ADVANCED MATERIALS

towards understanding the principles and dependency of the process. An ideal process would use inexpensively produced, gas atomized, fine and small sized powders of about 10 μm diameter with a compatible multicomponent binder system which provides a mild decomposition at relatively low debinding temperatures. Debinding, presintering and consolidation of injection molded parts in a Sinter-HIP furnace offers the possibility of a one step heat treatment which avoids handling of the debinded parts. Full density can be achieved by pressure assisted final stage HIP. In the USA, a multimillion dollar project, part of the Advanced Powder Processing program at Rensselaer Polytechnic Institute, is the beginning of a move from empirically based process development to a systematic development of the theoretical background.

The basic elegance and simplicity of the injection molding process must not lead to the assumption that fully dense parts of predictable final dimensions are produceable as easily as in plastic injection molding. Up to now the main problems arise after the actual molding, during debinding and sintering. Only complete control over all process parameters will result in high quality reproducable parts.

Macromolecular Physics in Lodz

By Hugh J. Byrne*

To the French Cistercians who founded the Abbey in Sulejow Lodz, Poland, the terms charge transport and activation energy had little meaning, and seldom were they to be seen meandering through the grounds digesting the importance of bipolarons and multiphoton resonances. However, for one week in September, the serenity of this decaying 12th century house of learning was disturbed as it played host to the 21st Euro-Physics Conference on Macromolecular Physics, held from 4–8 September.

The conference was focused on the topic of "Electrically and Optically Active Polymers", a field which has attracted the expertise of a diverse range of scientists including polymer and solid-state physicists as well as physical and synthetic chemists. Interest in these materials was generated by the discovery that it was possible to make thin films of polyacetylene, and was increased by the subsequent discovery that the conductivity of this material could be increased to metallic values by chemical doping. Since then, a great deal of activity has produced a large range of processible organic polymers whose properties have been studied. Of similar interest to the electrical properties of these materials are the optical and, in particular, the nonlinear optical properties. The highly delocalized π-electron backbone of these polymers should give rise to large nonlinear susceptibilities which may render these materials a possible alternative to inorganic materials in the developing fields of all-optical switching and signal processing. This conference was designed to review the progress and problems of understanding the nature and origins of these materials properties.

The key-note address was delivered by the conference chairman, *Prof. M. Kryszevski*, from the Polymer Institute of the Technical University of Lodz, who outlined the objectives of the conference. Particular importance was attributed to the necessity for a greater understanding of the dependence of the electrical and optical properties of these materials on their structure and morphology. In a field where the range of materials available is ever increasing and where the polymer morphology may vary from that of single crystal to that of solution, an understanding of this structure-properties relationship is as important as understanding the microscopic molecular properties. Indeed, the problems facing "homo polymerius" were effectively portrayed by *V. Enkelmann* from Mainz, FRG. In his presentation he described the number of possible inter and intra chain effects contributing to a bulk measurement of any polymer parameter. He stressed the need to control the macroscopic conductivity by means of molecular parameters. The approach taken was to move towards single crystal materials in which interchain hopping is controlled by the size of the molecular structure. In polythiophene and polyparaphenylene, substitution was employed to systematically control the interchain distance by steric effects. The temperature dependence of the conductivity was found to increase as the size of the substituent increased, indicating an increasing activation energy although the conductivity itself decreased. The transition from the dominance of interchain effects to that of intrachain effects was thus shown, and an empirical relationship between the activation energy and the interchain parameter was presented. A similarly strong correlation between the

---

[*] Prof. H. J. Byrne
Department of Pure and Applied Physics
Trinity College
Dublin 2 (Ireland)

structural and electronic properties of these systems was evident in the presentation of *P. Bernier* from Montpelier, France. NMR and ESR studies of the doping process of polyacetylene appear to confirm the stage-like nature of this process indicative of a step-wise restructuring of the material with increasing dopant concentration. They also reported that a new, dilute phase was identified. This correlation was highlighted by the work of *M. Stolka* et al. from Xerox in New York in which the charge transport in Si and Ge backbone polymers was studied over a wide range of temperatures, encompassing the glass transition temperature. At the glass transition temperature the activation energy of transport abruptly decreases to very low values, raising the comment from *H. Bässler* from Marburg, FRG, that transport in these materials is controlled by disorder.

