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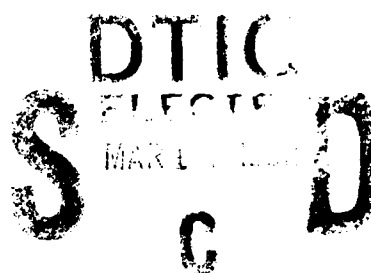
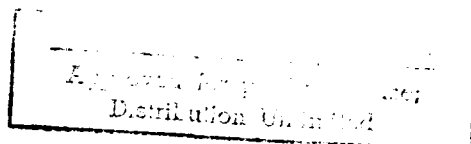


EOARD LR-90-070

PROCEEDINGS
of the
3rd OGAMM MEETING

4-7 SEPTEMBER 1990

KESWICK - ON - DERWENTWATER
CUMBRIA, ENGLAND



LIAISON REPORT

LT. COL. C. DYMEK

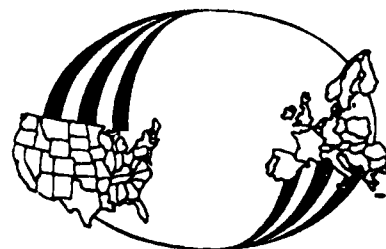
DR. V. DONLAN

Air Force Office of Scientific Research

EUROPEAN OFFICE OF AEROSPACE

RESEARCH AND DEVELOPMENT

92-07043



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**PROCEEDINGS OF THE 1990 OPTICAL GLASS AND
MACROMOLECULAR MATERIALS (OGAMM) MEETING**

by

Lt Col C. J. Dymek and Dr. V. L. Donlan

4-7 September 1990

ABSTRACT

The 1990 OGAMM Meeting was held at the Keswick Hotel in Keswick-on-Derwentwater, England from 4 to 7 September 1990. The OGAMM program is a highly collaborative multidisciplinary effort of about 20 US and European groups. It is designed to provide the technology base needed for the development of devices based on multifunctional materials. Because these devices are generally aimed at imaging, detecting, photonics, tracking, and communications systems, there is a strong emphasis on combining various nonlinear optical, electrical, thermal and mechanical properties. Reported advances in the ability to form reproducible pure samples of OGAMM materials, in theoretical modeling of their properties and behavior, and in refinement of techniques for measuring a range of properties have led to greater quantification in the understanding of these materials and their behavior. A world leading capability to characterize optical, electro-optical, and NLO properties/materials has been developed within the group and has become readily accessible to all participants in the OGAMM program.



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THE 1990 OPTICAL GLASS AND MACROMOLECULAR MATERIALS
(OGAMM) MEETING - AN OVERVIEW

by

Lt Col C. J. Dymek and Dr. V. L. Donlan

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

EUROPEAN OFFICE OF AEROSPACE
RESEARCH AND DEVELOPMENT

INTRODUCTION

The 1990 OGAMM Meeting was held at the Keswick Hotel in Keswick-on-Derwentwater, England from 4 to 7 September 1990. The OGAMM program is a highly collaborative multidisciplinary effort designed to provide the technology base needed for the development of devices based on multifunctional materials. Such a material - whether a glass, ceramic, polymer, or a composite containing them - can ideally be designed so that it possesses several properties which make it useful for the highly sophisticated devices needed for advanced SDI systems. Because these devices are generally aimed at imaging, detecting, photonics, tracking, and communications systems, there is a strong emphasis on combining various nonlinear optical, electrical, thermal and mechanical properties.

Dr. Don Ulrich, AFOSR/NC, provides the program management and inspired technical leadership which has made OGAMM a model for a successful collaborative effort on the cutting edge of technology. The importance of Dr. Ulrich's ability to get talented people to work together was particularly evident at this OGAMM review. Because of illness, he was unable to attend this meeting. The momentum he previously provided to this effort in the form of clear technical goals and quality of organization allowed this very important annual collaborative meeting to, in effect, run itself. The logistics requirements

were very nicely taken care of by Mr. George Gallagher-Daggitt from the SDI Participation Office at the UK MOD.

Funding for OGAMM comes primarily from the Innovative Science and Technology (IST) office of the SDI Organization. AFOSR/NC also provides some support to the program - about 10% of the IST total. A number of the grants in the OGAMM program have ended in FY90. Because of the high degree of interdependence among the participants in OGAMM and the clear benefits that have come from collaborative efforts, there was a strong sense of urgency that all elements in the program continue at the same or higher funding levels to maintain the excellent progress towards the technical goals. In this overview of the OGAMM program status, we will describe the current organizational and technical structures based on inputs we received at the meeting. These clearly reflect Dr. Ulrich's original concept of multifunctional materials development. We will also present the consensus view of the key technical issues and important recent achievements. Following the overview we give the summaries, provided by the six prime contractors, of the status in their respective areas, along with extended abstracts of each of the papers on the research efforts.

STRUCTURE OF OGAMM

The organizational structure of OGAMM is shown in Figure 1. The six prime contractors from the US, who receive the bulk of the IST funds, are listed in solid blocks. The general areas in which they work are indicated by the labels in the dashed blocks. Four of the primes have subcontractors from Europe and Japan.

The technical structure of the program is indicated in Figure 2. This gives a listing of key words which can be considered to characterize the phases in the progress from new materials ideas to device demonstrations. The starting point in the process is the production of interesting new materials. "Molecular engineering" of polymers and sol-gel processing of silica glass have been the most highly visible activities at this stage. Once new materials are identified and created, the various electrical and optical properties expected

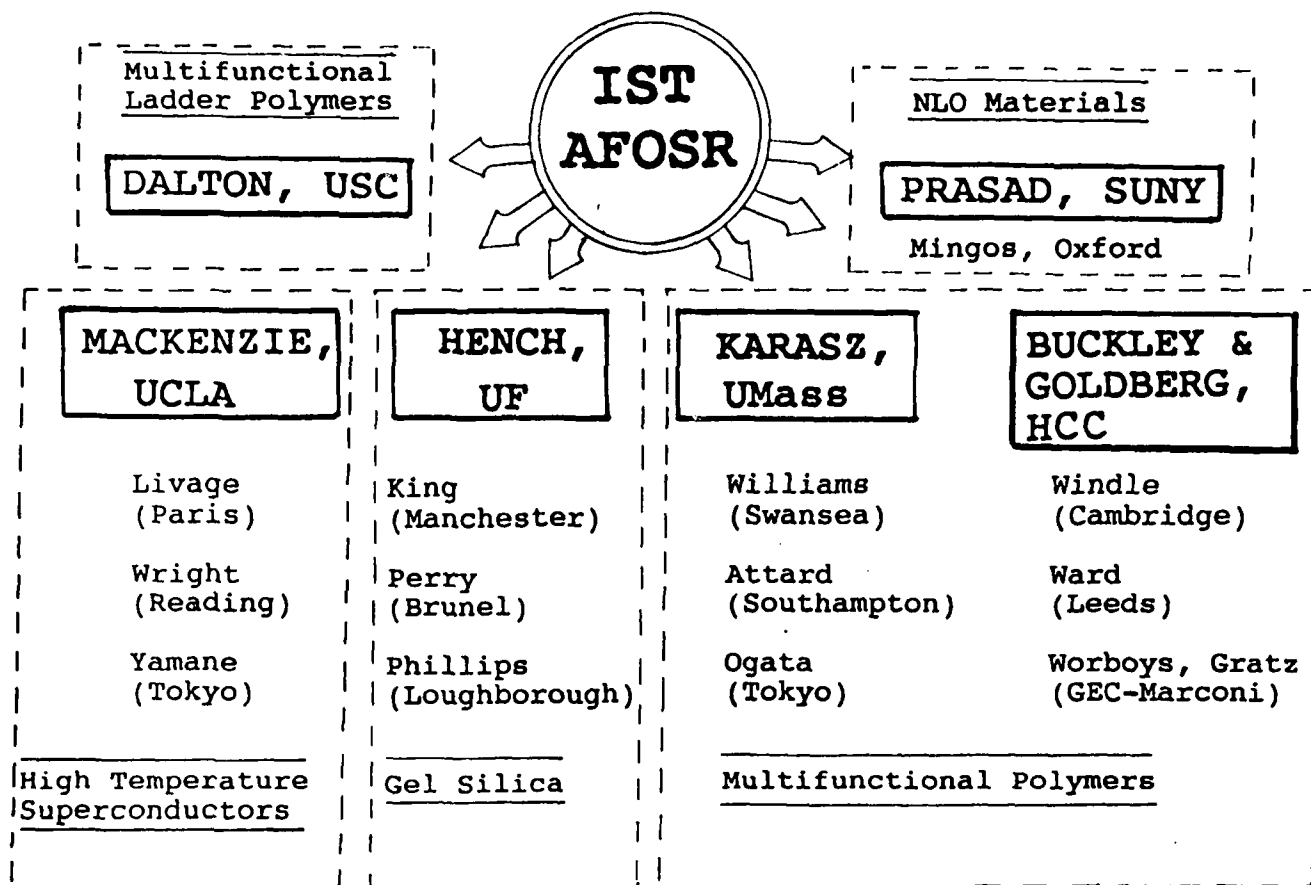


Figure 1.

OGAMM KEY WORDS

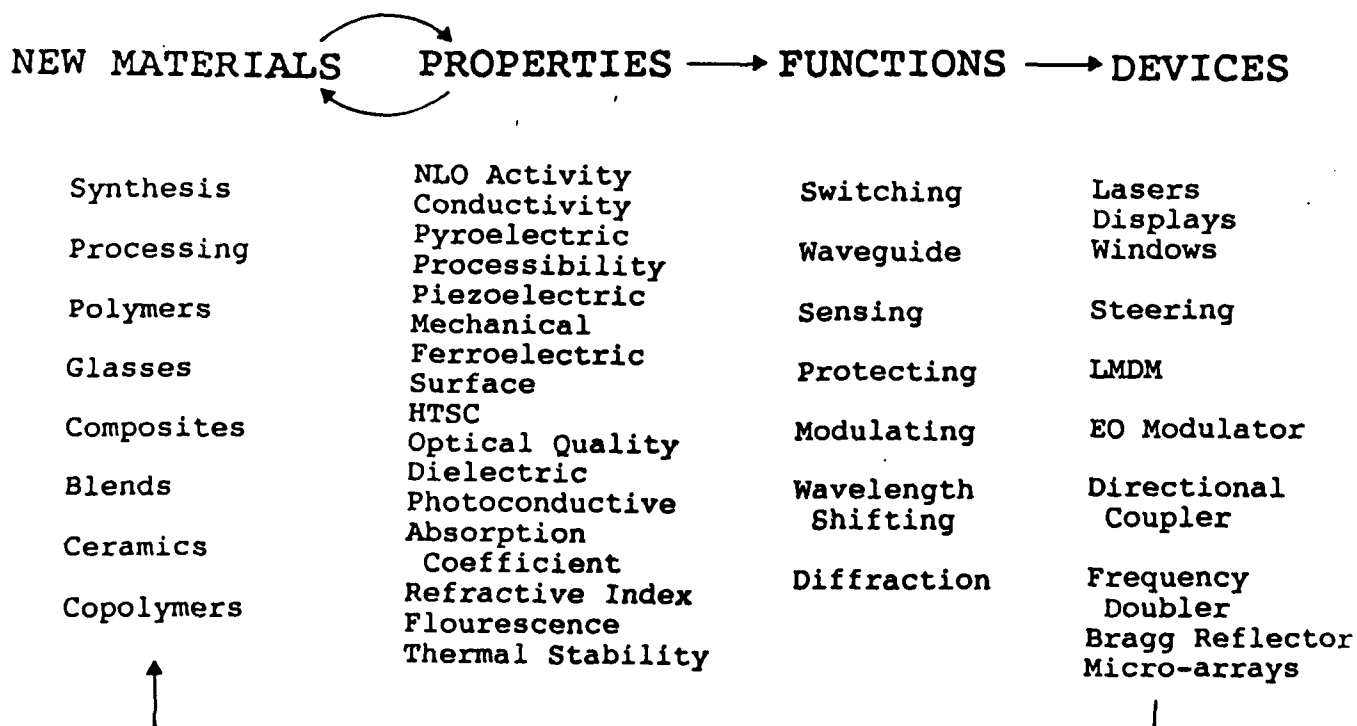


Figure 2.

for them are measured, and a range of other key aspects such as thermal stability and processability are evaluated. As the reverse arrow suggests, information about the properties can be used to suggest modifications to the materials' chemistry or processing. Next, the behavior of systems with interesting properties is studied to determine for which functions the material may be suitable. Finally, the materials with suitable functionality or, preferably, multifunctionality are incorporated into laboratory devices to evaluate their performance. These tested device concepts, along with the multifunctional materials used in them, represent the end products of the OGAMM program. However, as the dashed "feedback arrow" indicates, the test devices also represent stimuli for new material developments by magnifying both the defects and special qualities of the materials incorporated into them.

To go from basic research ideas to tested device concepts over the range of materials, properties, functions, and devices shown in Figure 2 might be considered overly ambitious at the present level of funding. However, some of the devices, indicated by circles, have already advanced well into the demonstration phase. Furthermore, unexpected combinations of polymer and gel silica materials have risen out of the cross fertilization which Dr. Ulrich built into this program. Other factors enhancing the productivity of OGAMM include close collaboration between workers with strong industry instincts (Hoechst Celanese, GEC, and Geltech) and those workers at universities whose reputations are built on good science.

PROGRAM ACHIEVEMENTS IN FY90

There are four achievements of the OGAMM group as a whole:

1. A combination of the ability to form reproducible pure samples of OGAMM materials, advances in theoretical modeling of their properties and behavior, and refinement of techniques for measuring a range of properties has led to much higher level of quantification in the understanding of these materials and their behavior.

2. In-depth interactions between organic and inorganic chemistry groups have resulted in better understanding of the fundamental chemistry of both classes of materials.

3. A world leading capability to characterize optical, electro-optical, and NLO properties/materials has been developed within the group and has become readily accessible to all participants in the OGAMM program.

4. The interaction of industry and university scientists provides a built-in mechanism for technology transfer and for commercialization. For example, all the gel silica samples used in the OGAMM program are commercially available from Geltech, and Hoechst-Celanese provides the basic polymer precursors. The strong technology transfer flavor of the program is also reflected in the number of patents that have been generated in the OGAMM effort to date.

There were also a number of accomplishments of major program goals of the prime contractors:

1. Demonstration of a dye laser in a gel silica matrix with properties superior to those of liquid systems. (Hench, King)

2. Demonstration of a designed multifunctional copolymer with oxynitro-stilbene and vinylidene cyanide side chains providing electro-optic and piezoelectric functions, respectively. (Buckley, Goldberg)

3. Development of a high $X^{(3)}$ NLO composite (10^{-9} esu) of gel silica and polyphenylenevinylene with high optical quality as well as thermal stability and mechanical strength. (Karasz, Prasad)

4. Development of the first processable metallated ladder polymer with useful levels of both $X^{(2)}$ and $X^{(3)}$ NLO activity and built in spectral flexibility (their NLO and optical spectra can be "tailored" by side chain modification). (Dalton)

5. Fabrication of tapes and fibers of high temperature superconducting materials from sol-gel processed $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$. (Mackenzie)

6. Development of a new class of frequency doubling materials based on two-component crystalline complexes. (Prasad)

KEY ISSUES

In a planning session during this OGAMM meeting, the prime contractors expressed their views on what the key issues are for this collaborative effort:

1. There is growing evidence that the surfaces in gel silica samples are stabilized by infiltration of dyes and other organic molecules. This includes increases in mechanical strength, photostability, and air/moisture resistance. A key question then is what is the mechanism by which the stabilization occurs.

2. It has become apparent that the ability to predict the effect of adding functional groups onto polymer systems is complicated by the interactions that the side chains containing these functional groups have with other side chains or with the main polymer backbone. How these interactions affect the properties and the expected multifunctionality must be fully understood to achieve the real control of properties needed for designing devices.

3. At an even more fundamental level, understanding the effect of adding functionally active groups to the backbone of a polymer on its electrical, mechanical, and optical properties is a science still in its infancy. Additional support for this aspect of OGAMM would contribute significantly to the achievement of an ability to design truly multifunctional materials. Thus, increasing the $X^{(3)}$ of polymers by two orders of magnitude while retaining optical quality and processability will require that Mother Nature has such a

material tucked away somewhere. But finding out where will require a few more clues on the rules of her game.

The justifiably optimistic view of this list of key issues is that it's hard to know the answers until you understand the questions. Much good science has been done under OGAMM to increase the understanding of the rules of the game, and good organization and luck have resulted in some preliminary successes. This group is building an impressive technology base for a number of critical SDI systems. We feel strongly that the OGAMM program is a successful model of the type of collaborative research efforts that the IST office is promoting.

