion equation. Because a photon is scattered once before it reaches the detector, the path length of photons is equal to the number of scattering events from the vesicles. By studying the DWS intensity correlation for temperatures above and below the bilayer transition temperature, the existence of shape fluctuations in these vesicles has been confirmed. [1] Hu Q, A.H. Krall and D.A. Weitz, Phys. Rev. E 52, pp.6896-6912 (1995)
CC0.3 SCATTERING FROM HOMOPOLYMER-BLOCK COPOLYMER BLENDS: PART II, DYNAMICS P. Falus, M.A.

Dynamic X-ray scattering measurements were presented of the dynamics of cylindrical polymer micelles, self-assembled in homopolymer-block copolymer blends. The emerging technique of Dynamic X-ray Scattering was used at the S-1D 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 2πr/λ > 2λL, where L is micellar length. Our Dynamic X-ray scattering results will be compared to what may be expected for the dynamics of hard cylinders.

CC0.4 LARGE-SCALE ALIGNMENT OF ABC BLOCK COPOLYMER MICRO DOMAINS VIA SOLVENT VAPOR TREATMENT. Kenji Fukunaga, Hubert Elia, Robert Magerle, Georg Krausch, Universität 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 micro phases 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.

CC0.5 EFFECTS OF SALT VALENCE ON THE SHEAR THICKENING OF DILUTE WORM-LIKE MICELLAR SOLUTIONS. Jennifer M. Politach, Department of Chemical Engineering, University of California, Santa Barbara, CA; David J. Flinn, 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 consisted of a cationic surfactant, cetyltrimethylammonium bromide (CTAB) and a complex salt, the alkaline earth [Sr2+] salt with either a monovalent counterion, sodium (Na+), or a divalent counterion, magnesium (Mg2+). Comparisons between the two salts are made by maintaining a constant CTAB-Salt 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 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. DMR9622710.

CC0.6 MOLECULAR-DYNA Simulations of Subsurface Defects in Nematic Liquid Crystals. J.J. Castro, A. Calles, R.M. Valladeas, 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 an anisotropic induced dipole-induced dipole and isotropic Maier-Saupe interaction, and the external anchoring (nematic-substrate) is describe by the Ragni-Papoular interaction. We compare our results with calculations based on lattice models and also with some other molecular dynamics simulations using different interparticle potential.

CC0.7 SALT EFFECTS ON THE PRE-AGGREGATION OF NANOPARTICLES. T. Zemb, S. Lycann, O. Spilla, L. Belloni, J. Barlett, E. Pinnin, J. Wellby, CEA Saclay, 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 formulation induces fragmentation of the droplets during drying, hence producing fine aerosols instead of porous powder of controllable granularity. We have correlated the SANS produced by the initial salt which gives the interparticle potential with the USAPEX spectra of the final powder produced. The right engineering amount of salt 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/silica colloidal solution.

CC0.8 EFFECT OF THE DIPOLE INTERACTIONS ON THE PHASE BEHAVIOR OF POLAR LIQUIDS: A SIMULATION STUDY. Godfrey Gumbs and Girija S. Dabey, 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.

CC0.9 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 in submillimeter) in pure water under nitrogen atmosphere at 30°C. One of the gel surfaces was chemically adhered on a glass plate by using Hind Silane (Phenom). 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 ±0.05°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 different by the equation of state of gels on the basis of Flory theory. The Weck's Flory-type free energy taken into account the uniaxial and biaxial mechanical constraint.

CC0.10 PARTICLE INTERACTIONS AND RHEOLOGICAL PROPERTIES OF POLYVINYL ACETATE SUSPENSIONS STABILIZED BY POLYVINYL ALCOHOL. Stefano Carra, Vinvel Spa, Villadossola (Vr), ITALY; Leonardo Malacarne, Sergio Carra, Dept. Chimica Fisica Applicata, Politecnico di Milano, Milano, ITALY.

