

TOPICAL WORKSHOP

**FLOW-DEFORMATION AND MOLECULAR
REORGANIZATION IN**

**POLYMERS WITH CRYSTALLINE AND LIQUID
CRYSTALLINE ORDER**

sponsored by

Division of Polymer Chemistry, Inc.

AMERICAN CHEMICAL SOCIETY

**April 5 - 8, 1986
Montreal, Canada**

Chairman: A. E. Zachariades

**Celanese Company, Dartco Manufacturing Inc. & IBM Corporation
are graciously providing support for this workshop.**

April 5, 1986

Dear Colleague:

Welcome to Montreal!

Please find enclosed in this folder a copy of the Program, a list of registrants and a copy of the abstracts of the papers to be presented at the ACS Polymer Division Topical Workshop on "Flow-Deformation and Molecular Reorganization in Polymers with Crystalline and Liquid Crystalline Order". The Program has been designed to provide state of the art knowledge of the molecular reorganization that occurs under flow conditions in melt, solution and solid state operations in order to obtain products with high modulus and strength. I think you will find the program stimulating. However the success of the Workshop depends to a large extent upon the active participation of all the attendees. I encourage you to contribute your ideas, express your thoughts and raise questions during the discussion sessions.

I look forward to meeting each of you.

With best regards,

A. E. Zachariades

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ACS Topical Workshop

"Flow-Deformation And Molecular Reorganization in Polymers With
Crystalline Order"

SPEAKERS & TECHNICAL PROGRAM

SUNDAY MORNING, APRIL 6, 1986

8:30 AM Welcoming Remarks - A. E. Zachariades

Session I Chairman - Roger S. Porter

9:00 AM A. Keller, and J. A. Odell, University of Bristol, England.
"Extensibility of Long Chains as Studied Through Extensional Flow in
Solutions".

9:40 AM Discussion

9:55 AM Coffee Break

10:10 AM P. Smith, DuPont Experimental Station, Wilmington, Delaware.
"High Performance Materials from Flexible Polymers"

10:50 AM Discussion

11:05 AM T. Kanamoto, K. Tanaka, M. Takeda, Science University of Tokyo, and
R. S. Porter, University of Massachusetts, Amherst, Massachusetts.
"Preparation of Ultra-High Modulus Morphologies of Polyolefins by Drawing
Single Crystal Aggregates of High Molecular Weights".

11:45 AM Discussion

12:00 PM Lunch

SUNDAY AFTERNOON APRIL 6, 1986

Informal Discussions or Free Time

SUNDAY EVENING, APRIL 6, 1986

Session II Chairman - J. F. Fellers

7:30 PM D. Baird, Virginia Polytechnic Institute and State University.
"The Effect of Flow and Thermal History on the Orientation and
Morphology of Thermotropic Polymers".

- 8:10 PM Discussion
- 8:25 PM J. D. Cloyd and R. H. Cox, Eastman Kodak Company.
"Effects of p-Hydroxybenzoic Acid Residue Level on the Melt Rheology and Extrudate Properties of Poly(ethylene terephthalate)".
- 9:05 PM Discussion

MONDAY MORNING APRIL 7, 1986

Session III Chairman - D. Baird

- 9:00 AM N. D. Field, R. Baldwin, F. Scardiglia, J. Duska and R. Layton, Dartco Manufacturing Inc.
"Morphology, Crystallinity and Orientation in a Copolyester Based on Biphenol, Terephthalic acid and p-Hydroxybenzoic Acid".
- 9:40 AM Discussion
- 9:55 AM Coffee Break
- 10:10 AM S. K. Garg and S. Kenig, Celanese Speciality Operations.
"Orientation and Gross Morphology in Injection Molded Thermotropic Liquid Crystalline Polymers".
- 10:50 AM Discussion
- 11:05 AM J. F. Fellers, J. E. Flood, G. W. Farrell and D. N. Lewis, The University of Tennessee.
"Design and Analysis of Processing Operations to Control Orientation in Polymer Liquid Crystals"
- 11:45 AM Discussion
- 12:00 PM Lunch

MONDAY AFTERNOON APRIL 7, 1986

Session IV Chairman - T. Asada

- 2:00 PM K. F. Wissbrun, G. Kiss, Celanese Research Company, and F. N. Cogswell, ICI, England.
"Flow Behavior of a Thermotropic Liquid Crystal Aromatic Copolyester".
- 2:40 PM Discussion
- 2:55 PM Coffee Break

3:10 PM G. C. Berry, M. Srinivasario and S. Se, Carnegie-Mellon University.
"Rheological and Rheo-optical Studies of a Nematic Polymer Solution".

