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NMR AND OPTICAL STUDIES OF PIEZOELECTRIC POLYMERS

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PROGRESS REPORT

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ELECTROACTIVE POLYMERS AND LIQUID CRYSTALS

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We briefly outline below the progress made during the grant period in each several areas dealing with piezoelectric polymers and liquid crystals, as well as in facilities improvement. A list of publications under this grant, including abstracts of presentations at meetings, is appended.

Polymers

Optical Studies: A Brillouin scattering study of electrically active polymers was completed by Zhimin Liu, forming the bulk of his Ph.D. thesis. He studied copolymers of 60, 70 and 80% vinylidene fluoride with the balance trifluoroethylene, as well as a copolymer with tetrafluoroethylene, measuring sound velocity and attenuation through the glass transition as well as the ferro-/paraelectric transition. Hysteresis of about 40 K was observed at the latter transition, with a sharper transition in decreasing temperature due to the greater difficulty in nucleating the more highly ordered ferroelectric phase. He also saw evidence for a two-step ferro-/paraelectric transition.

Neutron Scattering: For the past eight years we have collaborated with Jean-François Legrand of the Institute Laue-Langevin (ILL) in Grenoble, France on work with PVF_2 and its copolymers. In the early stages we collaborated on NMR experiments described elsewhere in this proposal. More recently, we have performed several neutron scattering and diffraction experiments at the ILL. Our neutron work began with incoherent quasi-elastic neutron scattering experiments at the ILL to probe the displacements of individual protons, associated with conformational changes of the polymer chains. We continued with quasielastic neutron scattering experiments on the ILL's IN10 backscattering Doppler spectrometer, and diffraction experiments under hydrostatic pressure on the ILL's D20 high flux neutron diffractometer. The nature of the change of proton motions across the ferroelectric-paraelectric transition of the crystalline portion of the 70/30 VF_2/TrFE copolymer was investigated. The high pressure experiments showed similar increases of this transition temperature and the melting point with increasing pressure. Recently we employed the high resolution neutron spin echo technique at the ILL. We found overdamped central modes which slow down upon cooling toward the ferroelectric Curie temperature with a critical behavior which scales with the dielectric anomaly. We attribute these modes to dipolar interactions perpendicular to the chain axis.

NMR: Graduate student Nick Pinto has continued our NMR studies of the deuteron spin-lattice relaxation time T_1 in a deuterated sample of PVF₂/TrFE copolymer, one of the samples investigated with neutron scattering as described above. These results support the idea that, in the paraelectric phase, kink-3-bond motions propagate along the molecular chains of the crystalline component in the paraelectric phase.

Theory and Modelling: We have extended both general studies of polymer chain statistics, and models which bear directly on electrically active polymers. In the first category is work exploring the nature of many linear chains, modeled as self- and mutually-avoiding walks on lattices, in the dense amorphous state. Results from our computer simulations of this model are related to predictions made using the $n=0$ vector model, an adaptation of the n -vector of magnetism (where n is the number of spin components). On the basis of scaling arguments the $n=0$ vector model for a many-polymer system had also been predicted to undergo a percolation-like transition to a phase in which a single chain occupies the lion's share of the system (an "infinite chain", in the thermodynamic limit). We have carried out a detailed examination of this proposal using Monte Carlo simulations in two and three dimensions, and a careful extrapolation of finite-size lattice results. No evidence for a percolation transition was found, and we conclude that it can occur only in the limit of zero statistical weight for chain end-points. We also showed that this is consistent with the properly formulated scaling arguments. Recently we modified these models of PVF₂ and copolymer chains in the crystalline state, to better take into account electronic polarizability and monomer randomness.

An obstacle to the understanding of polymer statistical mechanics is that there are few exactly solved polymer models. This led us, with W.A. Schwalm at the University of North Dakota, to consider models which are made solvable by the introduction of geometric constraints, with the idea that important physical properties may remain. We have studied the behavior of self-avoiding walks (SAWs) on the fractal 4-simplex lattice, a generalization to three dimensions of the Sierpinski gasket. Using exact recursion relations we studied how changing the stiffness of the SAW (the cost in energy of a bend in the SAW) can inhibit or promote a collapse transition in the SAWs. This led to a complete description of the rod-like-to-flexible-coil crossover in the scaling behavior of stiff walks with increasing length. We were also able to incorporate (exactly) repulsive or attractive interactions between adjacent chain segments -- interactions that can mimic the effects of good or poor solvents. We have developed a technique which further streamlines the renormalization analysis of this problem and will, we anticipate, lead to additional analytic (rather than numerical) results.