Polyvinyl acetate emulsions are commonly used materials for the coating industry, widely applied in the production of waterborne adhesives and coatings. Since conventional anionic surfactants are quite ineffective in the stabilisation of polyvinyl acetate-based emulsions, they are often replaced by nonionic polymer molecules, genetically related to so-called stabilizers. A variety of 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 emulsions are important but little completely understood. Particularly, 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 achieved by reducing the content of stabilizers, 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 expression, 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 controlled with a study hard sphere potential. The present attention is focused onto the low-viscosity regime, with the intention of extending the approach to high solids content in future work. A particular attention is hereby devoted to the extraction of the viscosity parameters of polyvinyl alcohol; the total amount adsorbed onto the polymer particles and the thickness of the adsorbed layer.

CC09.11

**FIRST-PRINCIPLES MOLECULAR DYNAMICS OF A  KNOT IN A  POLYMER STRAND.** Antonio Marco Saitta, Michael L. Klein, 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, an important interest in everyday life. We modelled this very general situation by studying the strain-induced breaking of the simplest polymer, i.e. polyethylene (A. M. Saitta et al., Nature 399, 48-51 [1999]). These ab-initio molecular dynamics calculations show that the chain resistance is significantly weakened by the presence of a knot, which also affects the rupture of 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 following in the range of "femtochemistry".

CC09.12

**INSERTION PROCESS OF A  PROTEIN SINGLE LAYER IN A  FREE STANDING BILAYER FILM OF LIPOSOMES.** J. J. Benatar, 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 insertion 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 demurrature 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 method opens the possibility for further studies, including the investigation of interfacial processes under perfectly controlled conditions, or the two dimensional crystallization of such proteins over very large areas. We apply this method here to the confinement of a model protein [BSA] associated to a non-ionic 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.

CC09.13


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-mol' mesogen shaped like the letter Z, composed of seven soft spheres bonded rigidly together with no intramolecular degrees of freedom. For strongly angled molecules, we find that the nematic phase alone provides 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.

CC09.14

**INTERACTION OF POLYMER WITH CLAYS.** Jyttehelen Lal, IPSN, A.N.I., Aragonne, IL; Loic Aubry, LLB, CE-SACLAY, GIF-Sur-Yvette, FRANCE.

Normally well defined synthetic monodisperse discotic liquid crystalline chys are known to form a gel phase at mass concentrations as low as a few percent in distilled water. Hydrophilic polymer polyethylene oxide was added to this gelling system and it was observed that it either prevents gelation or slows it down extremely depending on the polymer weight, concentration or the polyelectrolyte concentration. Small Angle Neutron scattering (SANS) was used to study these systems because this technique can in the structure of polymer layers be determined. The contrast variation technique is specifically used to determine 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.

CC09.15

**SOFT-PROPERTY PROPERTIES AND ASSOCIATION OF POLYBENZYL-P-PHENYLENES; NOVEL HIGH PERFORMANCE POLYMERS.** Richard Niro, Amit Selgani, Thomas A.P. Seely, University of Connecticut, Polymer Science Program, Storrs, CT; Richard Vain, Air Force Research Center, Wright-Paterson AFB, OH.

Poly(benzyl-p-phenylene) (PB) is a novel polymer that offers possibilities for use in high temperature composites. Fundamental study of polymers with this backbone has been performed previously due to the insoluble and infusible nature of these polymers. The polar benzyl group in PB allows the means to dissolve the phenylene backbone in organic solvents such as dichloromethane, tetrahydrofuran, and cresol. A series of PBPs 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 rod-like 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 fundamental characteristics can provide information about the conditions under which these high performance polymers can be processed.

CC09.16

**NON-DEBYE DIELECTRIC RELAXATION IN LIQUID CRYSTALS CONFINED TO RANDOM POROUS MEDIA.** G.P. Sinha and F.M. Allev., 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 axes has been broadened in bulk, is broadened when liquid crystal is confined in random porous media. We present results of dielectric investigations on alkylcyanobiphenyl (5CB and 8CB) confined in random porous matrices of two porosities (1 and 1000 Å) in various temperatures (10^3 Hz - 10^8 Hz) and temperature (140 K to 330 K). The dielectric behavior of 5CB and 8CB confined in random porous matrices is different from their bulk behavior. Novel 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 layer of the 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 spectral 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. Allev., Phys. Rev. E 58, 2081 (1998). This work is supported by DoD grant N00014-99-0-0566.