3:50 PM Discussion

4:05 PM M. M. Denn and R. C. Moore, University of California.
"Orientation Kinetics of Thermotropic Liquid Crystalline Polymers".

4:45 PM Discussion

6:30 PM BANQUET

Banquet Speaker - R. H. Marchessault, Xerox Research Center of Canada.
"Polymers and Systems".

TUESDAY MORNING APRIL 8, 1986

Session V Chairman - A. E. Zachariades

8:30 AM J. A. Cuculo, M. H. Theil, Y. S. Chen and K. S. Yang, North Carolina State
University.
"Cellulose Dissolution, Liquid Crystal Formation and Fiber Formation in
Ammonia/Ammonium Thiocyanate Solution".

9:10 AM Discussion

9:25 AM D. T. Grubb, Cornell University.
"Gel Drawing of High Modulus Polyvinyl Alcohol Fibers"

10:05 AM Discussion

10:20 AM Coffee Break

10:35 AM A. E. Zachariades, IBM Research Laboratory, and T. Kanamoto, Science
University of Tokyo.
"A New Model for the High Modulus and Strength Performance of Ultra
Drawn Polyethylenes".

11:15 AM Discussion

11:30 AM Open Discussion and Summary.

ABSTRACTS

EXTENSIBILITY OF LONG CHAINS AS STUDIED THROUGH EXTENSIONAL FLOW IN SOLUTIONS

A. Keller and J. A. Odell

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A general survey will be presented on a new field of experimental study developed in the Bristol laboratory. It consists of stretching out long chain molecules in solution virtually completely by means of elongational flow and of registering the course of this chain extension. It has turned out that this approach encompasses some of the most central and salient issues of physical polymer science. In the case of dilute solutions it provides, amongst much else, a method for characterizing the flexibility, length (i.e. molecular weight and its distribution) and strength (and alternatively mechanically induced fracture) of chains when in isolation. In semi dilute solutions it offers an approach to the assessment of interchain interactions in general and entanglements in particular. Conversely, the extending chains can affect the flow field which causes the chain extension to begin with in very specific, usually highly localised ways, which in turn affects rheological behaviour providing an approach, amongst others, to the flow modifying effect of polymeric additives.

HIGH PERFORMANCE MATERIALS FROM FLEXIBLE CHAIN POLYMERS

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High performance materials can be produced from common flexible chain polymers through tensile drawing, provided that nearly full extension and perfect alignment of the polymer molecules is achieved in the drawing operation.

The development of the Young's modulus with draw ratio, and the factors that limit the maximum draw ratio and the maximum achievable modulus will be discussed and illustrated with experimental results. In addition, theoretical estimates for the maximum tensile strength of oriented polymers will be addressed, in particular its dependence on the molecular weight.

PREPARATION OF ULTRA-HIGH MODULUS MORPHOLOGIES OF POLYOLEFINS BY DRAWING SINGLE CRYSTAL AGGREGATES OF HIGH MOLECULAR WEIGHTS

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Based on the previous studies of solid-state co-extrusion of single crystal morphology of high density polyethylene, superdrawing of ultrahigh molecular weight polyethylene (UHMW-PE) and of polypropylene (UHMW-PP) has been achieved by solid-state co-extrusion and tensile drawing of the single crystal mats precipitated from dilute solutions (0.05-0.2 wt-%). These techniques produced ultra-oriented films with draw ration (DR) 240 for UHMW-PE and 40 for UHMW-PP. Even higher DR were achieved by a combination of solid-state co-extrusion followed by tensile drawing at controlled rates and temperatures. The maximum DR attained for the mats by this drawing combination was ~350 for UHMW-PE and ~80 for UHMW-PP. Such superdrawn films exhibit tensile moduli and strength ≤ 220 GPa and 5.0 GPa, respectively, for the UHMWPE, and ≤ 34 GPa and 2.2 GPa, respectively, for the UHMW-PP. These moduli approach the yet uncertain theoretical maximum modulus values reported for the crystal for each of the two polymers. The two-stage drawing technique was applied for the preparation of superdrawn rods of UHMW-PE; ie., solid-state extrusion of single crystal powder followed by tensile drawing under controlled conditions. There were additional difficulties in achieving ultradraw for rod samples and the maximum DR that we could attain rather easily was 150. The temperature stability of drawn samples significantly increased with DR, as evaluated by the Young's modulus vs. temperature, linear thermal expansion, and DSC melting behavior.

