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SYNTHESIS AND CHARACTERIZATION OF POLY(VINYLDENE
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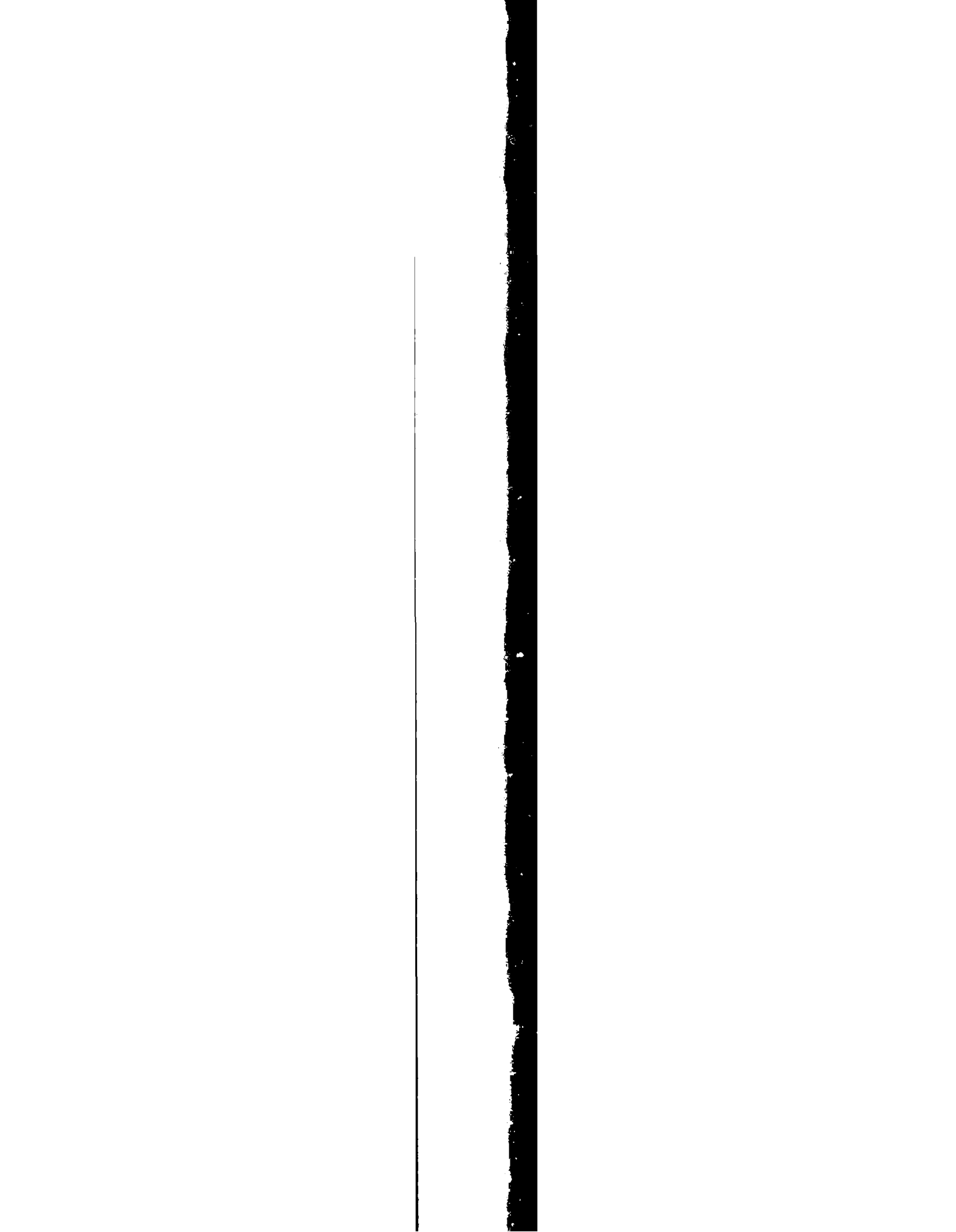
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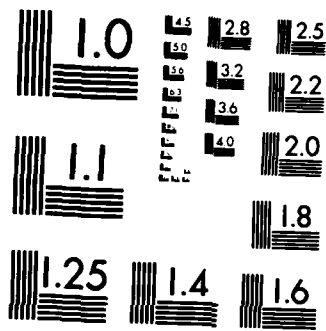
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FINAL REPORT

Synthesis and Characterization of Poly(vinylidene fluoride)

by

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SUMMARY OF ACCOMPLISHMENTS

Poly(vinylidene fluoride) (PVF₂) has been widely studied due to potential applications based on its ferroelectric nature, with both piezoelectric and pyroelectric devices possible. In order to understand and possibly to improve the physical performance of PVF₂, however, detailed knowledge of its molecular structure is essential. As a result, structural analysis of PVF₂, which involves characterization of both the polymorphism and the detailed molecular structure, has been a major area of research.

One major thrust under this contract has been to examine the influence of head-to-head defects on the crystallization and melting behavior of PVF₂. Such structural irregularities, formed by monomer reversal during polymerization, are thought to increase the free energy of the molecular chains and thus alter the chain packing in the crystallization region. In order to study this phenomenon, ten commercial samples and two samples synthesized in our laboratory were investigated. Ranges of physical parameters for these materials were: H/H content, 3.3 - 6.1%; molecular weight, 52,000 - 703,000; and bulk crystallinity, 36 - 50%. The primary experimental tool for the study of the crystallization behavior was differential scanning calorimetry.