CC09.17

**NMR SPECTRA FROM MONTE CARLO SIMULATIONS OF POLYMER DISPERSED LIQUID CRYSTALS; EFFECTS OF MOLECULAR MOTION.** C. Ciricotti, P. Pasini, Istituto Nazionale di Fisica Nucleare, Sezione di Bologna, Bologna, ITALY; G. Skrecz, S. Zumer, Physics Department, University of Ljubljana, Ljubljana, SLOVENIA; C. Zanoni, Dipartamento di Chimica Fisica ed Inorganica, Università di Bologna, Bologna, ITALY.

Polymer dispersed liquid crystal (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 Lebowitz-Liniger lattice spin model. We have applied the Monte Carlo (MC) simulation technique to this model and calculated a sequence of eigenvalues molecular configurations inside the drop for radial, linear, and random boundary conditions. Since the desterimeric NMR is an appropriate experimental tool widely
used to investigate PDL.C, we decided to interpret the output from 
MC simulations in terms of NMR spectra. Calculating the spectra, 
two types of effects have been included: fluctuation of molecular 
1 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 a broadened spectrum, which in the fast diffusion limit 
consists of one or two rather narrow lines, depending on the type of 
boundary conditions considered. In present non-spherical 
motion, a possibility of identifying the nemtic structure 
3 type from an inspection of the spectra has been discussed. Finally, we 
considered also cases where an external magnetic field was applied.

C02.18
CELL MORPHOGENESIS INDUCED BY DISRUPTION OF CYTOSKELETAL POLYMERISITY. Troy D. Moss, Samuel A. Sfran, and Alexander Benshalom. Weizmann Institute of Science, Institute of Physical Chemistry, 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 "pods". Quantitative measurements of the 
19 pearling instability give a square root behavior for the wavelength 
as function of drug concentration. We present a theory that explains 
these observations in terms of the interplay between rigidity of the 
sub-membrane cytoskeleton 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 
17 thickness of this supporting shell. The same considerations explain 
the shape of non-adherent edges in the general case of untreated cells.

C02.10
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 disordered 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 mesophase is 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 model is fully compatible with the well known Leslie-Erickson 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 
synchronous 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.

C02.20
LIQUID CRYSTALLINE ASPECTS OF STARCH GRANULES. Thomas A. Whelan, 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 main 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 plasticization (involving water or 
organic solvents) are required to permit long range structural 
correlations to develop which give rise to the characteristic SAXS peaks 
at 9 nm. These results are important in understanding the granule 
breakdown which occurs during processing (eg in thermoplastic 
starch) and consequences of the variation between species.

C02.21
POLYMER BLENDS: SYNTHESIS BY PHASE SEPARATION METHOD IN AN ACRYLIC SYSTEM. R. Velezquez, J. Reyes, A. Cabrera and V. M. Castro, Instituto de Fisica, 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 was made of methyl methacrylate 
monomer (MMA) and polymethyl methacrylate (PMMA) in 
concentrations of 10, 20 and 30% by weight of the monomer; each of 
the casting syrup was mixed with TEGDMA in a 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 instantly 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 especially constructed for these 
purposes. The tensile properties were also determined and the 
structural analysis was achieved 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.

C02.30
SINTER ASSEMBLY OF CARBON BLACK IN POLYMERS. Vahid 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 Tg or melt temperature Tm 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 
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 ion 
concentration. The critical ion concentration can be found higher 
above a critical salt concentration or after a certain time (percolation 
time) of special heat treatment of the composite melt in electrical field.

C02.23
SIMULATIONS OF BINARY LENNARD-JONES FLUIDS CONFINED IN A SLIT-PORF. Margarita Rivera and Hector D. Dominguez, University of North Carolina, Dept. of Chemistry, NC, and G. Ramos-Santiago, Instituto de Fisica, 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 simulation 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 kind interact through a 12-6 Lennard-Jones potential while 
the wall-particle interaction is via a 1-4-3 potential. Several values of the potential strength between particles of different 
species have been considered in order to simulate different 
xenotropic mixtures. We observed a stable phase as well as phase 
transition. 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. 52928-E.