The morphological changes on drawing of single crystal aggregates have been studied by x-ray wide-angle and small-angle scattering, and optical and electron microscopy. Supplementary information has been obtained by measurements of density, DSC melting behavior, linear expansion, and dynamic viscoelastic properties. The superdrawn films of UHMW-PE which show the maximum mechanical properties are extremely fibrillated and consist of macrofibrils with lateral dimension of 0.2-0.6 μm ; each of them is uniform but different from each other in the lateral size thickness. The macrofibrils consist of nearly perfectly crystalline microfibrils (~150 \AA wide) in which the molecular chains are extremely extended and oriented along the fiber axis. However, the existence of some defects and crystal distortion is indicated by the x-ray diffraction patterns; this is more significant for drawn UHMW-PP. Among several morphological properties studies in this work, the x-ray coherent crystal length, D_{002} , increases regularly with DR even for highly drawn samples and correlates well with the mechanical properties of highly drawn UHMW-PE.

THE EFFECT OF FLOW AND THERMAL HISTORY ON ORIENTATION AND MORPHOLOGY OF THERMOTROPIC

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In this paper we look at the effects of shear flow, and uniaxial and equal biaxial extensional flow on the development of orientation and morphology of several different liquid crystalline copolyesters. In general we observe that the degree of orientation as determined qualitatively by means of wide angle x-ray diffraction (WAXS) is quite low in all types of flow if the deformation is carried out isothermally. However, if the polymers are cooled and deformed simultaneously, then a much higher degree of orientation is achieved. Under the right conditions of deformation and thermal history we also observe biaxial orientation in the samples subjected to biaxial extensional flow. The value of this work rests in creating conditions which could be used in the design of novel processes for thermotropic polymer system. In this way it might be possible to translate the properties found primarily in fibers to other geometries.

EFFECTS OF p-HYDROXYBENZOIC ACID RESIDUE LEVEL ON MELT RHEOLOGY AND EXTRUDATE PROPERTIES OF PET

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Copolyesters of poly(ethylene terephthalate) (PET) and p-hydroxybenzoic acid (PHB) exhibit thermotropic liquid crystalline behavior. It has been found that the PHB level greatly influences the melt rheology and the properties of the extrudate of the copolyester. This paper presents the results of work studying the effects of PHB level on the viscoelastic behavior of the copolyester. The effects of viscoelastic behavior on the properties of the extrudate are then studied for extrusions in which the extrudate is prepared under varying amounts of elongational and shear flows.

**MORPHOLOGY, CRYSTALLINITY AND ORIENTATION IN A COPOLYESTER
BASED ON BIPHENOL, TEREPHTHALIC ACID AND
P-HYDROXYBENZOIC ACID**

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Thin plaques of copolyester based on biphenol, terephthalic acid and p-hydroxybenzoic acid were injection molded utilizing edge gating. The plaques were analyzed in the x, y and z directions using wide angle x-ray techniques. Distinctly different layers were apparent. The core was highly crystalline and highly oriented while the skin layer was much less crystalline and oriented. The orientation of the core along the midline and away from the gate was almost precisely perpendicular to the machine direction.

The high crystallinity is of interest since x-ray analyses of fibers indicate random -mer placement along the backbone of the polymer. Thermal analysis and x-ray diffraction at elevated temperatures are also described.

ORIENTATION AND GROSS MORPHOLOGY IN INJECTION MOLDED THERMOTROPIC
LIQUID CRYSTALLINE POLYMERS

BY

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Molding made from thermotropic liquid crystalline polymers display a marked layer (composite-like) structure and "color-bands" in the thickness direction. Both of these gross morphological effects influence the attainable mechanical properties of fabricated parts.

The mechanical consequences of these attributes have been quantified through layer removal studies. In addition, the influence of spreading radial flow in the vicinity of the gate, the fountain flow in the advancing melt front region, converging flow due to the flattening of the melt front and of shear flow on the formation of the layer structure and orientation development during mold filling has been studied.

The effects of the mold and melt temperatures on the gross morphology of molded samples have also been studied, and the influences of the relative proportions of the skin, intermediate and core layers on specific mechanical properties will be described.