OVERVIEW

MULTIFUNCTIONAL MACRO-MOLECULAR MATERIALS

by

A. BUCKLEY

Hoechst Celanese

In order to provide response to multiple inputs for light beam steering, sensor and/or system protection, multiple electronic functionality is being combined in macro-molecular assemblies. These may consist of polymers containing more than one functionality in each molecular species, or they may be designed molecular assemblies where discrete layers each contain specific functionality. Combinations of functionality could include, for example, non-linear optical responses together with piezo- and pyro-electrical responses or electro-optic responses together with photoconductive response to yield unique photorefractive properties. These are two parallel, but related, aspects to this program. A designed series of side chain polymers is being studied (HCC, U. of Cambridge, U. of Leeds) to develop a detailed understanding of the structure/property relationships. The effect of side chain orientation on the non-linear optic, piezo- and pyro-electric properties has been determined for both amorphous and liquid crystalline polymer variants. In parallel with this, device modeling concept demonstration activities are underway (HCC and GEC). These provide feedback to the chemistry and physics efforts and lead to the basic fabrication technologies for subsequent devices.

The continuing program will enhance electronic responses by both new chemistry and physics approaches. A second generation polymer system, designed to enhance piezo-electric response is currently being scaled up, and polymers containing photoconductive and electro-optic functions are being synthesized for initial evaluation. Device concept modeling and demonstration will continue with a device type being selected for assembly and demonstration. Because local field effects play a significant role in electronic responses, an additional effort in conjunction with Professor Haarer of University of Bayreuth is planned in order to more fully understand and exploit these effects. Significant developments in other parts of the OGAMM program

highlight further areas for cooperation, in this context joint experiments are planned with Professor J. D. McKenzie (UCLA).

Multifunctional Macromolecules

by

Harris A. Goldberg, A. J. East, Ilmar Kalnin, Joe Rafalko, and Ho-Nan Sung

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Summit, New Jersey 07901

A summary of a presentation made at the Third Annual OGAMMS review
Keswick, UK September 5, 1990

Background and Previous work:

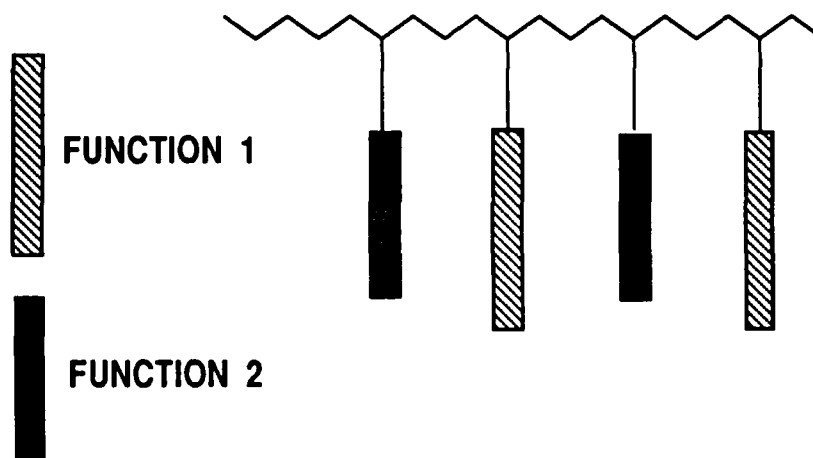
The focus of this program originally was to work on three tracks in parallel:

- 1) develop new multifunctional organic materials which would demonstrate techniques for designing functional materials and demonstrate multifunctionality;
- 2) develop applications which would require multifunctional organics so as to gain experience with the processing requirements and materials criteria one would want to design into new functional materials;
- 3) apply known techniques of polymer processing and morphology control to new functional polymers.

The third track involved collaboration with Leeds University, where there was considerable experience in processing of PVDF piezoelectrics, as well as Cambridge University with expertise in polymer morphology and characterization. In order to utilize standard polymer processing techniques, one of the first objectives was to make functional materials with high enough molecular weight to be processed in standard ways. The second track lead (in collaboration with GEC) to identification of the Light Modulated Deformable Mirror (LMDM) as a device concept which could utilize new processable organic piezoelectric materials as well as organic photoconductors. A spin off proposal aimed more specifically at developing the LMDM was prepared and submitted for funding. That work would be aim more specifically at utilizing existing materials in order to optimize multilayer designs.

The synthetic effort concentrated on two types of materials. The methacrylate polymers of oxynitrostilbene (and earlier work on oxynitrobiphenyl) was aimed at producing very high purity monomer and then high molecular weight polymer. This had been demonstrated by making >99% pure ONS-MMA monomers which led to high molecular weight polymers ($M_w > 500,000$ Daltons). Even with high molecular weights (degrees of polymerization more than 500 and in some cases over 1000) the films were still brittle and could not be processed as free standing polymers. Dielectric relaxation work (at Leeds) showed that the brittleness was associated with the disappearance of the β relaxation, presumably due to strong interactions between the side chain dipoles. Finally, significant progress was made in synthesizing PVCN-VA alternating copolymers which are well known as an amorphous, processable, piezoelectric polymer which can have piezoelectric activity equal to PVDF but with a high T_g (170°C) and thus much better thermal stability. It was this material that we planned to demonstrate the design of multifunctional materials by incorporating NLO active units while maintaining the piezoelectric active side groups (cyanide) of the PVCN-VA copolymers. The inherent multifunctionality (piezoelectric, pyroelectric, and electro-optic) which occurs in many polar side chain polymers was experimentally verified first using the ONS-MMA copolymers.

SIDE CHAIN POLYMER APPROACH TO MULTIFUNCTIONALITY



POTENTIAL FUNCTIONS:

- PIEZOELECTRIC
- PYROELECTRIC
- ELECTRO-OPTIC
- ELECTRICAL CONDUCTIVITY
- PHOTOCONDUCTIVITY

Recent Accomplishments: **Oxynitrostilbene-MMA Copolymers:**

During the last year, we have continued to synthesize high molecular weight ONS-MMA copolymers using both a 3 and 6 carbon aliphatic spacer from the main chain. Free standing films were prepared from copolymers containing 10/mole% ONS and mechanically tested. At room temperature these films showed brittle fracture at ca. 0.5% strain, beginning to yield plastically at ca. 70°C. The maximum fracture strains observed near the T_g (110-125°C) ranged from 56 to 78%. These films are the first example of this class of NLO active materials that have been tested and processed as free standing materials. We are presently working towards quantifying the ONS concentration dependence of the mechanical properties, as well as defining conditions under which we might induce backbone orientation.

Since we believed that interactions between the polar side groups may be responsible for the brittle behavior of these side chain polymers, experiments aimed at characterizing this interaction were begun. Pyroelectric and electro-optic measurements as a function of composition were completed, but to date have not provided any clear insights into this issue other than that both properties increase roughly in proportion to the ONS content in the copolymer. FTIR studies of both a 10-90 and homopolymer of ONS showed that a significant fraction of the nitro groups on the side chain are closely associated with another molecule (presumably another ONS). The fraction which is associated decreases with decreasing ONS content, and with increasing temperature above the T_g.

Finally, although careful GPC results have indicated that our ONS-MMA copolymers have very high molecular weights, we did not have a good calibration standard which had similar polar side chains. Such a standard had to be synthesized by reacting the acid chloride of ONS with polyhydroxy-styrene of known molecular weight. This material then

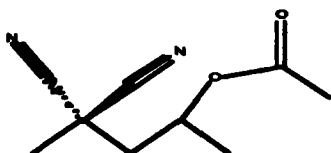
had a predetermined degree of polymerization and thus a known molecular weight. This work confirmed the validity of our earlier measurements for molecular weight by GPC.

Vinylidene-Cyanide Copolymers:

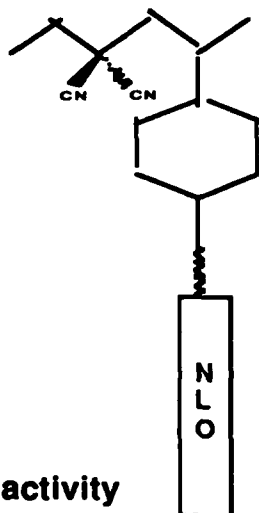
Having already demonstrated the synthesis of PVCN-VA copolymers, we synthesized several new polymers containing VDCN which have high pyroelectric activity. The most exciting of these is the copolymer of VDCN with acetoxystyrene. Hydrolysis of the acetoxystyrene unit then leads to a polymer which can be easily functionalized. We have made a copolymer containing 40-50 mole % ONS along with VDCN by this route.

VDCN MULTIFUNCTIONAL POLYMERS

PVCN - VA COPOLYMER



Schematic M3 Polymer



- Glassy polymer with superior Piezo/pyro performance
- High operating temperature ($T_g > 170^\circ\text{C}$)
- New backbone for Unique combination of NLO and Piezo activity
- Patented process and new compositions

PYRO AND ELECTRO-OPTIC PROPERTIES

(poled at $100 \text{ V}/\mu\text{m}$)

<u>POLYMER</u>	<u>$p(\mu\text{C}/\text{m K})$</u>	<u>$r(\text{pm}/\text{V})$</u>
M030NS-MMA(50-50)	3	10
M060NS-MMA(50-50)	3	11
PVCN-VA	7	1
PVCN-MO6)NS	5	10

PVCN-VA PYRO AND PIEZOELECTRIC RESPONSE IS KNOWN TO INCREASE BY A FACTOR OF 3-4 WHEN FILMS ARE STRETCH ORIENTED, MAKING ITS RESPONSE AS GOOD AS OR BETTER THAN PVDF.

The above table clearly demonstrates that we have achieved our goal of designing a side chain polymer which has most of its pyroelectric response coming from the VDCN side

group, and its electro-optic response coming from the ONS side group. The pyro response has been decreased a little due to the large volume fraction taken up by the ONS groups. The question of synergistic effects between the side chains is still under study.

Conclusions and Future Work:

We have achieved our original objectives of making high molecular weight electro-optic/pyroelectric polymers based on oxynitrostilbene. The strong dipolar interactions of the ONS side chains makes materials with large amounts of ONS brittle and generally not amenable to fabrication into free standing films. However, we have been able to process a 10 mole % ONS-MMA polymer (containing about 30 vol% ONS) as free standing films. Future work on the ONS-MMA system will build upon our ability to synthesize high molecular weight, high purity polymers over the entire composition range with a variety of spacer lengths. This system has all the features common to the best χ^2 active polymers, and thus serves as an excellent model system with which to do the fundamental materials science on these polar side chain polymers. Other recent results on these materials (especially the ONS-MMA system) will be reported by the groups at Leeds and Cambridge separately.

The most important accomplishment thus far is our demonstration that one can design the multifunctional properties of a side chain polymer by making copolymers containing the appropriate units. We have made (and patented) new copolymers based on VDCN backbones which have enhanced pyro/piezo-electric properties due to the cyanide side groups, and enhanced electro-optic properties due to the ONS side groups.

Our future work will concentrate on using this same design principle, but incorporating functionalities which we have determined to be advantageous for polymer based devices. Those functionalities are: piezoelectric and photoconduction for advanced LMDM's, and electro-optic and photoconduction leading to new organic photorefractive materials for optical signal processing and holography.

ACKNOWLEDGEMENTS:

First of all, we want to thank Don Ulrich and the SDIO-IST office for funding this program. In addition, the continued support and leadership of Alan Buckley and Jim Stamatoff have been essential to the success of this work. Finally we want to thank: Frank Haimbach and Duane Brikowski for mechanical testing, Dave Nikles for help with casting films, Dominick Cangiamo for NMR analysis, Frank Batitto and Rob Johnson for synthesizing the ONS-MMA polymers, Ray Carney for VDCN polymer synthesis, George Breckenridge for sample preparation and pyroelectric measurements, and Rich Keosian for electro-optic measurements.

Determination and Control of Structure in Multifunctional Side-Chain Polymers

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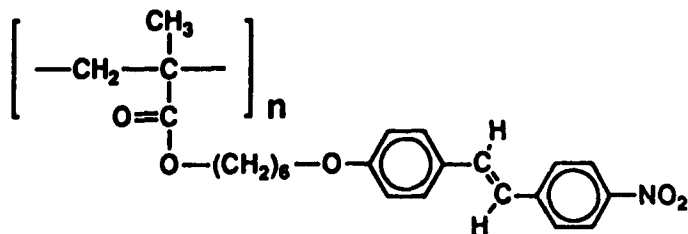
[* Principal Investigator in support of Hoechst-Celanese as Prime-Principal Investigator within the OGGAMS Project.]

Introduction

There is a need to develop active materials for key opto-electronic-mechanical devices which, while fulfilling all primary demands made on them, are easily fabricated in a form which can guarantee long term stability. Specially designed multifunctional polymeric molecules are showing promise for applications which involve the electro-optic effect, photo-refractive devices and those based on deformable mirrors. The polymeric approach to obtaining the desired properties is driven not only by the potential for ready manufacture of self supporting free films, but also by the fact that side chain polymers provide an excellent basis for creating *single phase* multifunctionality.

The major objective of this collaborative project between Hoechst-Celanese, Leeds University, GEC-Marconi and Cambridge University, is to develop devices to the proof of concept stage while at the same time moving forward the necessary scientific understanding. The Cambridge contribution has been the study of the influence of molecular formulation on microstructure, and the enhancement of useful properties through microstructural control.

The first side-chain system examined is essentially a polymethyl methacrylate polymeric backbone, with the active side group (-oxy nitro stilbene) attached to the backbone, through a flexible aliphatic spacer of $-(CH_2)_6-$, at the position where it takes the place of the methyl group of the ester. The repeat unit is thus:



C6ONS MA

These molecules form the basis of electro-optical devices while at the same time being a starting point for the creation of other multifunctional materials, particularly those which couple opto electrical and mechanical fields through photoconductive and piezoelectric activity. One important property of any material used in devices, particularly remotely sited ones, is long term performance. To achieve this aim it is desirable to have as high a glass transition temperature (T_g) as possible consistent with the maintenance of processability, and access to specific phase states such as liquid crystallinity. For this reason, random copolymer series have been examined consisting of units of the active methacrylates defined above and the non-active methyl methacrylate unit. The thermal characteristics of this system using the C6ONS unit, as determined by DSC and hot-stage microscopy are shown in Fig 1.

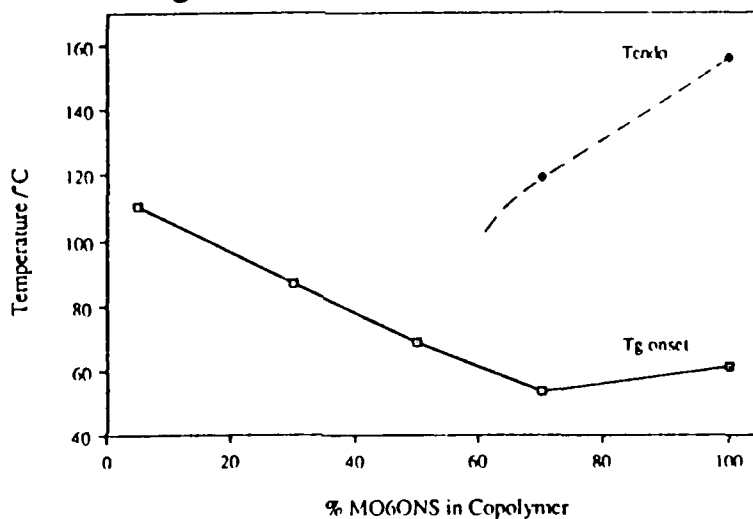


Fig 1 Variation of T_g and T_{s-i} with composition of the random copolymer.

The dilute end of the composition range has the advantages of the higher glass transition temperature and more tractable mechanical properties, while the compositions containing 70% and 100% active units showed a smectic liquid crystalline phase which could offer considerable advantages in tailoring the microstructure for optimum multifunctional action.

Structure of random copolymers

Wide-angle X-ray scattering (WAXS) data from unoriented samples of the series of random copolymers were compared with simulations of the scattering expected from a simple mixture of MOGONS homopolymer and PMMA (weighted according to the number of electrons from each monomer).

The homopolymer shows a strong interchain peak at about $19^\circ 2\theta$, which also appears in the 70% and 50% side chain substituted materials. In the 30% material, the peak moves to a slightly lower angle and a peak characteristic of the homopolymer PMMA backbone starts to emerge at about $30^\circ 2\theta$. In the 10% and 5% materials the $30^\circ 2\theta$ peak becomes more pronounced, and the $19^\circ 2\theta$ peak broadens towards lower angles. Both effects are

also seen in the simulated traces - the broadening of the $19^\circ 2\theta$ peak being due to greater contributions from the $14^\circ 2\theta$ interchain peak of PMMA.