We have recently developed, and are now analyzing results from, Monte Carlo simulations of chains of electrically active PVF₂ and PVF₂/TrFE copolymers. In this work our object is to model the conformational order/disorder transition within the chain that underlies the ferroelectric/paraelectric phase transition. In particular we are assessing the role of inter- and intrachain dipole-dipole forces in this process. So that we may use relatively rapid Monte Carlo methods in this study, we confine the monomers to the sites of a diamond lattice. In this scheme an all-trans chain lies along the lattice 110 direction, and the important kink-3-bond defect can be naturally accommodated. The trans/gauche energy difference, chain tension and a confining potential (to mimic the confining effect of neighboring chains) are also included in the model. We have found that the model displays relaxation of a stretched exponential form along its stochastic trajectory, and have studied the relaxation time as a function of temperature in order to determine appropriate sampling intervals. Our initial results suggest that in fact electrical

forces do play a dominant role in determining chain conformations, as compared to torsional (trans/gauche) energies at temperatures near the transition. In this simple model we observe the nucleation of stable GTG'TTG' sequences as the principal mode of disorder in the FE phase.

In a second phase of our PVF₂/TrFE simulations we have begun the development of a molecular dynamics simulation of linear chains in the crystalline phase. This is a multi-chain model in free space (rather than on a lattice) for which the equations of motion of the monomers are numerically integrated. Dynamic properties such as relaxation and time-dependent response, as well as time-averaged behavior can thereby be studied. Portions of this code are presently being tested.

Liquid Crystals

Optical: We are taking advantage of this 5-pass capability in beginning Brillouin scattering measurements in liquid crystals, which also have strong Rayleigh lines. Dr. Igor Siny of the Ioffe Institute in St. Petersburg is visiting this 1992-3 academic year. He, together with graduate students Tim Tu and Greg Pastalan, are improving the computer control of the interferometer and have already obtained strong signals from liquid crystal samples.

Phil Himmer for his recently completed M.S. work studied the Freedericksz transition in E7 liquid crystal material at room temperature in the nematic phase, fitting optical transmission data as a function of the magnetic field (which rotates the director) using the full Oseen-Frank free energy expression. This technique allowed us to measure the splay and twist elastic constants to within an accuracy limited by uncertainty in sample thickness and the anisotropy in the magnetic susceptibility. We are refining and extending this approach with the goal of measuring surface anchoring strengths, parameters which are necessary for the study of elastic energies in polymer-dispersed liquid crystals (PDLC's).

NMR: We have carried out preliminary ⁷Li NMR studies of a lithium stearate liquid crystal in the temperature range 21 to 178°C. This material has a crystalline-crystalline transition at 114°C, enters the smectic phase at 140°C and the isotropic phase at 174°C. Spin-lattice relaxation time (T₁) measurements up to 140°C indicate the presence of multiple time constants, which merge into one above this temperature.

NMR T₁ measurements made by us on the liquid crystal E7 show evidence of a phase transition at the clearing point at 61°C.

Thermal: An ac thermal diffusivity apparatus has been built by graduate student Greg Pastalan. By operating at different frequencies, we can determine both the specific heat and thermal conductivity of a small sample slab. This will be used to study both polymers and liquid crystals. The sample holder can operate in a dewar to allow observations over a wide temperature range. The sample cell contains two identical Melcor thermoelectric elements with the sample slab between, surrounded by a copper wall to insure temperature uniformity and stability. One element supplies an ac temperature wave, while the other one senses the phase-shifted and attenuated wave. A sensitive lock-in amplifier allows measurement of this wave from the amplifier's lower limit of 0.5 Hz up to 50 Hz where the wave becomes too weak to detect. Analysis of results agreed with theory down to 6 Hz. Below this frequency the measured wave was weaker than predicted, perhaps because of convection. We are building an evacuated sample holder in hopes of extending the useful frequency range downward.

Theory and Modelling: We reanalyzed the nematic liquid crystal elastic energy and showed that there are four normal distortion modes -- the splay, bend, twist and saddle mode -- such that the elastic energy is proportional to the sum of the squares of the four distortion amplitudes, with no cross terms. In previous treatments, parts of the saddle distortion energy have been included with the splay and twist energies, and the remainder has either been ignored or considered as a surface energy term because it can be mathematically expressed as a divergence. This can lead to confusion: The usual Freedericksz experiments, which purport to measure the splay or twist elastic constants, actually measure the averages (splay+saddle) or (twist+saddle), respectively, because the splay or twist distortion in those experiments occurs only in a plane. However, the radial director arrangement in liquid crystal droplets in PDLC sheets has the pure splay distortion, so attempts to analyze the elastic energy of such droplets using the splay coefficient obtained from a planar Freedericksz experiment geometry will lead to error.

A graduate student, Ruth Chien, is examining the phase behavior of a nematic liquid crystal in a micron-sized cavity located in a strongly electrically polarized medium, such as PVF₂. We are interested in learning the extent to which the polarization perturbs the radial and axial structures recently described by Kralj and Žumer.

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