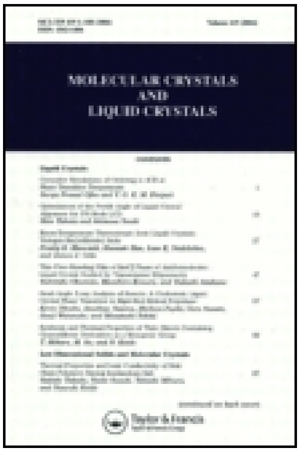

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Introduction to The Symposium on Order in Polymeric Materials

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INTRODUCTION TO THE SYMPOSIUM ON ORDER IN POLYMERIC MATERIALS

In the early stages of our studies[1,2] of the potential use of conjugated polymers as active elements for electronic and optical applications, it was readily apparent that structural order was a dominant consideration. Moreover, it also appeared likely that the ability to control crystallographic order would be of continued importance as research in these relatively new areas evolved. We were also cognizant of increasing activity in polymeric materials with liquid crystalline order, a more macroscopic situation. Hence, we felt that a short symposium, built around the theme of order, both microscopic and macroscopic, would provide a useful summary of the state-of-the-art of the several topics and might also serve as a stimulus for further investigations.

The specific topics selected for the symposium were solid state polymerization and the properties of materials derived from such processes, the physics and chemistry of polymer liquid crystals and related ordered materials, and the chemistry, electrochemistry, structure, and experimental and theoretical physics of conducting polymers. This article briefly introduces these topics and some highlights of their development to date.

X-ray diffraction in polymers dates to the observations reported in 1921 by Polanyi in naturally occurring fibers.[3a] While the modern study of polymers via electron diffraction dates from 1957,[4] electron diffraction in high polymers was reported as early as 1938.[3b]

SOLID STATE POLYMERIZATION

Solid state polymerization[5] provides the most convenient approach to highly ordered macroscopic polymer crystals.

Such studies date to gas-solid formaldehyde-trioxane reaction reported by Kohlschutter in 1930. The availability of high energy radiation sources stimulated investigation of the reactivity of crystalline monomers, and Schmitz and Lawson (1951) reported the study of ethyleneglycol dimethacrylate with an electron beam. Three-dimensional oriented chain growth was observed in the condensation polymerization of 6-aminohexanoic acid by Morawetz and coworkers in 1964.[6]

G.M.J. Schmidt's topochemical principle,[7] a structural concept which notes that groups undergoing reaction in the solid state ought to be in close (≤4.0Å) proximity, merges with solid state polymerization in the extensive studies of the reactions of conjugated diacetylenes ($RCH_2C{\equiv}C{-}C{\equiv}CCH_2R$) by G. Wegner and collaborators beginning in 1969.[5c,8] A prototype example is the lattice controlled polymerization of the bis-p-toluenesulfonate of 2,4-hexadiyne (PTS). The solid state polymerization of diacetylenes, by now investigated in many laboratories throughout the world,[9] allows synthesis of fully ordered macroscopic polymer single crystals with conjugated backbones. The diacetylene polymerization is amenable to mechanistic study, and this process, initiated by assorted types of radiation as well as thermally, has been widely studied for details of the initiating and propagating species. Numerous studies of the crystal and molecular structure of both monomers and polymers are available. The intense color associated with the conjugated backbone naturally stimulated interest in the spectral and other physical properties. The low energy spectral feature found in PTS polymer and others as well has been described as a charge-transfer exciton.[10] There has been substantial interest in high coefficients for both second[11] and third order[12] nonlinear optical processes. The latter may have subpicosecond response times with potential utility in optical communications. Electronic carrier mobilities comparable to silicon or gallium arsenide have also been reported.[13] Certain polydiacetylenes are also useful as time-temperature indicators and are under development for this purpose.[14]

Interest in the crystalline polymer derived from S_2N_2, that is poly(sulfur nitride), was stimulated by M.M. Labes and coworkers who have given a comprehensive review.[15] This polymer not only has the electrical properties of a metal but also provided, via the work of R.L. Greene and G.B. Street in 1975, the first example of a superconductor which lacked a metal atom. The details of the solid state polymerization were reported by MacDiarmid, Garito, and Heeger in 1976.

B.M. Foxman and collaborators have extensively studied the polymerization of nickel (cyanoethylphosphine) dihalide complexes and found the reaction characterized by product specificity, stereospecificity, and crystallographic specificity.[16] They have subsequently initiated studies of the solid state reactivity of vinyl and acetylenic monomers using metal carboxylates to orient the reactive moieties.[17]

Simultaneous polymerization and crystallization[5c,18] is another approach to macroscopic, defect-free single crystals of macromolecules. Recent examples include a preparative method for mixed metal coordination polymers[19] and the preparation of a polymer containing both polydiacetylene and polyacetylene moieties from a monomer produced by oxidative dimerization of 1,11-dodecadiyne.[20] Also, M. Hanack and coworkers have reacted hemiporphyrazine with iron (II) acetate in nitrobenzene to obtain single crystals of an oxygen bridged polymer with iron in a +4 oxidation state.[21]

Scheme 1 sketches a summary of the development of highly crystalline polymers, and a recent conference proceedings[22] details many current problems related to this topic.