The side groups in the liquid crystalline 100% and 70% materials are known to be segregated from the backbone because those materials are smectic. The data indicates that segregation also occurs in all the less substituted materials, as evidenced by the composite peaks at $14 - 19^\circ 2\theta$. This is further evidence for the proposition that the less substituted materials would be macroscopically liquid crystalline if the glass transition were lower, and suggests that short range order occurs in any case.

Alternating electric field alignment of C6ONS MA homopolymer

If an alternating electric field greater than $5 \text{ V}\mu\text{m}^{-1}$ is applied across a film of C6ONS MA homopolymer as it cools through the clearing point (156°C), an optically clear texture is formed instead of the usual highly scattering one. The effect is a little stronger at higher frequencies ($>500\text{Hz}$) and is much improved by slower cooling ($<5^\circ\text{C}/\text{min}$). It is shown in Fig 2.

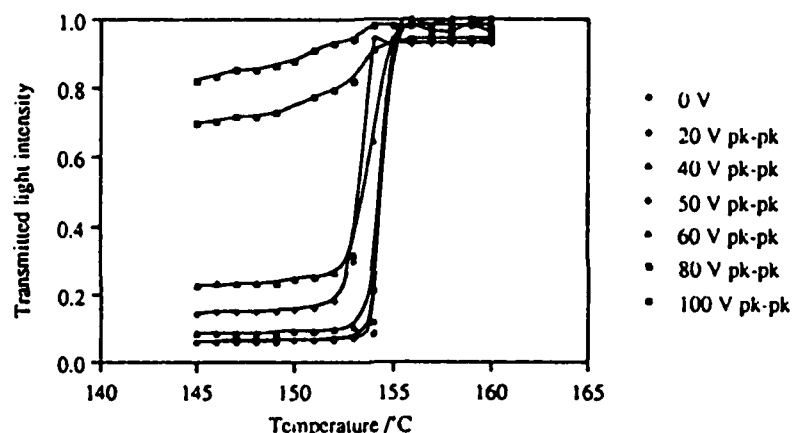


Fig 2 Changes in clarity of sample on cooling at 2°C m^{-1} at 1 Hz

This texture is homeotropic and uniaxial and displays a strong characteristic conoscopic image (Fig 3) which shows that the side groups have oriented parallel to the electric field, and thus to the film to form a large monodomain.



Fig 3. Conoscopic image showing the high quality of homeotropic alignment attained.

X-ray studies using a microcollimated beam incident in the plane of the film confirmed the strong orientation, with the smectic A layer peaks clearly visible, and the side group interchain peak contracted to the equatorial (estimated $P_2 \approx 0.7$)

A meridional scan in a reflection diffractometer (Fig 4) showed very strong first and second order peaks corresponding to a layer spacing of $33\text{\AA}$. This is consistent with a structure in which the side chains of neighbouring molecules are interdigitated.

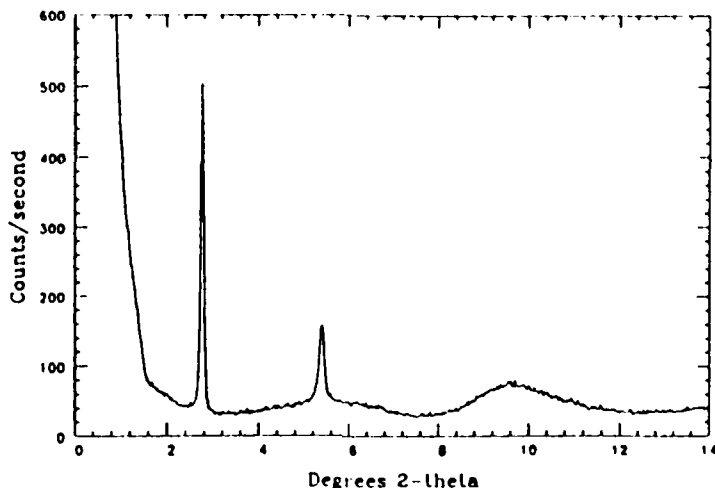


Fig 4. Meridional WAXS scan showing the highly ordered layer structure.

Conoscopic and X-ray studies of an annealed spin coated sample only $6\text{ }\mu\text{m}$ thick showed that it is also a large homeotropic smectic A monodomain, this having been induced by surface alignment from the indium tin oxide coating on the glass substrate.

Birefringence during a.c. alignment

Preliminary results from studies of birefringence in the C6ONS MA homopolymer during cooling from the isotropic phase in alternating electric fields have been obtained by sampling a quadrant of the conoscopic image at an angle to the optic axis using shining a laser beam.

On cooling in the absence of an electric field, or in weak fields, the birefringence rises briefly from zero (isotropic) as a thin polydomain smectic scattering texture forms at the surface; the measured intensity then falls again due to strong scattering. At stronger fields, the final birefringence is higher due to reduced scattering, and at very strong fields the sample goes into extinction due to the first interference ring of the conoscopic image. There was no evidence of any pretransitional alignment in the isotropic phase.

Acknowledgements

This collaborative work was initiated through the leadership of Don Ulrich, and has been made possible by our close association with Hoechst-Celanese at Summit NJ, the University of Leeds, and the device concept team at GEC-Marconi, London.

THE PRODUCTION AND MEASUREMENT OF POLAR ORIENTATION IN MULTIFUNCTIONAL MACROMOLECULES

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INTRODUCTION

The objectives of the main project are to demonstrate and optimise multifunctionality in novel polymers synthesized by Hoechst-Celanese. The particular combination of properties initially chosen are piezoelectricity, pyroelectricity and second order non-linear optical activity.

To maximise piezoelectric, pyroelectric or NLO activity, the active groups must all point in the same direction. In the original films they point in different directions and the film is inactive. An electric field is therefore applied at high temperatures to partially align the groups. When the field is removed at low temperatures the material is hard so the groups remain aligned even when the electric field is removed.

This operation is known as poling. The activity of the films depends upon the degree of alignment achieved and it is our task to study the poling process, develop methods of measuring the alignment produced by poling, maximise the alignment and to characterise the piezoelectric and pyroelectric properties of the materials so produced.

We have made progress in the following areas:-

1. Preparation of samples by solvent casting & dip coating.
2. Design and development of equipment for thermal and corona poling and the optimization of poling conditions.
3. Design and development of equipment for measuring the pyroelectric coefficient & thermally stimulated currents.
4. Measurement of piezoelectric coefficients.
5. Ageing of the pyroelectric response and its relation to relaxation processes seen in thermally stimulated current data and in dielectric relaxation spectra.
6. The measurement of orientation using IR spectroscopy.

In the first two years of the programme, advances were made areas 1-5 above. This year, after initial evaluation of Polarized Fluorescence and Raman Spectroscopy, Infra-Red spectroscopy was used to obtain orientation information to independently check the efficiency of the poling process.

MAIN RESEARCH FINDINGS

Hoechst-Celanese supplied two side-chain liquid crystalline polymers with a nitro-biphenyl or oxy-nitro-stilbene side group (mesogen) on a methacrylate backbone. After some work on the nitro-biphenyl polymer we concentrated most of our effort on the oxy-nitro-stilbene polymer with higher NLO activity. Several related polymers based on this side group have been supplied. The mesogen has been separated from the main chain by a 3 or 6 carbon spacer (denoted MO3ONS or MO6ONS respectively) and the mesogen concentration has been reduced by copolymerisation with MMA.

Processibility

Original samples of the homopolymer films were very brittle as cast and could only be handled on a substrate. Poling and the measurement of electrical properties were therefore carried out on samples cast on to thin glass substrates. We have related this brittle character to the absence of a room temperature β relaxation process as seen in Figure 1 which shows the dielectric loss of a range of copolymers.

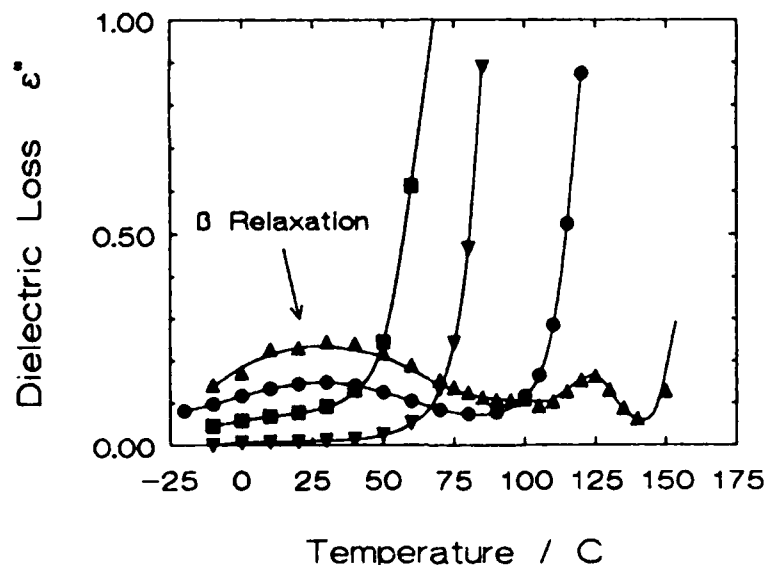


Figure 1. The dielectric loss of copolymers of MO6ONS and PMMA. Δ 0%, $\bullet$ 10%, $\blacksquare$ 30% and $\blacktriangledown$ 100% MO6ONS

Both PMMA and the 10% MO6ONS copolymer shown a large β relaxation and can be handled as free unsupported films.

Poling

The optimum poling temperature was found to be at or near the glass transition of the polymer. Poling at much higher temperatures, especially in the liquid crystal region, led to

breakdown due to high ionic conductivity. The potential self aligning properties of the liquid crystal polymers were therefore of little benefit.

The highest pyroelectric coefficients were obtained using high field corona poling. This often resulted in breakdown therefore comparative work was done by measuring the pyroelectric coefficient at relatively low poling fields.

Piezo- and Pyro-electric coefficient measurements.

Both piezo- and pyro-electric coefficients were found to vary linearly with poling field in the range studied. A maximum value of 7 pC/N was obtained for the hydrostatic piezoelectric coefficient and $3 \mu\text{C}/\text{m}^2/\text{K}$ for the pyroelectric coefficient. These are lower than can be obtained with PVDF but are in a polymer with significant NLO activity. Multifunctionality has therefore been demonstrated.

Ageing

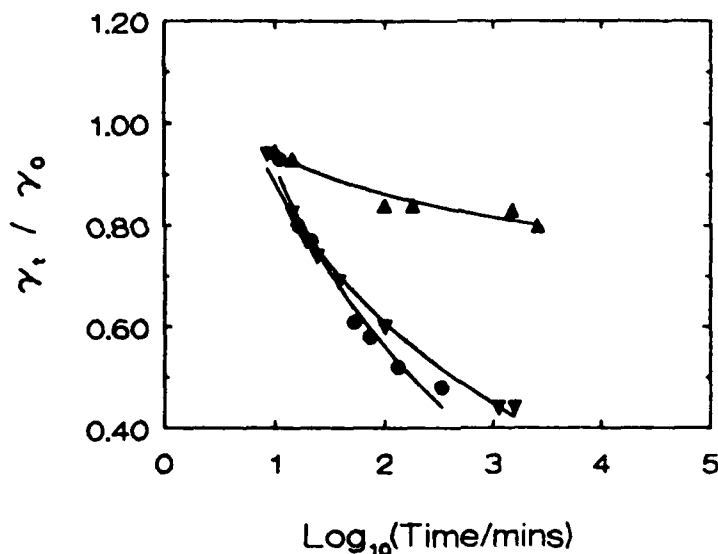


Figure 2. The decay of the pyro. coeff. of 10% MO6ONS.
 ▲ 15 μm thick, ● 35 μm , ▼ 65 μm free film.

The stability of any activity is obviously of prime importance. The homopolymers are relatively stable but PMMA itself and the 10% MO6ONS copolymers lose approximately 50% of their pyroelectric activity in a week. This is caused by the β relaxation which improves their ductility. Consequently, the homopolymers and higher copolymers which show no β relaxation are more stable but brittle. Surprisingly, as seen in Figure 2, the thickness of the film and the presence of a substrate affect the ageing process. Thin films on a substrate are more stable than unsupported thick films. This important observation needs further investigation.

IR Spectroscopy

Preliminary analysis of IR spectra for corona poled films of 10% MO6ONS using the NO_2 symmetric stretching vibration has given values of the orientation function $\langle P_2(\cos\theta) \rangle$ up to 0.15, implying $\langle P_1(\cos\theta) \rangle$ values of up to 0.5.

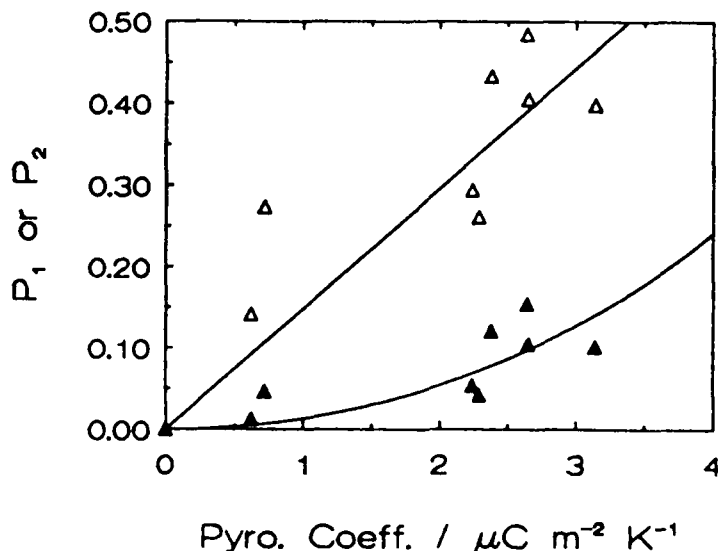


Figure 3. The orientation functions P_1 and P_2 from IR.
 $\Delta - P_1$ $\blacktriangle - P_2$

Correct interpretation of the IR data is important since the pyroelectric coefficient is directly proportional to P_1 . The maximum value of P_1 is 1 and if we are correct, therefore, we are within a factor of 2 of the maximum possible response from these materials even if they could be fully aligned.

FUTURE PROPOSALS

The new materials to be produced by Hoechst-Celanese will continue to be studied by us as at present. In addition, we will continue to develop IR and other techniques for the measurement of orientation.

In particular, our conclusions from the IR work rest upon the assumption that the copolymer films are isotropic prior to poling. From Dr. Windle's studies (Cambridge), it is known that the homopolymer films are preferentially aligned. Further tilted-film IR studies are therefore required to check the orientation in our unpoled films.

ACKNOWLEDGEMENTS

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Polymeric Optical Devices - A Multifunctional Approach

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Abstract

In principle, multifunctional macromolecules can combine a number of active material functions, such as optical non-linearity and photoconductivity, in one material. Consequently, multifunctionality may offer new options for device fabrication and implementation. However, practical materials are still some way away, partly due to the difficulty of optimising a material simultaneously for two separate properties. Therefore, the approach we have taken is to identify device configurations which rely on multilayers, each separate layer providing one of the active device functions. Progress on the fabrication of two proof-of-principle devices, a light modulated deformable mirror and a light modulated electro-optic layer, is described.

Introduction

The fabrication of through-plane optical devices may be simplified by the use of polymeric materials. Such materials do not require polishing which, for inorganics, can be both time consuming and expensive. Polymers can readily be prepared as large area thin films by techniques such as spin coating. Organic materials are currently available which exhibit active functions such as photoconduction, piezoelectricity and optical non-linearity.

The feasibility of obtaining macromolecular materials which exhibit a range of active functions has been considered. An example of such a material is polyvinylidene difluoride (PVDF) which is both piezoelectric and pyroelectric. However, multifunctional macromolecular materials are being considered which exhibit functions such as photoconduction and piezoelectricity, or piezoelectricity and electro-optical properties. This paper describes our approach at GEC-Marconi to identifying devices to which the multifunctional macromolecular concept might be applied. Progress with the fabrication and characterisation of two proof-of-principle devices, a light modulated deformable mirror (LMDM) and a light modulated electro-optic layer (LMEOL) are described. It is expected that these devices will help to suggest ways in which multifunctional macromolecules can be more fully utilised.

New areas of study have included the characterisation of a new processible piezoelectric copolymer, an investigation of faster organic photoconductors and modelling of interdigitated electrodes for use with electro-optic polymer films. Progress with each of these areas is reviewed.