C02.40
NEUTRON SPIN ECHO SPECTROSCOPY STUDIES OF SOFT 
CONDENSED MATTER AT THE NSF CENTER FOR NEUTRON 
SCIENCE.
The NIST Neutron Spin Echo (NSE) lab, with its state-of-the-art facilities, is a leading center for neutron research. The instrument suite comprises a unique combination of high-resolution, isochromat, and isochromix methods that are used to study the structure and dynamics of complex materials. The NSE spectrometers, which are housed in the Forschungszentrum Jülich, Germany, are equipped with advanced neutron optics and detection systems that allow for high-resolution, high-sensitivity measurements.

The NSE facility is particularly well suited for studies of liquid, amorphous, and disordered materials, including polymers, surfactants, and biological systems. The instrument suite includes a wide range of spectrometers, from small-angle neutron scattering (SANS) to high-resolution neutron spin echo (HRNSE), which enables researchers to explore a wide range of length scales and timescales.

### C00.25 MECHANISM OF STRESS PRODUCTION AND THE ENTROPIC NATURE OF STRESS IN MODEL POLYMERIC MELTS

Catalin R. Piciu, 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-scale 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 center of mass 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 contributions are nontrivially captured in the intrinsic description, with the entropic one becoming dominant at higher temperatures and later times of the stress relaxation history.

### C00.26 THERMALLY STIMULATED DESORPTION OF SELF-ASSEMBLED FILMS

Maria Raposo, Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologias, Departamento de Física, Monte Caparica, Portugal; Osvaldo 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 the desorption of gases adsorbed on solids, was adapted to study desorption of self-assembled films by placing the film in an aqueous solution and increasing the solution temperature at a constant rate. It was used to determine the effects of temperature, adsorption time, and temperature on the desorption of self-assembled films. POMA/PS 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 temperature was increased at a rate of 1 °C/min and monitored with the UV/Vis Spectrometer for several temperatures. From these spectra one can estimate the amount of polymer in the film and consequently determine the desorption amount, which was determined in relation to time and plotted as a function of temperature. Considering the Arrhenius process, one can estimate the activation energies of desorption, from which three types of interaction are associated with POMA/PS self-assembled films: van der Waals forces, hydrogen bonding and ionic forces.

### C00.27 STUDY OF THE [PEG/PPG/PEG] TRIBLOCK COPOLYMERS

Compared with lithium triflate. R.A. Silva, Universidade Federal de Minas Gerais, Department of Physics, Belo Horizonte MG, BRAZIL; G. Guanhart Silva, Universidade Federal de Minas Gerais, Department of Chemistry, Belo Horizonte MG, BRAZIL; P. Moreira, M.A. Pimenta, Universidade Federal de Minas Gerais, Department of Physics, Belo Horizonte MG, BRAZIL.

Polymer electrolytes, either polymeric or liquid electrolytes, are being used in lithium-ion 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 (Tramblock - poy (ethylene glycol) PEG/poly (propylene glycol) PPG/poly (ethylene glycol)PEG) copolymer complexed with lithium triflate (LiClO4) by using Thermal Analysis (TG and DTA) and Electric Conductivity measurements. The parameters studied are salt concentration from 12 to 58 % w/w and temperature. The Thermogravimetry (TG) measurement indicates that the Tramblock/LEIL system is thermally stable below T = 350°C. The glass transition temperature (Tg) obtained by the DSC results increases with salt concentration due to the decrease of the segmental flexibility in the polymer chain. The ionic conductivity increases and 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. These results indicate the precipitation of salt microcrystals in the polymeric electrolytes at salt concentration above 58%. Besides, the ionic association increases with increasing temperature. Despite the fact that the ionic association is a limiting factor for the conductivity, the increase of the conductivity with temperature is still higher for higher temperatures.
battery system. In 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. Consequently, 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 of 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 P. 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 and association of collagenous 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 crystal. The role of simple collagenous structures makes this system ideal for the controlled study of protein aggregation. We have investigated the growth mechanism of the crystal, retrieved, and imaged the crystal. Protein aggregation and the molecular properties (size, shape, and aggregation) were studied by atomic force microscopy (AFM) to collect kinetic, thermodynamic, and morphological information, respectively. In particular, we investigated the growth mechanism of the AFM and the other growth features by TEM and micromechanical analysis. We discuss the difference in these results and comment upon the molecular properties of the complex. Additionally, a comparison between the results obtained in this study and those obtained by TEM and the other growth features will be discussed.