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DESIGN AND ANALYSIS OF PROCESSING OPERATIONS TO CONTROL ORIENTATION IN POLYMER LIQUID CRYSTALS

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Kinematic, dynamic and rheological considerations have been used to design and analyze two processing methods for obtaining biaxial orientation in films. For the case of poly(p-Phenylene Terephthalamide) (PPTD) dissolved in H_2SO_4 , the basic steps are extrusion of the liquid crystalline solution through an annular die followed by expansion and elongational flow over a mandrel. For the case of melt processable thermotropic liquid crystalline polymers we have used a counter rotating annular die.

The mandrels used for the PPTD films include conical, hyperbolic and ogival shapes. Molecular orientation as well as mechanical properties were found to be dependent on mandrel shape. Wide angle x-ray diffraction (WAXS) techniques using orientation functions, pole figures and WAXS patterns were used to characterize the films. Mechanical properties as well as the above techniques indicate that a high degree of biaxial orientation can be obtained with a bias in certain film directions dependent on the mandrel used. Tensile strength and Young's modulus values were found to be on the order of 30,000 psi and one million psi respectively. They also can be equally distributed in the film plane dependent on mandrel shape. White - Spruiell orientation factors were as high as 0.49 and 0.5 for f_1^B and f_2^B respectively. There was also an attempt to quantify mandrel design so that one could predict the type of molecular orientation a particular mandrel shape would develop. Thin Shell Theory as well as the mandrel kinematics were used in this analysis.

Melt processing of tubes and films was achieved using an annular die consisting of a rotating inner core and a simultaneously counter- rotating outer cylinder. The inner core and outer cylinder rotation speed was used to vary the flow profile. Nitrogen gas can be fed through the inner core to inflate the tubes and produce thin films. The ratio of the tangential wall shear rate to the axial wall shear rate (R) was varied. The polymer chain axis orientation responds to changes in R . Films and tubes have been produced from hydroxypropyl cellulose (HPC), ethyl cellulose, cellulose acetate butyrate, polyethylene, and polystyrene. Optical birefringence, WAXS, mechanical properties, scanning electron microscopy, and pole figure analysis in conjunction with White-Spruiell biaxial orientation factors were used to evaluate the tubes and films produced. WAXS studies revealed HPC extrudates without die rotation to have White-Spruiell biaxial orientation factors of $f_1^B = 0.80$ and $f_2^B = 0.02$. With $R = 410$, the biaxial orientation factors were $f_1^B = 0.39$ and $f_2^B = 0.60$. Tubes and films with very high levels of biaxial orientation were developed using the described process.

**FLOW BEHAVIOR OF A THERMOTROPIC LIQUID
CRYSTAL AROMATIC COPOLYESTER**

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The rheology of a thermotropic aromatic copolyester, especially the steady shear viscosity, has been studied and found to be very different and more complex than that of analogous conventional isotropic polymers. The viscosity has a power-law dependence on shear rate over a wide range. The temperature dependence is very high below 300° C, and is comparable to that of isotropic polyesters above that temperature. The end correction for capillary viscometry is large, which is normally indicative of high melt elasticity, but nevertheless the extrudate swell is very small. The melt viscosity is shear and temperature history dependent. Unexplained effects that have been observed include a dependence of viscosity upon apparatus gap dimensions.

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RHEOLOGICAL AND RHEO-OPTICAL STUDIES ON A NEMATIC POLYMER SOLUTION

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Rheological and rheo-optical studies on nematic solutions of a rodlike polymer will be described. Behavior at very slow shear deformation in torsion is characterized by a decrease in the ratio M/ω , with M the applied torque and ω the rotational velocity. This is attributed to the effects of a pronounced boundary layer that decreases with increasing ω . Thus, for small ω , only a very thin layer of the fluid is in flow. For ω large enough, M/ω may approach a constant value over a range of ω for which the flow birefringence δn indicates a tendency for molecular orientation. With increasing ω , M/ω decreased and the orientation indicated by $\Delta\eta$ increases. If treated as a viscometric flow, these results indicate a viscosity η_κ that decreases with increasing shear rate κ . On cessation of flow, a complex pattern of disclinations develop, and is observed to gradually rearrange to a decreased number of disclinations, all apparently anchored at a surface boundary. In this process, the flow induced orientation is reduced.

ORIENTATION KINETICS OF THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

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The kinetics of orientation development and relaxation have been studied for two liquid crystalline polymer melts using x-ray diffraction techniques. Samples were oriented in magnetic fields of up to 6.3T for variable times, and allowed to relax for variable times outside the field prior to quenching. Orientation distribution functions were calculated from photon-counting intensity data using rigid-rod models for the liquid crystal molecules.