The importance and nature of interchain transport mechanisms were outlined by *A. A. Zakhidov* of Tashkent, USSR and the stabilization of solitons, polarons, and bipolarons by interchain coupling effects between neighboring polyacetylene chains was proposed. This stabilization leads to the possibility of interchain optical transitions, influencing the nature of the photoinduced absorption spectrum.

In terms of electrical conductivity, the most promising material at the present time is the so-called Naarmann polyacetylene. The question as to why this particular form of polyacetylene (and indeed, only some samples within a batch) shows such high conductivities ($\sim 10^5\ \mathrm{S\,cm^{-1}}$) was addressed by Dr. *T. Schimmel* of Bayreuth, FRG. The anisotropy of the conductivity was found to be ~ 50 but temperature independent, indicating a common limiting mechanism in both directions. This dependence was reported to fit best to the model of *Sheng* describing large, highly conducting regions separated by small gaps, with the rate of gap hopping being proportional to temperature. These barriers contribute to only 30–40% of any sample resistance and do not vary much between high and low conductivity samples. Transport is therefore deemed to be limited by the resistance of the high conductivity regions. As yet, however, the recipe for these highly conducting regions appears to be empirical.

The importance of new materials exhibiting new properties and of new processing techniques was also stressed in the key note address. The influence of the structural properties of poly(vinylidene fluoride) which has a strong piezoelectric activity, on the macroscopic polarization was discussed by *D. Geiss* from Taltow, GDR. It was demonstrated that even poorly crystalline polymers such as dye-doped poly(methylmethacrylate) can exhibit a significant piezoelectric activity upon poling. Polymer blends of poly(3-alkylthiophenes) were shown to exhibit improved mechanical properties by Dr. *V. Laakso* of Porvoo, Finland, whereas the soluble forms of polyacetylene described by *J. P. Pfleger* from Prague, Czechoslovakia, provided good optical quality materials for nonlinear optical measurements. In samples of poly(bis-alkylthio-acetylene) a dramatic increase of conductivity was observed by *H. K. Roth* from Leipzig, GDR, upon laser treatment. This increase is associated with a color change from red to blue-black and a loss of solubility, and the process appears to be similar to polymer doping. The advantages of this technique over doping is the high spatial resolution available by using small laser focal diameters.

Investigation of the nonlinear optical properties of organic conjugated polymers is a field of research equally as active as that of their electrical properties, and already device applications have become realistic. Exploiting the large second order polarizability of poled organic polymers, guided wave structures may be made which act as phase and intensity modulators. A 2X2 electro-optic switch has been realized, as reported by *G. Mohlmann* from Akzo in the Netherlands. Waveguide losses are as low as, or lower than, $1\ \mathrm{dB\,cm^{-1}}$, and further development should produce devices competitive with rival lithium niobate structures.

The second order nonlinearities utilized in these devices are not, however, intrinsic to the polymer backbone and exploitation of such an intrinsic nonlinearity for device applications appears to be further from realization. Highly conjugated polymers have been predicted to possess a large ultrafast nonlinearity which should be real in nature. Investigations of the nature of this nonlinearity using the technique of third harmonic generation were carried out by *F. Kajzar* of Saclay, France and also by *D. Neher* from Mainz. In the latter case, the materials studied were substituted polyphenyl acetylenes and poly(3-decylthiophenes) whereas in the former, they were poly(thienylthiophene) and poly(dithienyl benzene). In all cases a strong resonant enhancement of the process was observed. The influence of such multiphoton resonances on the degenerate four wave mixing signals at 1.064 μm in a range of polymers was discussed by *H. J. Byrne*, from Dublin, Ireland. In the case of poly(3-butyl thiophene) a strong three photon enhancement was observed, whereas in the much studied polyacetylenes poly 3 and 4 (BCMU) a two photon enhancement was observed. In poly(anthracene phenylenine) however, the nonlinearity is purely third order although a large imaginary contribution is measured. It appears therefore that in all cases, the nonlinearity is dominated by imaginary contributions, and it was suggested by *Byrne* that this represents an inherent limit to the material polarizability since all resonances in these materials are localized by virtue of the strong excitation-lattice coupling. The ultrafast nature of the nonlinearities in polyacetylene/poly methylmethacrylate copolymers was demonstrated by *Pfleger*, who also showed the detrimental effect of doping on the polymer nonlinearity. This observation highlights the divergence of the disciplines of electrically active and (nonlinear) optically active polymers.