The first project of interest was to examine lamellar thickening during alpha phase crystallization. Such thickening will be reflected by the increase in the melting temperature as a function of time during crystallization. The surface nucleation theory for homopolymers predicts that the thickness should increase linearly with the logarithm of the crystallization time. In fact, this is precisely what is observed for the material from Solvay (Solef 1010) crystallized at 410, 420 or 425K. There appeared to be no effect of the H/H defect until the H/H content dropped to 3.6%, at which point a break in the isothermal thickening curve occurred, similar to that observed for polyethylene below 400K. Consideration of the isothermal thickening behavior as well as available literature indicating that the heat of fusion decreases with increasing H/H content led to the conclusion that the H/H defects may be incorporated in the crystalline regions.

In a second study, Hoffman-Weeks plots of melting temperature versus crystallization temperature were prepared in order to determine the equilibrium melting temperature, T_m^0 , as a function of the H/H content. The Hoffman-Weeks plots showed breaks, as found earlier by Prest and Luca as well as Morra and Stein. Extrapolation of the higher slope led to equilibrium melting points that depended fairly strongly upon the H/H content: T_m^0 values dropped from 463K to 452K as the H/H content increased from 3.2 to 5.2%. In this same series of samples it was found that the crystallinity of the alpha phase material decreased from 55 to 40% as the H/H content increased from 3.2 to 5.2%, for samples of comparable molecular weight.

In the third study on crystallization and melting behavior, high temperature crystallization experiments were performed in order to determine the influence of the H/H content and the molecular weight on the solid state transformation from the alpha to the gamma

phase. This transformation is of potential interest because the gamma unit cell is polar, in contrast to the alpha unit cell. All results were derived from analysis of the melting endotherms obtained by differential scanning calorimetry, which showed contributions from melt-crystallized alpha phase, melt-crystallized gamma phase, gamma phase formed by solid state transformation from alpha and an additional low melting alpha peak attributed to the interlamellar crystallization that occurs during quenching.

The extent of the transformation appears to increase with the percentage of the gamma spherulites in the crystalline regions, but to decrease with the content of the interlamellar amorphous layers. The results support Lovinger's proposal that the transformation proceeds more rapidly in the longitudinal direction toward the alpha nuclei than in the transverse direction. Moreover, the two competing factors -- the percentage of the gamma spherulites and the interlamellar amorphous content -- increase with either the H/H content or the molecular weight. As a result, the alpha to gamma transformation is a complex function of the H/H content and the molecular weight. In addition, the excess free energy of the H/H content in the alpha polymorph and the equilibrium melting temperature of the no defect PVF₂ are calculated from the analytical treatment due to Morra and Stein. The results of the experiment and theory are inconsistent.

The second major thrust of our research has been an examination of the thermal degradation of PVF₂ in solution. The motivation for this effort is that although there are over 1000 papers on the morphological, processing or electrical properties of PVF₂, there are very few on the stability. The available reports on the thermal and radiation-induced degradation indicate that dehydrofluorination, chain-scission and branching occur. Since these changes in molecular structure would almost certainly change the morphology, and thus the electrical behavior, the topic seemed quite significant.

Solution degradation of PVF₂ has not been investigated previously, and has been the focus of our work. Our specific objective was to study the thermal and chemical degradation in N,N-dimethyl formamide and related basic solvents. The key experimental tool in this effort has been ultraviolet/visible spectroscopy because dehydrofluorination leads to conjugated polyene sequences in the PVF₂ that may be easily monitored by absorption techniques. The degradation was found to be enhanced by increasing basicity of the solvent or other additives. The peak absorbance of the dehydrofluorinated PVF₂ increased linearly with the degradation time, which could be explained by a kinetic model originally developed by Kelen for the dehydrochlorination of poly(vinyl chloride). In addition, the degradation rate was found to decrease with the polymer concentration and the molecular weight, exhibiting the characteristics of a diffusion controlled reaction.

PUBLICATIONS

1. L. T. Chen and C. W. Frank, "The Influence of Head-to-Head Defects on the Crystallization of PVF₂," *Ferroelectrics*, 1984,

57, 51-62.

2. L. T. Chen and C. W. Frank, "The Influence of the Head-to-Head Defect and the Molecular Weight on the Alpha to Gamma Solid State Transformation of Poly(vinylidene fluoride)," submitted to *Macromolecules*.
3. L. T. Chen and C. W. Frank, "Solution Degradation of Poly(vinylidene fluoride)," submitted to *Macromolecules*.

PERSONNEL

Lien-Tai Chen, graduate student

Miriam Shmueli, visiting scholar

Curtis W. Frank, principal investigator

AWARDS AND HONORS

Invited Paper, "The Influence of Head-to-Head Defects on the Crystallization of PVF₂," U.S.-Japan Seminar on Piezoelectric Polymers, Honolulu, Hawaii, July, 1983.

Invited Paper, "The Influence of Molecular Structure on Crystallization and Solid-State Transformation in PVF₂," Symposium on Advances in Piezoelectricity and Ferroelectricity in Polymers, American Physical Society, Baltimore, MD, March, 1985.

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