**CC9.31**

**DISORDER IN HIGHLY CHARGED BILAYERS IN THE ABSENCE OF SALT**
Marique Dubois, CEA, Saclay, FRANCE; Thomas Zemb, CEA, Saclay, FRANCE; Bruno Deme, IIL, Grenoble, FRANCE; Thadeeus Guik-Kreywoyt, Golno-Yvette, CGL-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 per cent is observed. The same situation is obtained with mixed anionic and cationic single chain surfactants, which associate as ion pairs. The set of Bragg peaks associated with the lamellar phase (SAXS and SANS) progressively widen and finally transform in an inflection point only in the descending branch of the scattering curve. Samples are characterized by SAXS, SANS and cryofracture experiments, as well as osmotic pressure control. The different physical origins of this distortion of Bragg's peak during swelling of an electrostatically cross-linked system, i.e. transition from the ordered to the disordered phase, correlated by ion doping and dissociation in micelles will be discussed.

**CC9.32**

**DYNAMICS OF DNA FRAGMENTS IN PORES AND IN SOLUTION**
Ullyana Molnay, Boston College, Dept of Chemistry, Newton, MA.

Osogon and "tube" reptation models are generalized to describe the mobility of an 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 1-D measure of fragment. Experimental measurement of gel mobility for DNA fragments of form Np(N)n, where n = 1,11,14 and 19 have substantiated this phenomenon. A model for the free solution electrophoresis mobility of oligo DNA relevant to the caption 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 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-trace, that takes into account a wide range of low and the high frequency vibrations of both backbone and the transverse frictional drag forces. Dynamical motions of the "probe" chain are accompanied by vesiculation response of the "vesicular" 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 lower than that of the same molecule with a bend at its end. Finally, generalization of the above model for the determination of binding parameter 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**
Hong Wang, Cristiana Geiger, Linhu Chen, Brian I. Swenson, David G. Whitten, Los Alamos National Laboratory, Chemical Science and Technology Division, Los Alamos, NM; University of Rochester, Center for Photoninduced Charge Transfer, Department of Chemistry, Rochester, NY.

The structure of organic gels formed from cholesteryl-substituted silylene derivatives in octane or octamethyl by an intermolecular interaction between the cured polymer and the solvent. Langmuir-Blodgett film, 20-58 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 photoinitiation of the film, it still keeps the fibrous structures microscopically. Hereafter, the helical twisting characteristics disappeared in most of cholesterine units. Interestingly, all the united fiber bundles seemed cracked from the center, with two parallel fibers forming boundaries to keep the fiber bundles in shape. When the gel was warmed 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. Govers
**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 GELS**
Yong Li, Ramanathan, Guanghui Liu, Karl Ludwig, Boston University, Dept of Physics, Boston, MA; Geshmar Kandall, Institute of Macromolecular Chemistry, Prague, CZECH REPUBLIC; Jyotsnam Lall, Argonne National Lab, Argonne, IL.

We have used small x-ray scattering (SAXS) and small angle neutron scattering (SANS) to study the micelle structure of a polyethylene/PS-block-polyethylene (PE/PBIH-3.5 block-polyethylene) triblock copolymer in dilute and concentrated solutions in solvents selective for either the outer P5 block (dioxane) or for the middle PBI block (heptane or decane). Equilibrium structure factors were measured over the temperature range of 20 to 90 C for different concentrations of the copolymer, ranging from 4% to 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 micelle 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 Graessling were used to describe the x-ray scattering and Lorentzians for the liquid-like peaks.

**8:45 AM CC10.2**

**X-RAY SCATTERING FROM HOMOPOLYMER-BLOCK COPOLYMER BLENDS**
Alfredo M. Bertiocchi, 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 revokes cylindrical morphology at low block copolymer composition. 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.
College Park, MD: University of Waterloo, Waterloo, Ontario, Canada

Arborescent polymers are highly branched materials synthesized by grafting multiple generations of macromolecular precursors on a central core. They 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 differ in a length scale due to being built at a higher density. This research studies the structure and self-assembly behavior of thin films of second [G2] and third [G3] generation arborescent graft polyethylene synthesized from 5k and 3k Mw micronic 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. Thin film polymers form self-assembled hexagonal macromolecular monolayer films during solvent evaporation when cast on ice-cold carbon TEM grids. Real-space imaging of the projected structure by TEM and of the surface structure by SEM reveal 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 3-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.