As the intensity of research increases in this area, the number of realistic applications increases. As previously mentioned, electrooptic switching devices based on poled polymers are already approaching the standards set by their rival lithium niobate based devices. The strong mechanical properties of *Laakso*'s poly(3-alkyl thiophene) blends make them good materials for antistatic packaging. An impressive piece of precision work with a wide range of applications was presented by *J. Kikas* from Estonia. Spectral hole burning of dyes in polymer matrices produces holes with a spectral width as low as 10^{-2}–10^{-3} cm^{-1}. With this resolution, up to 10^3 holes may be burned per inhomogeneous band. The listed applications of such hole burning techniques included frequency selective optical memory, space and time domain holography, and the materials may be used as narrow band optical filters. Application of an external electric field gives rise to stark shifting of the holes, an effect which may be exploited as an optical modulator.

Within one week it is only possible to cover a small portion of the current developments in this expanding field. Presented above is merely a cross-section of the week, but a number of issues were, however, highlighted. Firstly, whereas the nature of the optical and nonlinear optical properties of conjugated polymers are still considered to be primarily determined by interchain effects, the material structure and morphology appears to be critical for the electrical properties. This structure-properties relationship was discussed at length, resulting in the recognition of the need for well defined structures, and systematic studies. In such a way, understanding and enhancement of electrical properties may be achieved through manipulation of material structure. On the other hand, in the case of the nonlinear optical properties of conjugated polymers, the suggestion of an intrinsic molecular limit to the magnitude of the response infers the need for further systematic studies on well defined molecular structures. The division between the two fields of research is highlighted by the fact that good electrical properties require material doping, a process which as a devastating effect on the nonlinear optical properties.

Despite the continuing complexity of both areas, progress towards an understanding of the dominant physical processes involved is being made. The resulting feeling of optimism was reflected in the atmosphere of a conference designed as an exchange between Eastern and Western Europe, held in a country in transition from one political idealogy to the other. Amidst this political, economic, and scientific complexity, the conference was a success.

Surface Modification Technology in Neuchâtel

By Peter K. Bachmann [*]

The "Third International Conference on Surface Modification Technologies" (SMT III) was held from 28 August–1 September in Neuchâtel, Switzerland. After Phoenix, Arizona and Chicago, Illinois, SMT III was the first of this series of conferences to take place outside the United States of America.

Neuchâtel, beautifully located at the foot of Mount Chaumont and at the shore of Lake Neuchâtel was chosen because it is also the home of the University of Neuchâtel and of CSEM, the Centre Suisse d'Electronique et de Microtechnique S.A., a private, non-profit R&D organization active in the fields of microelectronics, optoelectronics, sensors, micromechanics and material science. CSEM and TSM jointly organized and sponsored SMT III along with many other Swiss scientific societies, Swiss government agencies and the University of Neuchâtel, which provided the rooms and the infrastructure for the conference.

The objective of the "Surface Modification Technologies" conference series is to bring together physicists, chemists, metallurgists, manufacturing engineers, and other materials scientists from around the world to interact and utilize each other's capabilities in the cross pollination of ideas, and, indeed, 82 contributions from 20 different countries including Europe, Asia, Australia and North America are listed in the technical program. Quite interestingly for a conference held in Europe, the USA with 22 papers outnumbered Switzerland with 13 and West Germany with 10 contributions. Japan, on the other hand, had only two entries.

The sessions offered to an audience of approximately 160 participants included ● Diamond and Related Coatings, ● Characterization of Coatings, ● Physical Vapor Deposition, ● Chemical Vapor Deposition, ● Laser Alloying, ● Alternate Coating techniques, ● Laser Surface Treatment, ● Coatings for Space Applications, ● Ion Implantation, ● Electroplating, ● High Temperature Coatings, and were accompanied by an additional half-day poster session.

1. Wear and Corrosion Resistance

Similar to other coating oriented conferences, SMT III illustrated that many practical applications of modified surfaces are related to improved wear resistance or increased

---

[*] Dr. P. K. Bachmann
Philips Research Laboratories
P. O. Box 1980, D-5100 Aachen (FRG)