Light Modulated Deformable Mirror

A schematic diagram of the basic light modulated deformable mirror (LMDM) is shown in Figure 1. Details of its fabrication have been previously described [1]. It should be noted that this is just one example of this class of device, in other types the glass support need not be used and the active layers could be sufficiently thick to be self supporting or a thin membrane stretched over an aperture. The operation of this optically addressed device is simple in principle. A voltage is applied across both the photoconductor and the piezoelectric layer. With no light incident on the photoconductor its impedance remains high and very little voltage is applied to the piezoelectric layer. At higher incident light intensities the impedance of the photoconductor is reduced so that more of the voltage falls over the piezoelectric layer. This results in the piezoelectric layer deforming, the magnitude of the deformation being proportional to the incident light intensity.

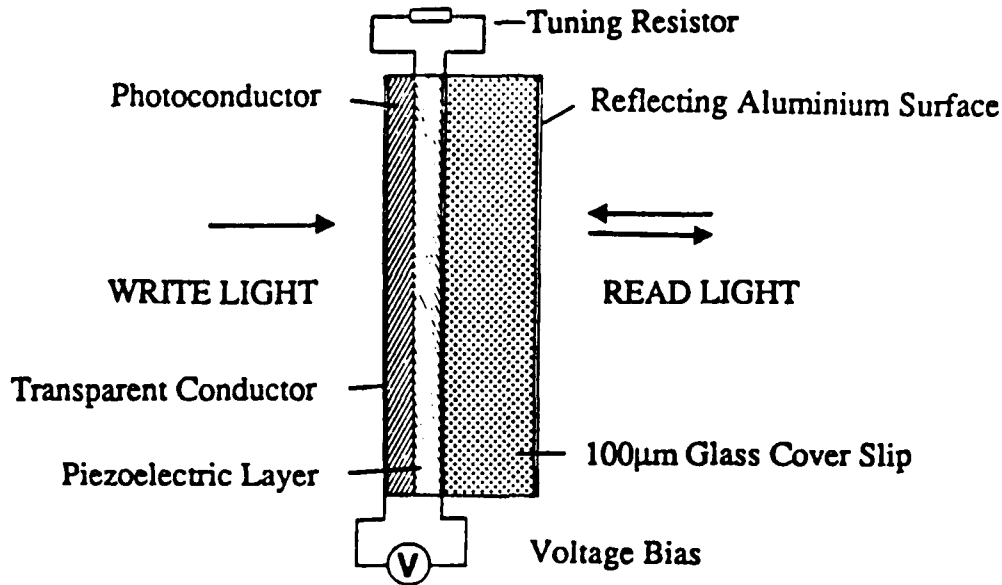


Figure 1: The light modulated deformable mirror

During the past year the design of the LMDM has been modified to include a tuning resistor placed in parallel with the piezoelectric layer. This has removed the requirement to impedance match the piezoelectric layer to the photoconductor. Previously, the high impedance of the piezo layer meant that the impedance of the photoconductor had to be correspondingly high so that only a low doping concentration of TNF could be used in the PVK photoconductor. Consequently, the carrier mobility in the photoconductor was low and this limited device response speed. By using a parallel resistance the impedance of the piezo layer is reduced so that a higher concentration of TNF can be used, with the result that device response times (due to both the photoconductor response and the RC time constant) have been considerably improved in the last year. A summary of performance data is given in Table 1.

Parallel Resistance (M Ω)	No. of fringes movement	Expected drop across piezo layer	Deduced R_L (M Ω)	τ_{on} (ms)	τ_{off} (ms)
6.5	1.5	13.0	43.5	48	84
22	3.5	30.5	50.0	100	270
44	4.5	39.1	68.4	140	400
66	5.5	47.8	71.9	170	660
88	6.0	52.5	80.6	180	900
110	6.5	56.2	84.7	230	1175
134	7.0	60.0	89.0	270	1400
161	7.5	63.0	94.5	280	1700

Table 1: Summary of LMDM performance and response time

It is clear from Table 1 that as the magnitude of the parallel resistance is increased, the number of fringes deformation increases. However, a corresponding increase in the response times (τ_{on} and τ_{off}) is observed so that a trade-off exists between the required level of mirror deformation and the timescale on which this occurs.

An initial study of the deformation of membrane mirrors has been completed and the expected response of the LMDM to various write light functions is shown in Figure 2. It is clear that using a combination of these functions to illuminate the photoconductor could facilitate the correction of complex wavefront aberrations.

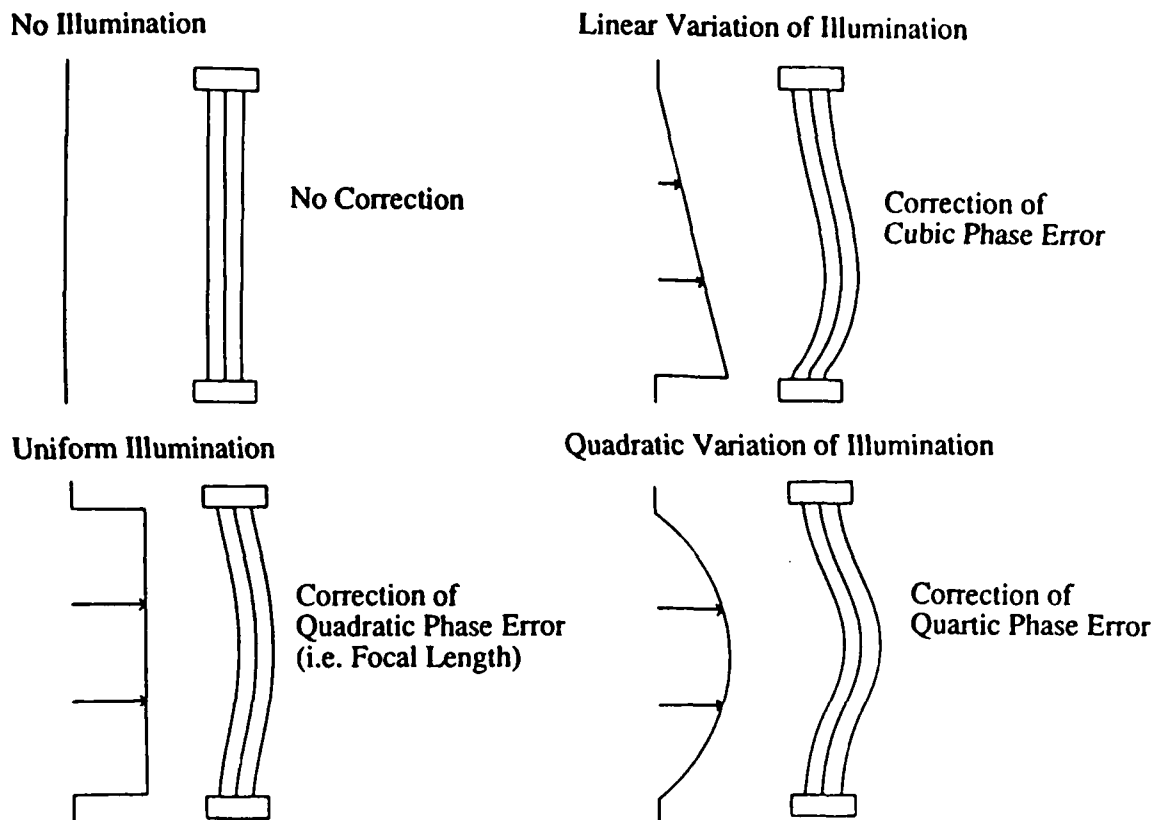


Figure 2: Response of a membrane LMDM to given write light functions

Electro-Optic Dual Layer

The Electro Optic Dual Layer (EODL) is the second proof-of-principle device and its operation has been previously demonstrated [1]. The device consists of an electro-optic layer and a photoconductor which are separated by a light blocking conducting layer. A voltage bias is applied across the whole device. The impedance of the photoconductor in the dark state is chosen to be greater than that of the electro-optic layer and so most of the applied potential falls across the photoconductor. On illumination, the impedance of the photoconductor becomes lower than that of the electro-optic layer and so most of the potential falls across the electro-optic layer, resulting in a change in the birefringence, or phase retardation. Thus in principle the operation of the dual layer is simple. However, if the optimum operating conditions are to be achieved, the correct impedance matching of the photoconductor and electro-optic layer is essential. As with the LMDM, the impedance of the electro-optic layer (cf piezo layer) is necessarily high (to achieve good poling efficiency) and so only a low TNF doping concentration can be used to avoid excessive lowering of the photoconductor (PVK) impedance.

We have recently begun the fabrication of a new design of EODL which uses resistors placed in parallel with the electro-optic layer (to lower the impedance) and amorphous silicon (α -Si) as the photoconductor. α -Si has a considerably faster response time than the TNF-PVK photoconductor and so limiting device performance can be probed. The design under fabrication is shown in Figure 2 and consists of an array of EODL's. This approach means firstly, that many EODL's are fabricated at one time, and secondly, an eventual reduction in device size can be envisaged to obtain a pixellated device.

Evaluation of Alternative Piezoelectric Polymer

The piezoelectric polymer used in the fabrication of the LMDM was a commercially available, stretch oriented, poled film. During the year an alternative piezoelectric polymer has become available from Hoechst Celanese. This material is a copolymer of vinylidene dicyanide and vinyl acetate. The advantage of this material is that it can be processed from solution by casting or spin-coating and so exploits the processibility aspect of the macromolecular concept.

We have carried out extensive characterisation studies of this material, determining the film thicknesses obtained as a function of both spin speed and spin time for solutions in N,N-dimethylacetamide. Glass transition temperatures T_g in the region of 140°C have been measured. The electrical breakdown strength of the films has been determined as a function of poling temperature. Such measurements are important as the piezoelectric coefficient must be optimised by applying the largest possible field.

Although no measurements of the piezoelectric coefficients have been made, the copolymer is expected to exhibit only approximately one third of the activity of PVDF as the films cannot be stretch orientated when incorporated directly into devices, as we have done. However, there are fabrication advantages to be obtained by the use of a processible piezoelectric polymer and so device fabrication/performance trade-offs must be considered. Work is continuing to incorporate the copolymer into LMDM's and evaluate their performance.

Enhanced Macromolecular Photoconductors

In both of the proof-of-principle devices, the performance characteristics have been determined by the response time of the photoconductor. The mobility of the charge carriers (holes) in the TNF-PVK systems studied is quite low ($\sim 10^{-6} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$) and the large number of traps has caused dispersive charge transport. A number of alternative photoconductor structures and materials have been identified which have faster response times.

The problem of charge mobility has traditionally been overcome by using a layered structure in which the holes and electrons are transported in separate layers, each of which is optimised for transport of the appropriate charge carrier. Thus the charge carrier generation layer can be used to generate the electron hole pairs and conduct the electrons, whilst the holes track through an adjacent layer to the electrode. Two hole transporting materials of interest have been identified, namely N,N-diphenyl-N,N'-bis (3-methyl phenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) and poly (phenyl methyl silylene). Both of these materials exhibit hole mobilities several orders of magnitude higher than those of TNF-PVK and sources of these materials are currently being sought.

Interdigitated Electrode Arrays

The use of poled electro-optic films for through plane optical devices requires that incident light enters the film at $\sim 45^\circ$ to the plane to experience non-zero birefringence. From a device viewpoint it is preferable to operate the device with light at normal incidence. This possibility arises if interdigitated electrodes are used to pole and drive the polymer film. A finite element routine was used to determine the electric field and resulting birefringence for a given set of film thicknesses and electrode spacings. The electrode width was 5 μm and the polymer was modelled on a silica substrate, as shown in Figure 3.

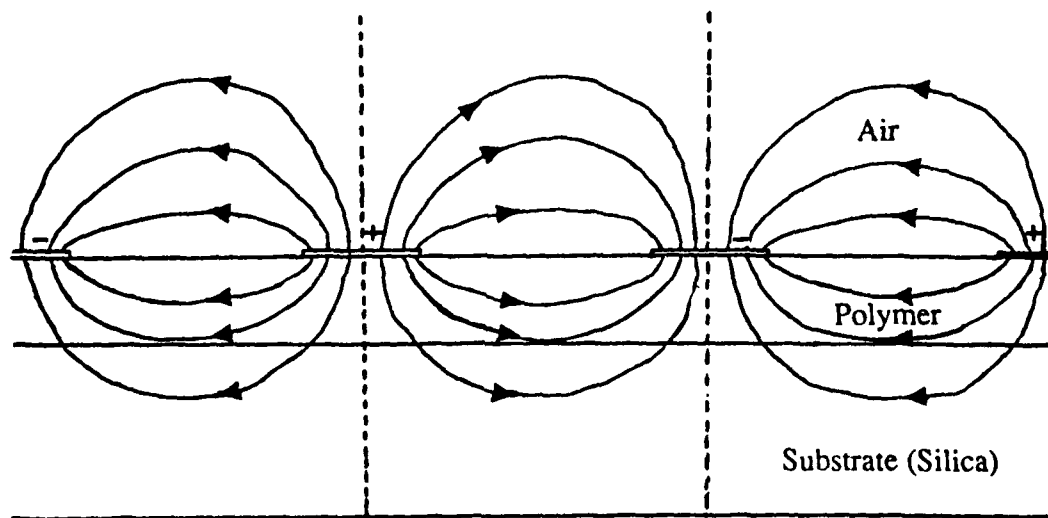


Figure 3: Electric field arising from an interdigitated electrode structure

We have found that it is possible to vary the electrode spacing and the polymer thickness so that uniform birefringence is obtained in the region between the electrodes, as shown in Figure 4. In such a configuration the electrodes must be light blocking. However, we have also considered the possibility of using two polymer films, one either side of a silica substrate, each with a set of interdigitated electrodes displaced relative to the other. In this geometry the electrodes could be transparent and a uniform birefringence may be obtained across the device aperture.

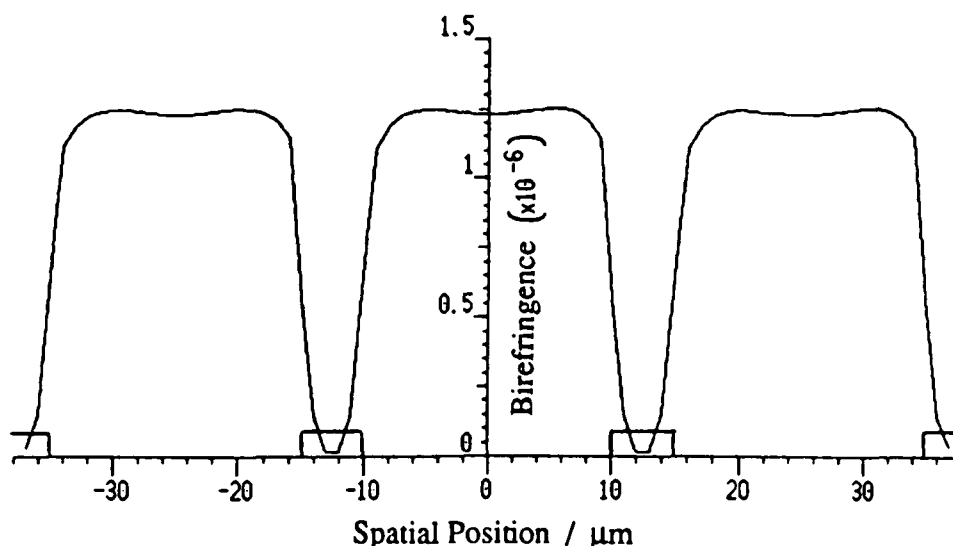


Figure 4: Variation of birefringence with position across the electrode structure for a 10 μm polymer film with an electrode width of 5 μm and a spacing of 20 μm . Light incident normal to the polymer film.

Summary

We have continued our studies of both of our proof-of-principle devices and further advances in device performance have been obtained. The use of a parallel resistance has reduced the effective impedance of the piezoelectric and electro-optic polymers so that faster photoconductors can be used. These studies have highlighted the way forward and new piezoelectric polymers and photoconductors are being characterised for inclusion in our devices. Important and valuable lessons have been learnt from our device programme and these have been fed back into the materials design and synthesis programme.

A novel application of interdigitated electrodes has shown that it may be possible to fabricate devices which operate with light impinging at normal incidence. Such a feature would greatly simplify the implementation of through plane devices in optical systems.

References

- [1] Worboys, M.R., Griffith, M.S. and Davies, N.A., *Mat. Res. Soc. Symp. Proc.*, **175**, 135 (1990).

Acknowledgements

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OVERVIEW

MULTIFUNCTIONAL POLYMERS

by

F. E. KARASZ

University of Massachusetts

The aims of the group are to produce and characterize new polymers which have combined electrical, optional and mechanical properties/functions which can be exploited in devices. The polymers are divided into two classes: conjugated systems and mesogenic (liquid crystalline) macromolecules. The conjugated systems are of the polyphenylene vinylene (PPV) type and include derivatives, analogs, copolymers and blends. The liquid crystal polymers are of the side chain type, where known active groups are pendant to flexible chain backbones. In addition, there is a related study of these and other polymers in ultra-thin film form produced by Langmuir-Blodgett techniques.