The samples showed measurable residual orientation from the fabrication process. Total orientation was time-, temperature-, and field strength- dependent; the time and temperature dependence could not be resolved in earlier experiments using diffraction patterns recorded on film. The orientation process appears to consist of an elastic deformation of an orientable entity (a domain) relative to its neighbors, followed by viscous flow. Relaxation initiated at time scales that are short relative to the viscous flow process appears to be elastic, while relaxation over longer time scales appears to be a Brownian process.

CELLULOSE DISSOLUTION, LIQUID CRYSTAL FORMATION
AND FIBER FORMATION IN AMMONIA/AMMONIUM
THIOCYANATE SOLUTION

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Cellulose dissolves in the solvent ammonia/ammonium thiocyanate ($\text{NH}_3/\text{NH}_4\text{SCN}$) to form isotropic and anisotropic solutions depending upon the polymer concentration. The cellulose solutions are being characterized by several methods including viscometry, ^{13}C NMR and light scattering. Isotropic solutions have been wet spun to produce conventional type cellulosic fibers.

Major emphasis is now being directed to the anisotropic (liquid crystal) solutions. These solutions are also being characterized. Both the cholesteric phase and what is believed to be the preferred nematic phase can be formed by proper control of certain parameters. Preliminary experiments indicate that fibers can be formed from either of the phase types. But, fibers from the presumed nematic phase, from first indications, seem to be the most interesting. Both wet and dry jet-wet spun extrusion techniques are being studied.

It is believed that this solvent system will provide much useful scientific information about cellulose. Of great significance is the potential for replacing the viscose process, which is multi-stepped, polluting and expensive. It may be possible to prepare a new family of cellulosic fibers varying in properties from rayon-like to Kevlar^R types. This opens new end uses and markets for a cellulose-based fiber. Cellulosic fibers could be used in conventional fabrics, in heavy duty industrial type usage, body armor, etc.

**GEL DRAWN HIGH MODULUS FIBERS
OF POLY(VINYL ALCOHOL)**

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Formation of a dilute solution and quenching to a gel, followed by drawing the gel has been a successful route for obtaining high modulus, high strength fibers. Polyethylene gel drawn fibers have been the most studied, and the first to become commercially available. In principal any linear polymer may benefit from gel processing, as it depends on its effect on the network of physical entanglements which is always present. Several materials have been processed to give high modulus fibers or tapes. We have investigated gels of medium molecular weight poly(vinyl alcohol), drawn isothermally and in a zone heating device. High draw ratios and reasonably high modulus can be obtained, but the mechanical properties of the material are strongly sensitive to water. Absorbed water softens the fiber and reduces its maximum use temperature.

A NEW MODEL FOR THE HIGH MODULUS AND STRENGTH PERFORMANCE OF ULTRA DRAWN POLYETHYLENES

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Many structural models have been proposed to explain the remarkable enhancement of the mechanical properties of drawn polyethylenes under uniaxial flow conditions. These models show that the enhancement of the tensile properties with draw ratio depends on the development of crystal continuity, crystalline bridges or taut tie molecules which connect crystallites longitudinally. Whereas the analytical techniques used for the characterization of the highly drawn polymers provide satisfactory correlation between the degree of chain extension and orientation for the drawn polyethylenes of low draw rates i.e. $DR < 30-40$, they do not provide adequate information for the relation of the tensile properties and the molecular organization at $DR \gg 30$. Thus, the structural models proposed hitherto cannot predict the mechanical performance of the superdrawn states and account for the disparity between the experimentally determined and the theoretically calculated tensile modulus and strength values. In this presentation we discuss the development of a morphological model which is based on the description of the tensile modulus and strength as a function of the macro-fibrillar dimensions (aspect ratio) of fibrillar ultra-high molecular weight polyethylene structures which were obtained by extrusion and drawing compacted single crystal mats to draw ratios up to and above 200. The model assumes the existence of crystalline continuity, taut-tie molecules and crystalline connections within the micro and macro-fibrils and concentrates on the load transfer mechanism between adjacent macro-fibrils. It appears that the tensile modulus is more sensitive to the fraction of the intra-fibrillar connections whereas the tensile strength is sensitive to the fraction of the inter-fibrillar connections between adjacent macro-fibrils. According to this model, the highest tensile modulus and strength values that can be obtained are 212 GPa and 13.3 GPa i.e. significantly close to the theoretically calculated values.

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