CONDUCTING POLYMERS

Polymers with significant dark conductivity have attracted substantial attention for over two decades. The electrical properties of poly(sulfur nitride), noted in the previous section,[15] were initially reported by Labes and coworkers in 1962. The activities of the 1960s, which include study of polyacetylene $(CH)_x$, in various forms, the use of charge transfer oxidants to render poly-p-phenylene $(C_6H_4)_x$ conductive, and observation of structural order in TCNQ salts of polymeric cations, have been summarized in a book.[23]

The considerable current interest was stimulated by the availability of a partially crystalline $(CH)_x$ film, prepared in 1971 by Shirakawa and Ikeda using Ziegler-Natta chemistry, and which may be isolated as either *cis* or *trans* forms, to take up both charge-transfer oxidizing and reducing reagents, commonly termed "dopants." Such doping, reported in 1977 by Shirakawa, MacDiarmid, and Heeger, gives materials with

SOLID STATE POLYMERIZATION AND ITS CHEMICAL AND PHYSICAL CONSEQUENCES

DIFFRACTION IN POLYMERS
- X-Ray (1921)
- Electron (1957)

SOLID STATE POLYMERIZATION

Trioxane, Kohlschutter (1930)
Ethyleneglycol Dimethacrylate, Schmitz and Lawton (1951)
6-Aminohexanoic Acid, Morawetz (1964)

TOPOCHEMISTRY

G.M.J. Schmidt (1964)

DIACETYLENE POLYMERIZATION
G. Wegner (1969)
- Structural Studies, V. Enkelmann
- Mechanisms of Polymerization
- Nonlinear Optics (1976)
- Charge Transfer Excitons, Philpott
- High Carrier Mobility, E.G. Wilson (1979)
- Time-Temperature Indicators (Allied Corp.)

REACTIVITY AND POLYMERIZATION OF OTHER CONJUGATED SYSTEMS

Sulfur Nitride, $(SN)_x$ Labes (1962, 1973); MacDiarmid, Garito, Heeger (1975); Street, Greene (1975)
Ni $(CEP)_2X_2$, B.M. Foxman (1977)
Crystalline Acetylenes

Scheme 1

metal-like conductivity over a significant temperature range. The doping process may also be accomplished electrochemically and this has led to the investigation of such materials for battery applications.

Conformational excitation in trans-$(CH)_x$, termed solitons, were initially discussed theoretically by Pople and Walmsley in 1962. Further theoretical treatment, including real time dynamics, has been given by Su, Schrieffer, and Heeger, and there is considerable experimental and theoretical interest in the role of solitons in the electronic structure and doping of trans-$(CH)_x$. Several review articles summarize the extensive studies of Heeger, MacDiarmid, and coworkers.[24]

Much attention has also been paid to the issue of crystal structure and morphology in both pristine and doped $(CH)_x$.[24,25,26] The sensitivity of both pristine and doped $(CH)_x$ to air and moisture has stimulated substantial interest in extending the useful lifetime of the material. Preparation and characterization of blends of $(CH)_x$ with polyethylene[27] and polybutadiene[28] has been one approach in the quest for both long term stability and processability.

The interest in the properties and potential applications of $(CH)_x$ naturally stimulated investigations of other conjugated polymers, and major new work in $(C_6H_4)_x$ as well as the processible poly-p-phenylene sulfide has appeared.[25,26] Anodic electropolymerization of pyrrole, thiophene, and other electron rich molecules has also proved a useful approach to conductive polymeric materials.[25,26,29] Polymeric metal macrocycles, prototype phthalocyanine, including both transition[30] and main group[31] elements, provide additional classes of conducting polymers, including an example of a cyano bridged material which is conductive as synthesized.[30]

Details of problems of current interest are given in recent conference proceedings.[22,32,33]

POLYMER LIQUID CRYSTALS AND MACROSCOPIC ORDER

The first example of liquid crystalline order in macromolecular materials was provided by nature; studies of the rod-like tobacco mosaic virus were reported before 1940. Several polymers with aromatic groups, such as poly(γ-benzyl-L-glutamate), poly(1,4-phenyleneterephthalamide) (Kevlar), and the polyesters of p-hydroxybenzoic acid[34] (Ekonol) and its copolymers, have stiff chain structures which impart outstanding mechanical properties to the materials. For example, Kevlar, with a density of less than twenty per cent that of steel, has a tensile modulus comparable to steel. The literature of the chemical and physical properties of these materials is available in readily accessible books[35-37] and review articles.[38,39]

Theoretical interest in the nematic-isotropic transition stems from L. Onsager's approach (1949) involving repulsive interactions of a gas of impenetrable rods and P. Flory's extension (1956) of the lattice model of solutions of flexible chains to rigid rods. More recent work done by de Gennes and Pincus[40] using a mean field approximation predicts a first order phase transition from a nearly coiled to nearly rigid conformation accompanied by simultaneous development of long range nematic order.

There is considerable experimental and theoretical interest at present in long range correlations in the 10Å-10^4Å range.[41] Polyelectrolytes and monodisperse polymer (e.g., polystyrene and polyacrylates) latices provide examples of such systems.[42] First produced in 1947, the colloidal latices exhibit diffraction phenomena with visible light. Problems of current interest include the role of solvent dielectric constant in the interactions among the charged colloids and the study of phase transitions as a function of density and coulomb screening length.[43]

ORDERED POLYMERS IN MONOLAYERS AND MULTILAYERS

While the polymerization of surface active monomers oriented at a gas-water interface is a variant of solid state polymerization, there is a sufficient interest in this relatively recent[44] development to warrant separate treatment. Two volumes of the journal Thin Solid Films give an overview of current activities in monolayers and multilayers produced by Langmuir-Blodgett techniques.[45] Applications of these layers could be in integrated optics, as barrier layers in Josephson tunnel junctions, as electron beam resists, and in derivatized electrodes.

Polydiacetylenes have been prepared as monolayers and multilayers.[5c,8] Values of the third order nonlinear susceptibility $\{\chi^{(3)}\}$ comparable to those reported in single crystals of PTS[12] have been deduced from intensity-dependent index of refraction measurements in a 5000Å multilayer of a polydiacetylene, and a large resonant enhancement of $\chi^{(3)}$ was also observed.[46]

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