The advantages of the PPV materials are versatility, high activity (electrical conductivity up to 10^4 S/cm and non-linear optical $\chi^{(3)} \sim 10^{-8}$ esu) and, most importantly, processibility. The latter is confirmed by the nature of the precursor synthetic route. By modifying the chemical structure, the electronic structure and hence the electrical/optical/mechanical properties, can be tailored. The liquid crystal polymers (primarily aromatic azo side groups attached to styrenic and acrylic backbones) can also include copolymers/blends of side groups of different functionalities. An extensive characterization of these materials and their non-linear optical effects has been carried out in collaboration with other OGAMM participants. The same strategy has applied to high temperature ultra thin films.

Progress in Polyphenylene Vinylene

F.E. Karasz

University of Massachusetts

Poly-p-phenylene vinylene (PPV) has been a major focus of investigations in the present program. The major features of PPV are illustrated in **Fig. 1**.

Synthesis. The parent polymer can be readily synthesized in large quantities from available monomers. The chief feature of the synthesis is the route to PPV via an intermediate precursor polymer which is water or methanol soluble. The precursor can be cast into a film or other structure which, by thermolysis at 200°C or higher, is converted to PPV. During the thermolytic reaction a transient plasticity is conferred to the film as a result of the evolution of low molecular weight species.

The mechanism of the polymerization reaction has been extensively studied in the last year. It involves a sulfonium ylid formation followed by a diradical initiator formation and an addition reaction to form the precursor polymer. The latter can be derivatized in a number of ways to form very stable non-ionic intermediates which can, in principle, be purified or subjected to the usual polymer characterization procedures.

The transient plasticity conferred to precursor films during thermolysis permits the development of highly isotropic structures. Uniaxial extensions of ten to fourteen are readily obtained. These highly oriented films have been characterized in terms of their morphological, mechanical, electrical and optical behavior. In addition, biaxially oriented films have been produced which have been studied optically.

The versatility of the so-called Wessling synthesis of PPV has been used to obtain derivatives, analog and copolymers of PPV. **Fig. 2** indicates a number of polymers that have been prepared. An object of this synthetic variability is to

PPV and Derivatives:

Some Potential Advantages

- Easily synthesized (100+ g.)
- Intermediates isolatable: purification and solution characterization
- Processing versatility:
high uniaxial and biaxial anisotropies
- High electrical conductivities in doped forms
- Substantial off-resonance χ^D activities
- Blendable with electro-optically inert matrices:
 - a) organic polymers (PEO,...)
 - b) inorganic (SiO_2 +)
- Copolymers synthesized

Figure 1

modify the electronic structure to systematically change the properties of the PPV parent polymer. For example, alkoxy electron withdrawing group on the phenylene ring can lower the band gap to permit doping (see below) by less oxidative species (e.g. I_2 vs. AsF_5) and consequently improve the stability of the electrically conducting films. The thienylene analogs have also been shown to be more stable. Longer chain alkoxy derivatives confer solubility to the PPV itself (i.e. as distinct from the precursor polymer), usually at the expense, however, of reduced electrical conductivity. Several permutations of the monomers shown in Fig. 2 have been combined into random copolymers whose properties are currently under investigation.

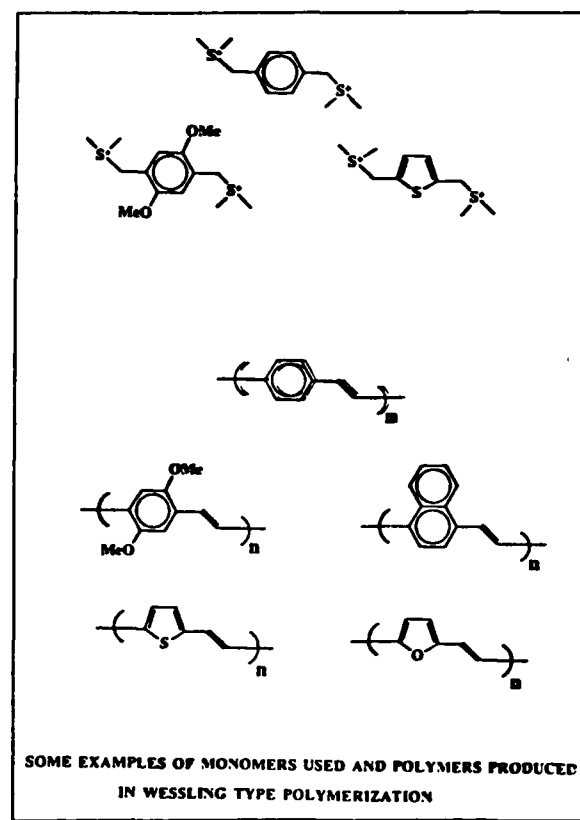


Figure 2

Electrical Properties. Initial interest in PPV was as a model conjugated system which is capable of being oxidized or reduced ("p- or n- doping") to yield highly conducting polymer structures. Indeed oriented PPV films can be doped by AsF_5 to conductivities of the order of 2×10^4 S/cm [For comparison, copper at room temperature has a conductivity of about 8×10^5 S/cm.] This feature, together with the advantageous synthetic route described above, still makes PPV a major candidate for electrical applications in a wide variety of systems. The mechanism of electrical conduction including bipolarons has been the subject of intensive experimentation and discussion. As already indicated, however, the band gap in PPV is such as to demand the use of highly active oxidizing agents leading to poor stability. The monomethoxy derivative, in contrast, can be doped with I_2 and this system has been shown to have a relatively high stability in ambient conditions over periods of weeks or months. The conductivity is somewhat lower, ~ 10 S/cm, but this is because optimal conditions for achieving high anisotropies have yet to be found.

Characterization. PPV itself is an insoluble and infusible solid showing no melting or glass transition before decomposition (at about 400°C *in vacuo*). However advanced and in some cases novel solid state polymer characterization

techniques have been used which have yielded substantial information about this polymer in its pristine and doped forms. The same techniques are now being applied to the derivatives, analogs and copolymers described above.

PPV in oriented form is a highly crystalline polymer. The crystal structure has been deduced in great detail by X-ray techniques. Recently (in collaboration with Prof. M. Winocur, University of Wisconsin) the structures of the alkali metal doped forms have been investigated. Dopants are essentially intercalated between PPV chain or sheets (cf. graphite) and as doping proceeds a variety of channel phases can be obtained, **Fig. 3**. In highly oriented PPV the crystalline domains are relatively small (perhaps ~ 50-100 nm) and a fraction of the material therefore resides at inter-lamellar ("grain") boundaries in a less oriented form (shown by NMR). Nevertheless, because of the very rigid chain conformation, a "fringed micellar" structure is not inappropriate to describe the overall morphology. It is not yet known how derivatization, etc.

affects the morphological features in comparison with the parent PPV.

Solid state NMR has also been extremely useful in elucidating the fine structure of PPV. Deuterated PPV (either completely or selectively deuterated forms have been prepared) has yielded detailed information concerning chain conformation and structure and has also been instrumental in confirming the presence of "ring-flip" motion of the phenylene group in PPV. Very recently two dimensional NMR techniques have been devised for the study of solid PPV, and novel information is beginning to emerge.

Optical Properties. PPV in common with other conjugated systems is of interest with respect to its potential non-linear, $\chi^{(3)}$, optical activity. Measurements (with Prof. P. Prasad, SUNY Buffalo) have indicated that in

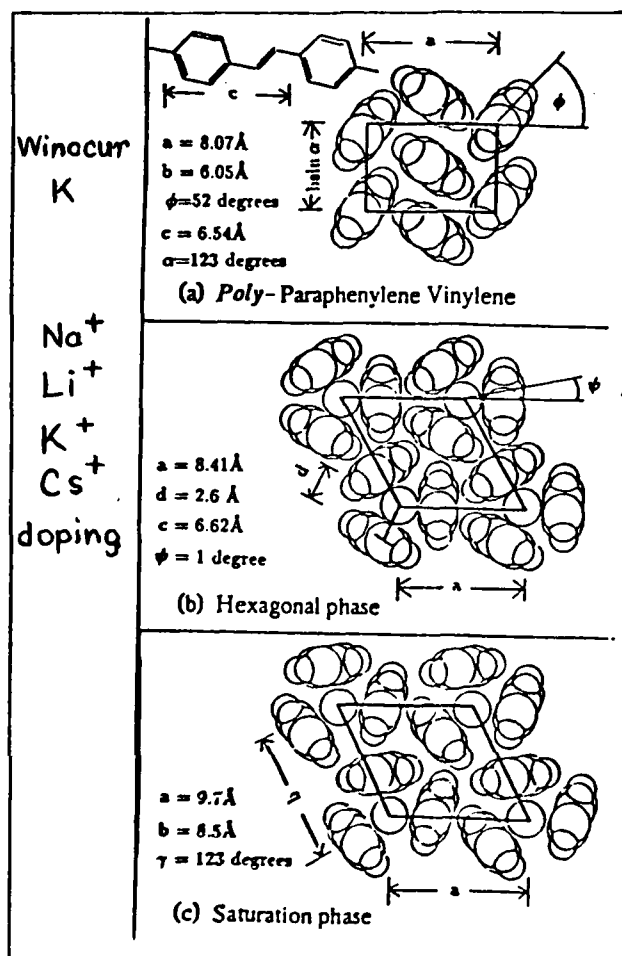


Figure 3

carefully purified, oriented films, $\chi^{(3)}$ s of the order of 10^9 esu can be achieved. Biaxial films have also been studied. These values are off-resonance results with less than picosecond half lives. Derivatives are also being examined.

Blends. The existence of the water soluble precursor polymer offers the possibility of forming multi-component systems with electrically inactive second polymeric components. Several such systems have been studied in some detail, including PPV-polyethylene oxide blends. There are many characteristic properties of such blends which have been described elsewhere; an important advance found in alloys in which the second component has a low T_g is the greatly increased doping kinetics in such blends. Diffusion of dopants into pure PPV is slow and is possibly impeded by side reactions. However PPV-PEO films of any thickness can be quickly doped, presumably because of the ready pathways offered by the PEO to the diffusing species. It should be noted that PPV-PEO blends, while not compatible in the thermodynamic sense nevertheless appear to possess a molecularly dispersed morphology. Direct electron microscopic and indirect electron percolation experiments provide this information.

Molecular dispersion to form very highly transparent blends has also recently been found in PPV blends with sol-gel formed silica, studied in collaboration with Prof. P. Prasad. In this case advantage is again taken of the mutual solubility of the precursor polymer with (in this case) the TMeOS precursor of the silica. Under optimal conditions PPV-silica blends were produced over a wide range of compositions with excellent wave guiding characteristics and the high $\chi^{(3)}$ characteristic of PPV. This approach is being extended to other blends.

**Progress Report 1990 OGGAMS Meeting
Keswick, Cumbria, England
September 5-7, 1990**

**Functional Polymers and Guest-Host Polymer Blends
for Optical and Electronic Applications**

Contract F49620-87-C-0111

Graham Williams, Professor of Chemistry, University College of Swansea, SA2 8PP, in collaboration with **Professor F.E. Karasz**, University of Massachusetts, and **Dr. G.S. Attard**, University of Southampton, U.K.

Introduction

There is considerable interest at the present time in synthesizing and investigating the physical properties of organic multi-functional polymer materials which may find application for high-density optical information storage, for non-linear optics or as passive or active optical elements (e.g., diffraction gratings, optical waveguides, Fresnel zone plates, transient phase gratings, optical modulators). The materials should possess good optical and mechanical properties, should exhibit reproducible behaviour and should retain the particular function (e.g., second harmonic generation (SHG) of laser light) for long periods of time. The present research has been concerned with studying certain physical properties of novel liquid-crystalline (LC) side chain polymers and guest-host polymer systems in order to obtain a fundamental understanding of their properties in terms of physico-chemical principles. The knowledge thus gained is essential if future devices based on materials of this kind are to have the desired properties and are to function in a controlled and reproducible manner.

Aims of Research

To study the dielectric, electrical and optical properties of novel LC side chain polymers and guest-host polymer materials. One aspect of the work involves a study of the macroscopic alignment behaviour of the LC polymers when they are subjected to different electrical/thermal treatments. The alignment behaviour is monitored in the optical microscope but we have used dielectric relaxation spectroscopy to monitor, and determine quantitatively, the nature and extent of macroscopic alignment, using methods we have developed theoretically and demonstrated experimentally [1,2]. The dielectric spectra for samples of different macroscopic alignment (homeotropic, planar, intermediate) are very different. The analysis of such spectra gives information on the dielectric relaxation functions and hence the anisotropic reorientational motions of the mesogenic groups in the LC state. The kinetics of alignment and disalignment processes in the LC polymer films which were subjected to electrical/thermal treatments can be followed using dielectric relaxation spectroscopy and the relationships between the alignment behaviour and the optical properties of the films can be investigated. The electrical poling of aligned LC polymer films provides a means of forming a material which may be used for SHG of laser light. One aim was to study the retention of poling in different materials. Further work involved a study of amorphous materials which contain functional groups attached to the chain or as guest molecules. In addition, studies were made of the electrical conductivity of Iodine-doped *cis* 1:4 poly(isoprene) (natural rubber).

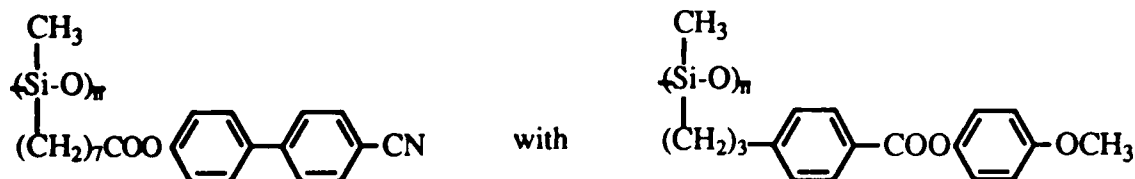
Experimental

A system capable of measuring the dielectric and electrical properties of organic materials over a range of frequency (10 - 10^5 Hz) and temperature has been established at Swansea with the aid of the Grant. Computer programs, developed in-house, allowed measurements to be made semi-automatically. Samples of LC polymers, 5 - 100 μm thick were subjected to directing electric fields using a power source built in-house which operates in the ranges dc to 300V , 5 Hz to 300 kHz, thus allowing different macroscopic orientations of a LC polymer film to be prepared for a given sample. A programmable hot-stage on a polarizing optical microscope was modified in order to incorporate a dielectric cell, thus allowing dielectric/electrical experiments and optical studies to be made simultaneously and provided a direct link between the state of alignment of a material and its optical properties. The optical textures could be recorded either with a camera or a CCTV/VCR programmable system purchased through the Grant. The dielectric properties at ultra-low frequencies (10^{-1} to 10^{-4} Hz) and thermally-stimulated currents from poled films (electrets) were measured using additional equipment.

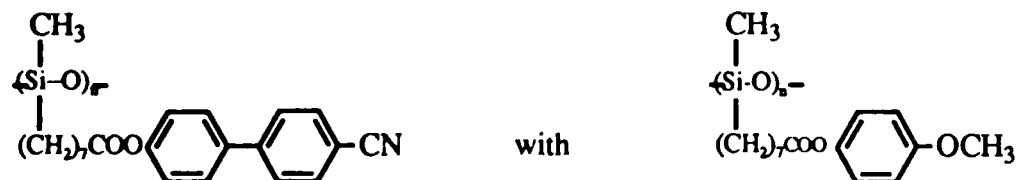
Materials

A number of LC polymer materials were investigated and included the following:-

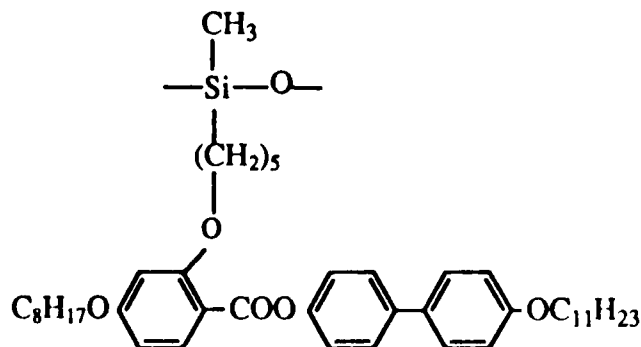
1. S16. Copolymer (50:50). T_g 16°C ; T_c 117°C



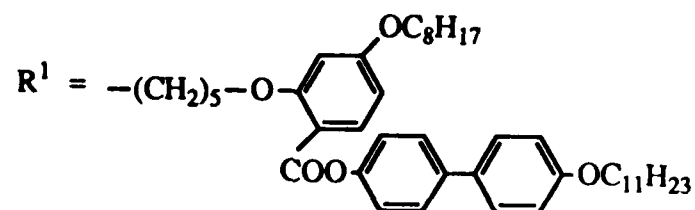
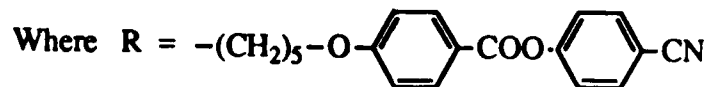
2. S15. Copolymer (50:50). T_g -6°C ; T_c 74°C .