9:15 AM CCI010

BIOACTIVE AMPHIPHILIC DENDRIMERS. Chris Z. Chen, Stonet 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 non-microbial 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-(dimethylamino)-carboxylic acid (DMAC) and tert-butyl alcohol (tBA) to form different dendrimeric structures. The electrophilic properties of these novel dendrimers have been investigated using recombination E. coli bioluminescence techniques. Because of the high density of functional groups, the porous structure and the associative behavior of the dendrimeric structures makes them more potentially useful as animal and human counterparts. Preliminary results on the mode of action of these biocidal dendrimers will also be discussed.

9:30 AM CCI010


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 recent examination of nanoscale transition phenomena shows that this does 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 probable present and the free volume model is too simplistic. Further, we have measured the density of the new 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 cannot 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 CCI010

SELF-ASSEMBLY OF ARBORESCENT GRAFT POLYSTYRENE. Tamara E. Cochrane, R. D. Gawlik, M. Gharib, R. A. Black, School of Engineering, Institute of Technology, Hoboken, NJ; *University of Maryland, College Park, MD.

Arborescent polymers are highly branched materials synthesized by grafting multiple generations of macromolecular precursors on a central core. They 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 differ in a length scale due to being built at a higher density. This research studies the structure and self-assembly behavior of thin films of second [G2] and third [G3] generation arborescent graft polyethylene synthesized from 5k and 3k Mw micronic 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. Thin film polymers form self-assembled hexagonal monolayer films during solvent evaporation when cast on ice-cold carbon TEM grids. Real-space imaging of the projected structure by TEM and of the surface structure by SEM reveal 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 3-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 CCI010

RHEOLOGICAL CHARACTERISTICS OF SOLDIER PASTES. Douglas Lee, William J. Walker, Jr., William M. Culc, New York State College of Ceramics at Alfred University, Alfred, NY; Peter Borgeson, Universal Instruments, Binghamton, NY.

The soldier 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 99 wt %), and characterized over a range of temperatures to systemically 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 (beyond 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 103 s-1) was a function of both variables, with a maximum at low temperature and low metal content.

10:45 AM CCI010

VISCOELASTIC PROPERTIES OF A COLOIDAL SUSPENSION. Raúl Enriguez-Siegert, Cecilia Noguer, and Guillermo Ramírez-Santiago, Instituto de Física, Universidad Nacional Autónoma de Mexico, Mexico City, DF, Mexio.

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 thickening 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.

Work partially supported by CONACYT grants No. 30155P and 297961F, as well as by DGAPA-UNAM grants No. IN-100197, IN-100565 and IN-110297.

11:00 AM CCI010

PHASE SEPARATION UNDER SHEAR OF BINARY MIXTURES CONTAIN HARD PARTICLE S. Feng Qin, Valeriy Ginzbarg, Gaoqwen Peng, Anna C. Baluc, Chemical Engineering Department; David Jansen, 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 with 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 CC110.10
QUANTIFYING DYNAMICAL HETEROGENEITY IN MODEL GLASS-FORMING LIQUIDS VIA FOUR-POINT DENSITY CORRELATIONS. Thomas H. 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 temporally 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 [5]. We discuss the possible implications of our results for $T_g$, shifts under confinement, and the possibilities of new experimental measurements.


11:30 AM CC110.11
MAGNETIC- AND ELECTRO-OPTICAL STUDIES OF UNIAXIAL AND BIAXIAL FIELDS. James E. Martin, Sandia National Laboratories, Albuquerque, NM.

We have conducted large scale 3-D simulations of magneto- and electro-optical studies of uniaxial 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 apparent in 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 single 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 CC110.12
CONFOCAL MICROSCOPY STUDIES OF ELECTRO-RHEOLOGICAL FLUIDS. Jijka Dassargues, Seth Freuden Dept. of Physics, Brandeis University; Alfon van Blaaderen FOM Institute, AMSTERDAM.