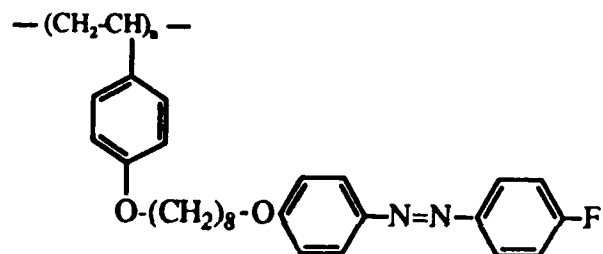
3. D6. Polymer with transverse LC group. T_g 9°C ; T_c 61°C .



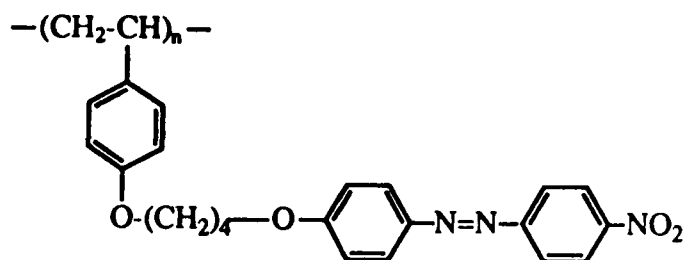
4. JSH. Copolymer with longitudinal and transverse LC groups. T_g 6°C; T_c 120°C.



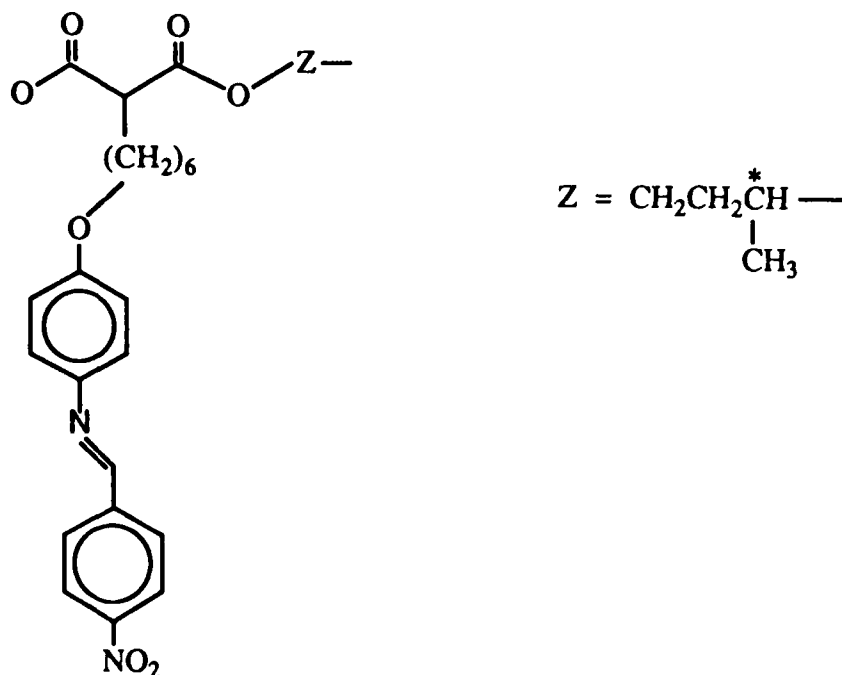
5. JSD2. Photoactive polymer. T_g 55°C; T_c 117°C.



6. GA2. Photoactive polymer. T_g 70°C; T_c 155°C.



7. Chiral-nematic polymer. T_g 5°C; T_c 51°C.



Materials S15 and S16 were provided by Dr. Matsumoto of Kuraray Ltd, D6 and JSH by Prof. Gray and Dr. Lacey of Hull University, JSD2, GA2 by Dr. Attard of Southampton University and the chiral nematic polymer (7) by Prof. A.C. Griffin of the University of Southern Mississippi.

Results and Discussion

Methods were developed which allowed all LC polymers to be aligned macroscopically. All materials could be aligned by cooling from the melt in the presence of a strong low frequency a.c. voltage. Some polymers, D6, JSH, polymer 7, could also be P-aligned by cooling in the presence of a strong high-frequency a.c. voltage. Only polymers D6, JSH and polymer 7 could be aligned $H \leftrightarrow P$ directly for samples in the LC state using high or low frequency voltages. As one example of our extensive data, figure 1 shows the dielectric loss spectra for H and P aligned samples of JSH compared with that for an unaligned sample. The loss spectra are very different and it is evident that the dielectric method provides a means of determining the nature and extent of alignment of intermediately and aligned materials. By measurement of the real or imaginary parts of the complex dielectric permittivity $\epsilon(\omega)$ for a sample, its degree of alignment may be determined as the director order parameter S_d using the relation

$$\epsilon(\omega) = (1 + 2S_d) \cdot \epsilon_{\parallel}(\omega) / 3 + 2(1 - S_d) \cdot \epsilon_{\perp}(\omega) / 3 \quad (1)$$

where $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the principal permittivities of the dielectric tensor and are obtained from measurements of the H and P samples respectively. S_d is equal to 1, 0, $-1/2$ for H, P and U samples, respectively. Hence S_d can be determined for different samples as they align or disalign in response to the application or removal of electric fields or by surface forces. As one illustration, figure 2, shows a family of loss curves for a sample of D6 which was prepared in different states of alignment. The continuous curves were calculated using eqn. 1 for different values of S_d .

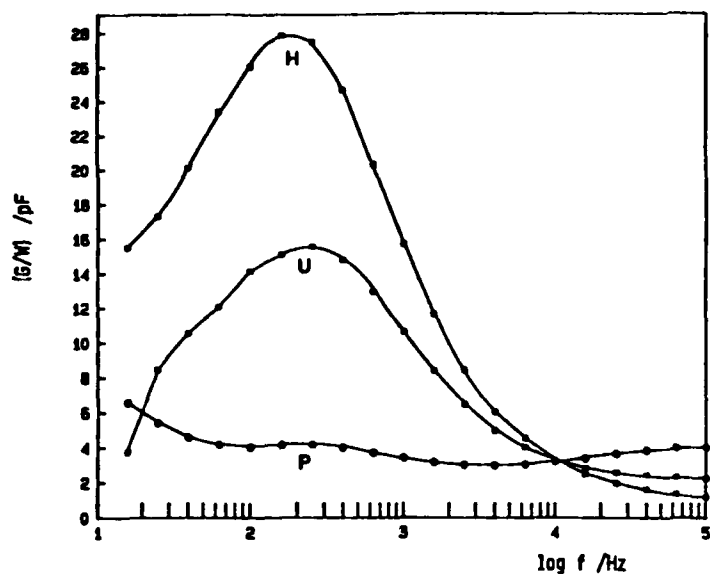


Figure 1. Dielectric loss spectra for homeotropic, planar and unaligned samples of JSH at 70°C. Note the isosbestic point at 10^4 Hz.

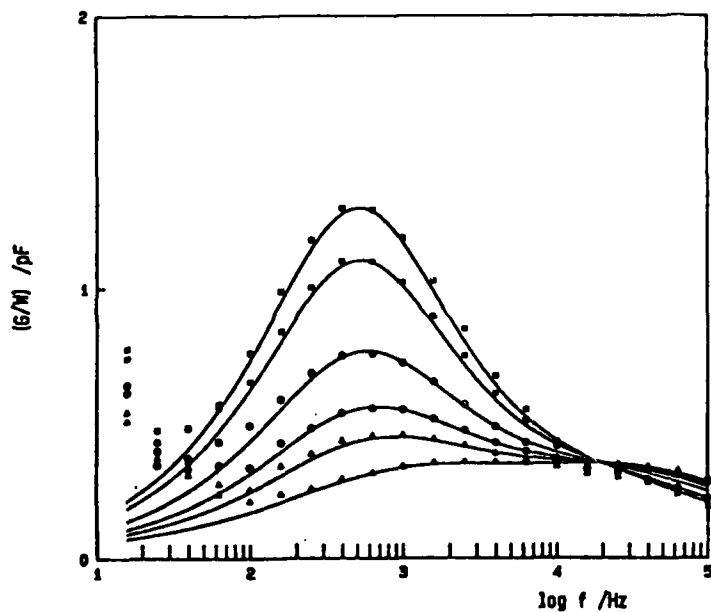


Figure 2. Dielectric loss spectra for a sample of D6 at 52°C in different states of macroscopic alignment. The continuous curves correspond to fits using eq. 1 with S_d equal to 1.0, 0.71, 0.31, -0.15, -0.30 and -0.50 ($\square$, $\blacksquare$, $\circ$, $\bullet$, Δ , $\blacktriangle$, respectively).

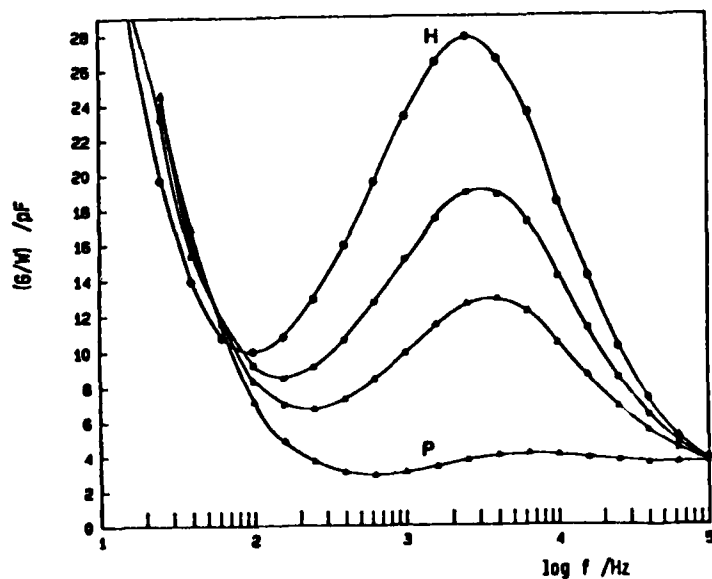


Figure 3. Dielectric loss curves for a JSH sample at 70°C; Freshly prepared in the P-aligned state (Δ), after 3 hours ($\blacktriangle$) and 16 hours ($\blacksquare$) following removal of the directing field. Also shown is the curve for the fully H-aligned sample ($\bullet$)

The detailed results of all our studies will not be given here but may be summarized as follows:-

The dielectric loss spectra for JSD2 and GA2 were obscured at low frequencies by space-charge-related conductivity. This was reduced significantly by application of a d.c. field to the melt sample which sweeps the extraneous ions to the electrodes. These ions are rendered ineffective on cooling into the LC state. This electrical 'cleaning' of the sample has an advantageous effect on the alignment behaviour in the LC state and improves the poling behaviour through a reduction of the space-charge contribution.

Bulk and surface induced disalignment of LC polymers may be followed using dielectric relaxation spectroscopy. Figure 3 shows the variation in loss spectrum as a sample of planarly-aligned JSH polymer spontaneously realigns the H-aligned state due to surface forces at the electrodes. Such changes have been monitored simultaneously in the optical microscope. The ability to align materials varies systematically with chemical structure and the thermal/electrical conditions. Electrohydrodynamic instabilities, due to dielectric heating at the 'cross-over' frequency could be generated in samples in a reproducible way. These anomalies could be avoided and the thermal/electrical conditions could be arranged so that samples of optimized alignment and optical quality could be prepared. S15, S16, JSH and 7 possessed excellent alignment behaviour. D6 disaligned readily, following preparation in H or P aligned states, being due to bulk disalignment of the LC phase involving the release of the field-induced strain in the backbone and spacer units. JSD2 and GA2 exhibited large low frequency space-charge dielectric loss and were particularly difficult to align, although electrical cleaning led to a substantial improvement in the alignment behaviour.

Poled samples of the different LC polymers were prepared by first aligning a sample homeotropically and then poling just above T_g , followed by cooling into the glassy LC state. All samples lost their stored electrical polarization when aged at room temperature, and the kinetics for the process has been investigated. Since SHG capability requires the poled electrets to be stable, methods are being explored which will prevent this aging process, especially for JSD2, GA2 and 7.

The dielectric loss curves for the H and P aligned samples of the different polymers have been analyzed in order to obtain, in each case, the four orthogonal relaxation modes which arise from the anisotropic motions of the dipole moment components $\mu_{\parallel}$ and $\mu_{\perp}$ of the mesogenic group with respect to the LC local director n [2,3].

A part of the results for JSH are being published [4,5] while those for D6 have been submitted [6]. Further papers concerned with the other LC polymers given above are in preparation. In addition, work with guest-host polymers, including iodine-doped *cis* 1:4 polyisoprene, not described here due to lack of space, is being written for publication.

Further Work

In a recent proposal to AFOSR the research teams at Amherst, Southampton, Tokyo and Swansea have identified target areas in which they can make significant and original contributions. The Swansea component will involve work with functional side chain polymers (amorphous and/or liquid crystalline) for integrated optical circuits, and for optical processing and for digital, analogue, and holographic information storage. The new work, which will be both experimental and theoretical, will emphasize the multi-functional

nature of the new materials to be investigated, e.g., each of the polymers JSD2 and GA2 above are multi-functional in the sense that they are (i) liquid crystalline, (ii) photoactive (photobleachable) and (iii) capable of NLO such as SHG and third harmonic generation.

Acknowledgements

We thank Dr. Donald R. Ulrich for his support and encouragement of our research work. We gratefully acknowledge the support of the AFOSR(SDIO/IST) through Contract F49620-87-C-0111.

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**REPORT ON SUBCONTRACT UNDER PRIME CONTRACT
F49620-87-C-011**

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**[1] INVESTIGATION OF THE ROLE OF PHASE ULTRASTRUCTURE IN THE
PERFORMANCE OF $\chi(2)$ N.L.O. SIDE-CHAIN POLYMERS**

Synthesis:

• In the initial stage of the research program we devised and optimised a protocol for the synthesis of multifunctional side-chain polymers which enabled us to routinely prepare high purity materials (low ionic impurities) and to achieve batch reproducibility. Our choice of synthetic intermediates and synthetic strategy allows the easy and low-cost preparation of homologous series of functional polymers. This development was central to our subsequent ability to investigate detailed structure property relationships in these complex systems.

Materials:

• Although we have synthesised some poly(acrylate) systems, the bulk of our research has been on poly(styrene) derivatives. This polymer backbone was chosen so as to confer a high glass-transition temperature to the resulting multifunctional polymers. We regarded a high T_g as an important material parameter since it potentially enhances device reliability and lifetime. Investigations of the role of sub- T_g motions and volume relaxation type effects in the ageing of poling, and consequent reduced n.l.o. performance are in progress in collaboration with Prof. G. Williams at Swansea.

• The manner in which n.l.o. chromophores assemble in the fluid state has important implications on the processing of the materials and on their performance. In order to achieve an understanding of the relative contributions of the different structural components that make up a side-chain polymers to the phase ultrastructure, we carried out a systematic investigation of several polymers with different chromophores having high second order hyperpolarizabilities. By studying homologous series in which the length of the flexible spacer chain is varied from 3 to 12 carbon atoms we were able to explore the entire spectrum of transitional behaviour for a given material.

- We also studied blends of selected side-chain polymers with low molar mass mesogens in order to obtain insights into the potential of such systems for enhanced processing of high quality n.l.o. thin films.

Results:

- The clearing temperatures of the liquid crystalline materials we prepared were found to be very sensitive to relatively minor changes in the chemical structure of the n.l.o. chromophore. For example, changing the terminal polar group on an azo chromophore from nitro to fluorine resulted in a 30-50°C drop in the clearing temperature. The information obtained from a comparative study of materials with different n.l.o. chromophores is essential for the rational design of multifunctional polymers whose transitional properties are optimised with respect to processing.

- In Figure 1 we show the transitional behaviour of two poly(styrene)-based homologous series which illustrate the fundamentally different behaviour of materials with large ground-state dipole moments (e.g. chromophores with cyano- or nitro- terminal groups) and materials with lower ground-state dipole moments (e.g. materials with fluoro- or alkyl- terminal groups). These differences are also reflected in the thermodynamics of the order-disorder transitions in the systems investigated.

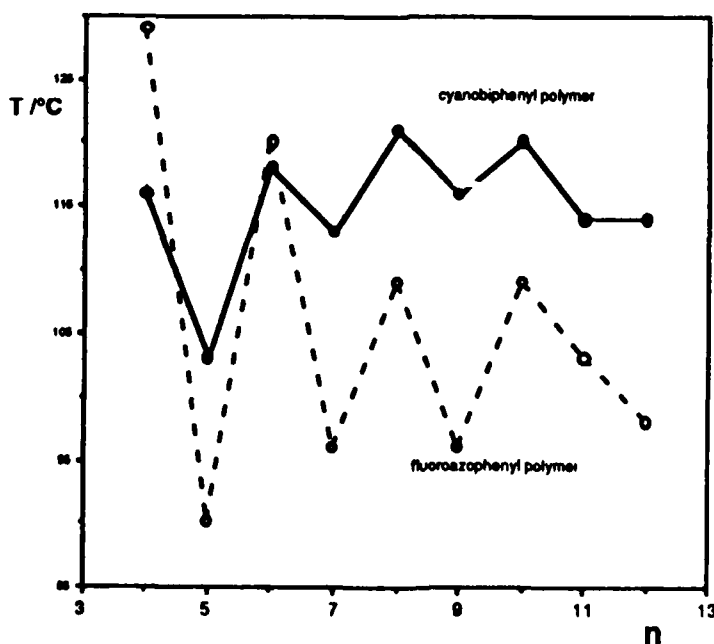


FIGURE 1

- The phase ultrastructure was also found to be critically dependent on the choice of n.l.o. chromophore. Chromophores with large ground-state dipole moments resulted in polymers exhibiting interdigitated mesophases with a high degree of dipole-dipole correlations. Conversely, materials consisting of

relatively weakly polar chromophores tend to form highly interdigitated mesophases in which the dipole moments of neighbouring chromophores are largely uncorrelated. These considerations are illustrated schematically in Figure 2.

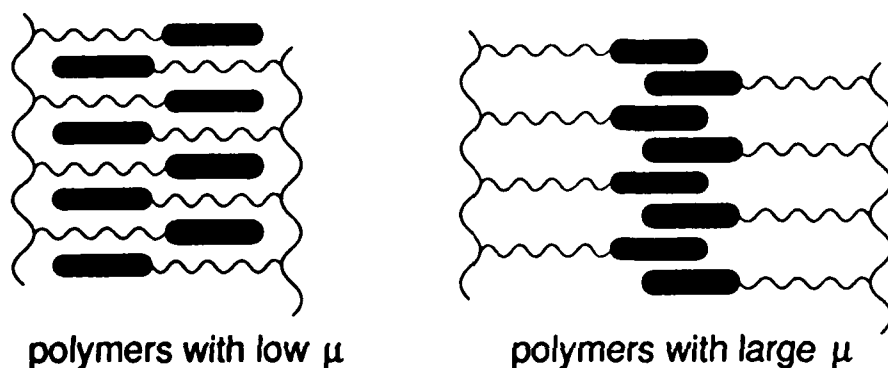


FIGURE 2

- In order to establish a coherent framework within which to analyse dipole-dipole correlations we developed a new statistical thermodynamic theory, based on pair orientational interaction energies, which relates the macroscopic second order susceptibility to the molecular second order hyperpolarizability. In our theory the dipole-dipole correlations occur explicitly, and this has enabled us to assess their detrimental impact on the efficiency of poling in both liquid crystalline and amorphous systems. The torque resulting from strong polar interactions may also provide a mechanism which drives the sub- T_g relaxation of the polar order that occurs in many proposed $\chi^{(2)}$ polymers.

- Our research strategy which combines synthesis, materials characterisation, and mathematical modelling has enabled us to embark on the rational design of new amorphous and liquid crystalline homopolymers, copolymers, and polymer-monomer blends in which dipole-dipole correlations are minimised. We anticipate that these materials will show the high $\chi^{(2)}$ performance and operational stability required by device engineers.

[2] EXPLOITATION OF LIQUID CRYSTALLINITY IN THE PROCESSING OF POLYMERS WITH ANISOTROPIC ULTRA-STRUCTURE AND OF BULK SINGLE CRYSTALS FOR N.L.O. APPLICATIONS

Design concepts :

- The principal design concept underlying this novel class of materials is the use of liquid crystallinity as an aid to processing new materials. This can be achieved in two ways. Suitable monomers could be designed which contain readily polymerisable units and which exhibit highly ordered mesophases. The response of these fluid phases to magnetic, flow, or electric fields can then be used to prepare monodomain samples, following which the monomers are polymerised in situ, by, for example, uv radiation. The resulting polymer network will have the orientationally anisotropic ultrastructure of the parent mesophase, and cannot be prepared by conventional polymerisation techniques. Alternatively, liquid crystalline monomers can be designed so that they exhibit a sequence of liquid crystalline phases of increasing dimensionality as a function of decreasing temperature. By using magnetic fields it would be possible to prepare macroscopically aligned mesophases which on cooling form a net-shape single crystal of high optical quality. The advantage of these approaches to new n.l.o. materials is that they are based on monomers which can be synthesised with a degree of chemical purity which is impossible to achieve in most side-chain polymers.

Results :

- A number of monomeric rod-like mesogens containing diacetylenic units have been synthesised which exhibit highly ordered liquid crystalline phases. Exposure of these mesophases to uv radiation results in the formation of an anisotropic poly(diacetylene) network which cross-links the mesogenic groups. The polymerisation does not lead to any significant disruption to the mesophase ultrastructure. Attempts to obtain monodomains by using magnetic or electric fields are currently in progress.
- We have synthesised a new class of polymerisable transition metal containing discotic mesogens which can be processed from their discotic melts into highly ordered single crystal fibres of any length, and whose diameter can be controlled in the range between 6 μ m and 150 μ m. The fibres have excellent optical homogeneity and surface smoothness as illustrated by Figure 3.

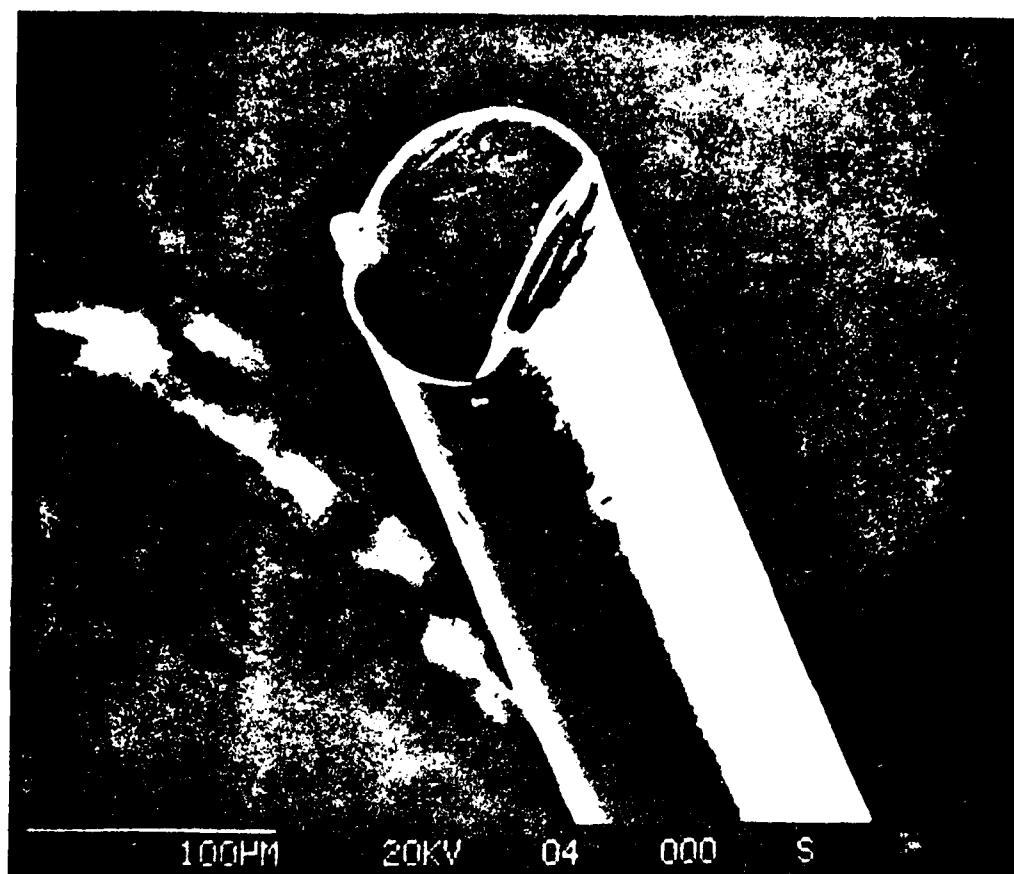


FIGURE 3

Post-processing uv-induced polymerisation of these fibres has been demonstrated to occur without disruption to the crystal ultrastructure. The resulting fibres have a $\chi^{(3)} \sim 7 \times 10^{-12}$ esu as a consequence of a highly ordered poly(diacetylene) network. We have conducted extensive X-ray diffraction investigations on these materials in order to understand the ultrastructures of the mesophase and of the solid state. Research on extending this approach to materials with larger $\chi^{(3)}$ values is in progress.

- We have discovered that a number of dimeric rod-like mesogens with large second order hyperpolarizabilities can be transformed into net-shape highly oriented crystals by cooling in a magnetic field > 1.2 Tesla. By a judicious choice of chemical structures we have been able to minimise the extent of dipole-dipole association in the mesophases. We are currently engaged in an attempt to process non-centrosymmetric thin-film single-crystal planar waveguides by using the combination of a magnetic field and a poling field.

Thin Films of Functional Polymers

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ABSTRACT: It was found that acetylated poly(vinyl alcohol)s(PVA) having long alkyl side chains form stable monolayers at air/water interface which were easily deposited onto various substrate as multilayers thin films which had regular orientations of aligned acetylated PVA molecules.

Non-linear optically (NLO) active moieties such as p-nitroaniline were incorporated into the acetylated PVA which was spread onto water so as to form monolayers with well-oriented structures. The monolayer film of the acetylated PVA having NLO moiety was deposited onto quartz as multilayers thin film which exhibited a strong activity of second harmonic generation (SHG).

INTRODUCTION

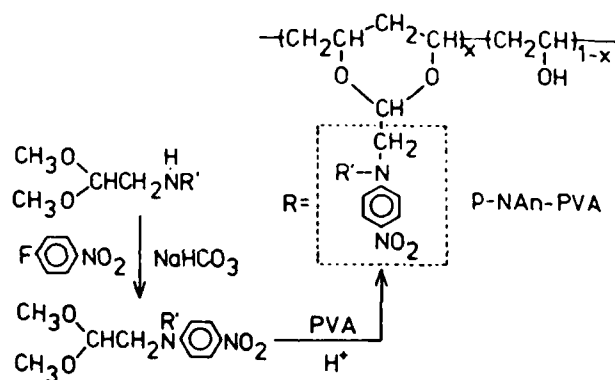
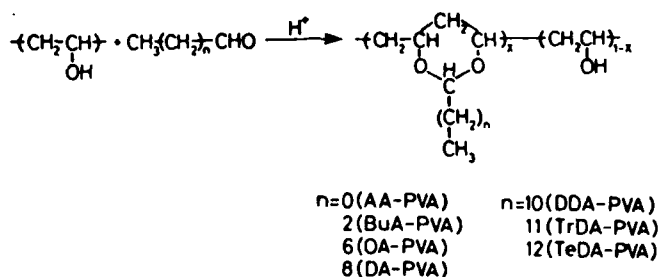
It is well known that the Langmuir-Blodgett method is one of the best methods to obtain very thin and uniform films that can be controlled to molecular dimensions. Various kinds of amphiphilic molecules such as long chain fatty acids or dye-stuffs with long alkyl chains are known to form a stable monolayer at air/water interface with regular molecular orientations. However, these thin films are mechanically weak because the aligned molecules are not covalently bonded together. A great interest has been focused on the possibility of creating oriented LB films from synthetic polymers.

Organic NLO active materials are known to exhibit very strong activities for SHG or third harmonic generation (THG) in comparison with inorganic materials, but they are based on a single crystal or electrically poled polymers having NLO active moieties which have various problems of processability or stability of poled structures of NLO groups within the polymers. The SHG activity requires a noncentrosymmetric and highly polar structure in which donor and acceptor groups are uniformly oriented.

It was expected that acetylated PVA having long alkyl chains might have an amphiphilic character owing to the existence of both hydrophilic alkyl and hydrophilic OH groups so that the acetylated PVA might form a stable monolayer at air/water interface by means of the LB method, which could be deposited onto various substrates as multilayers thin film with highly oriented structures. Moreover, it was expected that various NLO active moieties could be incorporated into the acetylated PVA which might form a stable monolayer, so that SHG active thin films would be obtained.

RESULTS AND DISCUSSION

Following acetalized PVAs were synthesized by reacting PVA with aldehydes in benzene in the presence of catalytic amount of hydrochloric acid. Acetalized PVA having NLO active moieties were synthesized by the acetal exchange reaction as shown below:



Properties of the acetalized PVAs are summarized in Table I which shows that acetalized group content was in the range of 60 to 80 mol% and glass transition temperatures (T_g) decreased with increasing length of alkyl groups. No significant change of decomposition temperatures occurred.

These acetalized PVAs were spread on water in 0.01wt% benzene solution to form monolayer thin film at air/water interface. The monolayer film could be deposited onto quartz plate as multilayers thin films as shown in Fig. 1.

1.

Table I Properties of Acetalized PVA			
Polymer	X(mol%) ^{a)}	T _g (°C) ^{b)}	T _d (°C) ^{c)}
AA-PVA	61	116.0	340
BuA-PVA	72	60.0	317
OA-PVA	75	25.0	337
DA-PVA	74	21.5	337
DDA-PVA	73	13.0	350
TrDA-PVA	78	3.0	337
TeDA-PVA	76	4.8	347

a) Determined by elemental analysis.

b) Measured by DSC.

c) Measured by Tg-DTA.

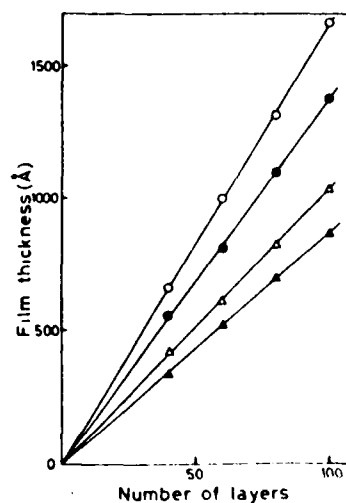
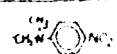
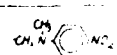


Fig 1 Effect of methylene length of acetal side chain on film thickness as measured by ellipsometry. (○) TeDA-PVA, (●) DDA-PVA, (Δ) OA-PVA, (▲) BuA-PVA

Properties of acetalized PVAs having various NLO active groups are summarized in Table II in which the deposition conditions to obtain monolayer film are described together. Almost perfect monolayer thin film was obtained when a small amount of OA-PVA was added as a support, and the Z-type deposition of multilayer thin films was possible, which was very important to attain noncentrosymmetric structures of aligned molecules for the SHG activity.

Table II Properties of Acetalized PVA

	side chain	X	T _g (°C)	Limiting area (Å ² /unit)	Addition ratio of OA-PVA	Z-type Deposition ratio
OA-PVA	$-(CH_2)_4-CH_3$	0.819	34.0	33.61	—	—
BA-PVA		0.775	—	30	—	—
p-NBA-PVA		0.419	135.7	—	5wt%	0.62
m-NBA-PVA		0.506	98.2	11.47	15wt%	0.30
p-NAn-PVA		0.88	73.8	4.41	1wt%	0.17
DN-PVA		0.591	86.4	2.75	1wt%	0.41

*1 Reported value

*2 Z-type deposition ratio: $\frac{\text{deposition ratio during down process}}{\text{deposition ratio during up lift process}}$

Fig. 2 indicates electrical properties of the thin films of the acetalized PVAs in terms of temperature dependences of logarithms of electrical conductivities. In case of number of layers N was over 5, the conductivity of the thin films was in the order of 10^{-16} – 10^{-17} S cm⁻¹, which was similar to that of the film prepared by conventional spin-coating method. On the other hand, the conductivity of monolayer thin film of OA-PVA increased to 10^{-13} S cm⁻¹, possibly owing to a tunneling current.

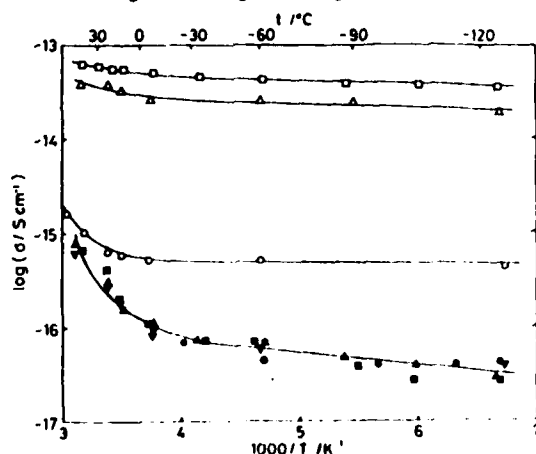


Fig 2 Temperature dependence of conductivity for Al/N-OA-PVA/Al.
(○) N=1, (Δ) N=2, (□) N=4, (▴) N=5, (◐) N=6, (●) N=8, (●) N=10

X ray analyses of the LB films obtained from the acetylated PVAs having NLO active moiety indicated a well-ordered structure when they were deposited onto quartz plate as multilayers thin films. When p-nitroaniline (p-NAN) was incorporated into the acetylated PVA and it was spread on water with a support of stearamide (1wt%), it formed a perfect monolayer which could be deposited as Z-type thin films on quartz plate. The structure of the NLO active PVA is illustrated in Fig. 3.

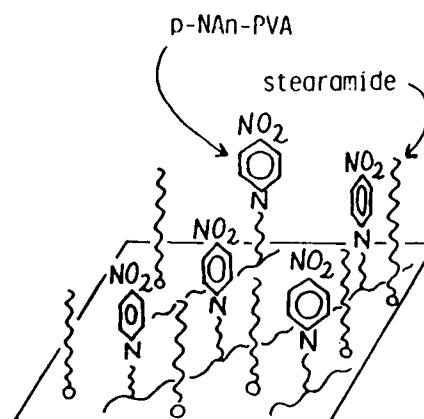


Fig.3 LB structure of p-NAN-PVA mixed with stearamide

The SHG activity of the multilayers thin films of p-NAN-PVA was measured by means of Maker-fringe method using Q-switched Nd:YAG laser operating at $1.064 \mu\text{m}$ with polarized beam. Fig. 4 indicates the fringe pattern of the thin film of p-NAN-PVA. A strong fringe pattern was observed in pp direction in comparison with ps direction. The fringe pattern of pp beam was 7 times larger than that of ps direction, indicating that the SHG activity was dependent on the orientation of the NLO active moiety in the acetylated PVA. No significant relaxation of the fringe pattern was observed, possibly owing to strong hydrogen bonding between acetal and hydroxyl groups.

These results indicate that the acetylated PVAs having NLO active moiety are quite stable to attain a high SHG activity and further research will be carried out.

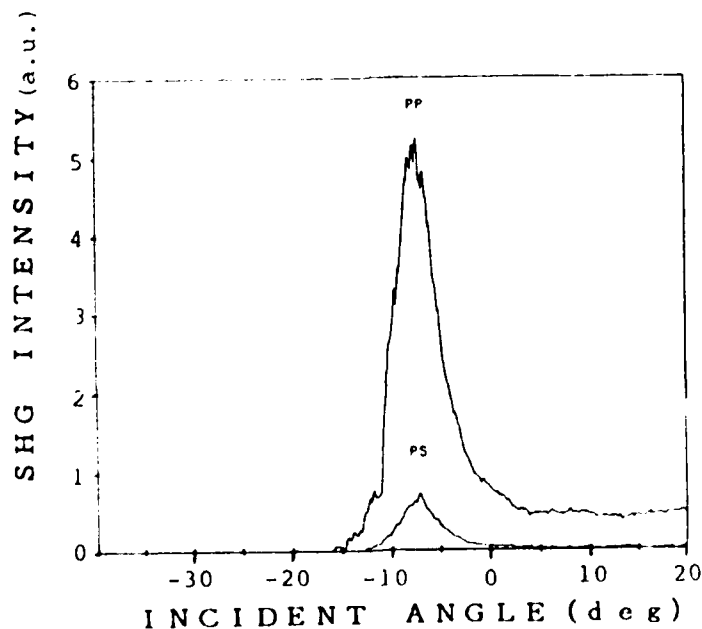


Fig. 4 SHG of p-NAN-PVA (slit type substrate)

OVERVIEW

MULTIFUNCTIONAL MOLECULAR MATERIALS FOR PHOTONICS AND NONLINEAR OPTICS

by

P. N. PRASAD

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The goal of our program is development of chemically processed novel composite structures for applications in the newly emerging field of photonics and nonlinear optics. In our photonics research laboratory, we have developed a comprehensive research program which focuses on the following areas. (1) Theoretical modeling using ab initio and semi-empirical calculations coupled with experimental investigation of nonlinear optical behavior of sequentially synthesized chemical structures. This has the objective of identifying molecular building blocks with enhanced nonlinear optical response, (2) Use of orientation control and composite structures to introduce and optimize the necessary multifunctionality, (3) Experimental studies of nonlinear optical and electronic behavior using femtosecond pulses to investigate ultrafast switching and frequency shifting, (4) Investigation of device processes in optical waveguides and fibers; optical bistability for optical memory operation, and optical recording media.

During the past three years of support, we have achieved the following important goals:

- . Development of a new class of composite materials consisting of sol-gel processed inorganic glass (silica, V_2O_5) and a conjugated polymer (PPV) for applications in waveguiding for nonlinear optics (a patent filed).
- . Development of a new class of binary crystalline complexes for frequency doubling (patent filing procedure initiated).

- . A new nonlinear optical process in a hollow core silica glass fiber (filled with organic liquids) with potential applications in frequency shifting and broad band amplification.
- . Use of composite material for successfully demonstrating two dimensional grating formation.
- . Demonstration of power limiter behavior for sensor protection using a planar waveguide configuration.
- . Use of Langmuir-Blodgett films to make a surface plasmon electro-optic modulator.
- . Demonstration of a femtosecond optical gate using the polymer/silica composite.

Future plans, as proposed, will be focused on the development of composite structures to introduce multifunctionality. We plan to develop binary crystalline complexes, a new class of second-order nonlinear material, for efficient frequency doubling. We plan to fabricate electron donor-accepter Langmuir-Blodgett heterostructures and investigate the nonlinear optical response, photoconductivity and electrical conductivity. We also propose to investigate both the physics of the new nonlinear optical processes and its application using the organic liquid filled hollow core fiber. We propose to further explore the novel composite structures between a sol-gel processed inorganic oxide and a conjugated polymer. There are exciting possibilities in this class of materials, such as redox coupling of the two systems which can yield significant change in their nonlinear optical and electronic response. For this purpose new polymeric structures will be synthesized. In the current proposal, an active interaction with Professor Miyota at Tokyo University of Agriculture and Technology is also proposed. Professor Miyota is conducting topical research in the field of Langmuir-Blodgett films which would benefit us.

MULTIFUNCTIONAL MATERIALS FOR PHOTONICS AND ELECTRONICS

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The objective of our research is to develop chemically processed multifunctional heterostructures optimized for the newly emerging technologies in the field of photonics and electronics. We have developed a comprehensive program in our Photonics Research Laboratory where the strategy for optimization of the molecular materials includes four principal stages: (i) optimization at the molecular level, (ii) optimization at the bulk level, (iii) experimental studies, and (iv) investigation of device processes. This comprehensive approach with an interactive feedback between different stages has been the key to the great success we have achieved. We describe below the success we have achieved at each stage.

(i) Optimization at the molecular level:

Our strategy for optimization at molecular level focuses on identification of functional molecular units with enhanced nonlinear optical response which provides key functions for photonics. Two approaches have been used: (a) Theoretical modeling using AB-initio and semi-empirical quantum chemical calculations and (b) molecular design and synthesis of sequentially built and systematically derivatized structures followed by experimental study of their nonlinear optical response. We have made significant progress in each approach. We have used time dependent coupled perturbed Hartree-Fock method at the ab-initio level to compute the nonlinear optical coefficients at different optical wavelengths. However, the ab-initio calculations which are exact require a large computational time even on a supercomputer, which we have used, and are not practical for large molecules and polymers. Therefore, we are developing an approximate method, a semi-empirical method, specifically INDO, to the level of sophistication where it can be reliably used to predict the nonlinear optical response of a large molecule or a polymeric structure. We have synthesized a large number of sequentially built and systematically derivatized organic and organometallic structures and investigated their nonlinear optical response. These studies have yielded some very valuable information on functional groups which may enhance nonlinear optical response and also improve processibility.

(ii) Optimization at the bulk level:

Here our goal is to optimize for necessary multifunctionality by control of design at the bulk level. We have focused on design which would enhance nonlinear optical response, produce low optical loss, and introduce other necessary bulk properties such as mechanical strength, environmental and thermal stability and high optical damage threshold. The two broad approaches taken are: (a) orientation control for enhanced response. For this purpose we have used successive monomolecular layer deposition of Langmuir-Blodgett film heterostructures and electric field poling of bulk structures for second-order nonlinear material; and stretch orientation of polymeric structures for third-order nonlinear optical material. (b)

Composite heterostructures. We have developed several new classes of composite structures which are extremely promising.

We have developed new heterostructures which are binary crystalline complexes that show second-order nonlinearity ranking among the highest. These crystalline complexes do not possess the structural features that have been used in the past for the design of second-order nonlinear material. We have obtained highly efficient phase-matched frequency doubling in our heterostructures.

We have prepared, to our knowledge, the first compatible blend between an inorganic polymer, such as silica glass or V_2O_5 gel, and a π -conjugated optical nonlinear polymer, poly (p-phenylene vinylene), homogeneously mixed over large composition ranges. This composite material was prepared by combining sol-gel processing techniques applicable to the silica glass with the preparation of the organic polymer from a water/alcohol soluble sulfonium salt precursor. These composite materials combine the high $\chi^{(3)}$ of the conjugated polymer with the extremely low optical loss in an inorganic glass.

(iii) Experimental Studies

Here our goal has been to use a number of experimental techniques to understand the mechanisms of electronic and nonlinear optical response. A major strength of our program is the availability of the large number of techniques using the most sophisticated state-of-the-art femtosecond lasers to probe the details of nonlinear optical response down to 50 femtosecond resolution. A combination of these techniques have permitted to separate the resonant response created by a real excitation from a purely electronic off-resonant response, determine the sign of the nonlinear coefficient, resolve its real and imaginary components, determine its time-response under different experimental conditions, and evaluate the role of multiphoton absorptions. All of these are important in relation to device processes. For third-order nonlinearity, we have used a combination of degenerate four wave mixing, optical Kerr gate, and transient absorption coupled with optical waveguide studies.

(iv) Investigation of Device Processes

We have investigated many device prospects. The sol-gel processed inorganic oxide: PPV composite has excellent optical quality and excellent surface finish for application in optical recording. Using a 1 μ m thick film of silica: PPV composite on a glass substrate we have successfully fabricated a two-dimensional grating by crossing femtosecond pulses at 602 nm.

Using an optical waveguide configuration, we have obtained a power limiter behavior in the optical output-input relation, useful for broadband sensor protection. With a considerable effort in material processing, we were successful in forming a low loss planar optical waveguide of a $\chi^{(3)}$ material of a soluble polydiacetylene, poly-4-BCMU for this purpose. 100 picosecond pulses at 1.06 μ m were coupled into the film using a grating coupler at an optimum coupling angle determined by the refractive index of the waveguiding film. The output from the waveguide is decoupled using another grating. As the input intensity is increased, the output from the

waveguide increases initially. But as the refractive index of the film for a third-order nonlinear optical material is intensity dependent, the coupling is not optimum at high intensity. As a result, the output power levels off because of inefficient coupling at high intensity. The observed power limiter behavior is shown in Figure 1.

We have also used a film of the silica: PPV composite material to demonstrate femtosecond optical gate action. The schematics of the optical gate operation and the observed optical gate output are shown in Figure 2. We have used 60 femtosecond pulses from an amplified colliding pulse mode-locked laser at a repetition rate of 8 kHz. The beam is split into two portions: a weak probe signal and a strong gating (control) pulse. The probe pulse passes through a polarizer (1) and then through the film and finally through a cross-polarizer (2). In the absence of the control pulse, no output from the gate is produced. The presence of the strong control pulse creates an optically induced birefringence so that the polarization of the probe signal is now rotated which produces a signal output through the cross polarizer. In other words, the control pulse acts as an optical valve which opens the optical gate. By delaying the probe pulse with respect to the control pulse one can get information on the time response of this optical gate. The signal output from this gate plotted as a function of the time delay is also shown in Figure 2. One can see that the response time is in femtoseconds.

Frequency shifting, optical amplification and pulse shaping will play important roles for optical processing. We have observed novel nonlinear optical phenomena in an organic liquid core hollow fiber which can conveniently be used for optical amplification and pulse shaping. By using a long interaction length (250 cm) provided by the fiber we have observed novel superbroadening ($> 200 \text{ cm}^{-1}$) of stimulated scattering added on the Stokes side of the pump (Rayleigh) line and the stimulated Raman scattering lines of several liquids (eg benzene) containing anisotropic molecules. To explain these effects, we have proposed a photon scattering model of Rayleigh-Kerr optical effect and Raman-induced optical Kerr effect.

For device applications, we have demonstrated the application of this broadening in high gain amplification of a broad band optical signal. For this purpose a hollow core fiber system filled with liquid benzene was used. Using 4 picosecond dye laser pulses as the pump source, stimulated amplification of the accompanying $\approx 550 \text{ cm}^{-1}$ broad spontaneous emission was achieved. The results are shown in Figure 3. Top: a strong laser pulse (532) is accompanied by a weak broad band (shown with a $\times 10^3$). Bottom: by passing this signal through a hollow core silica fiber filled with benzene, amplification of the broad background at higher power is revealed.

POWER LIMITER ACTION

poly 4BCMU OPTICAL WAVE GUIDE

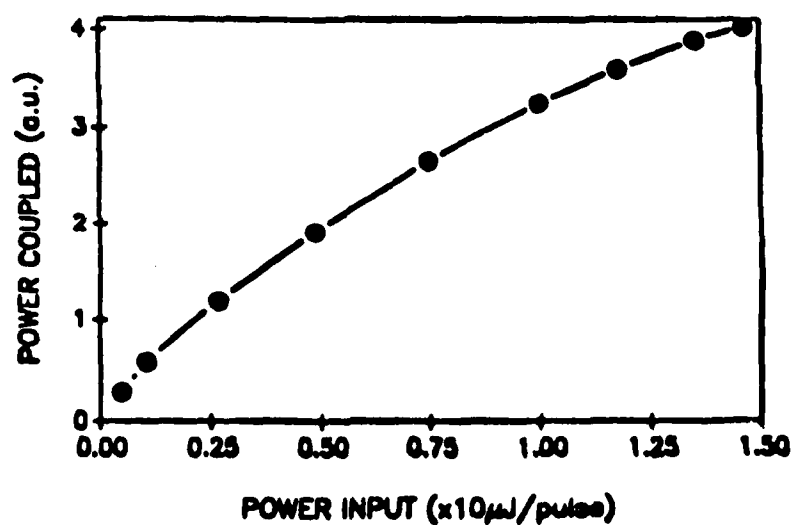


Figure 1

FEMTOSECOND OPTICAL GATE USING NOVEL SOL-GEL PROCESSED SILICA:PPV POLYMER COMPOSITE

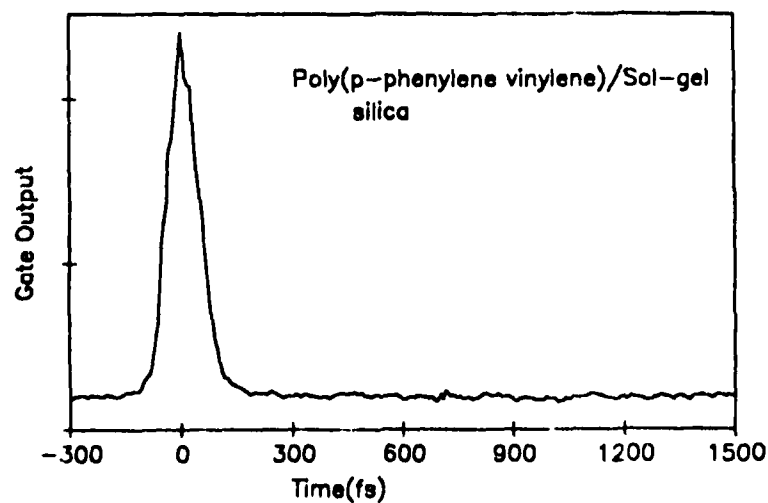
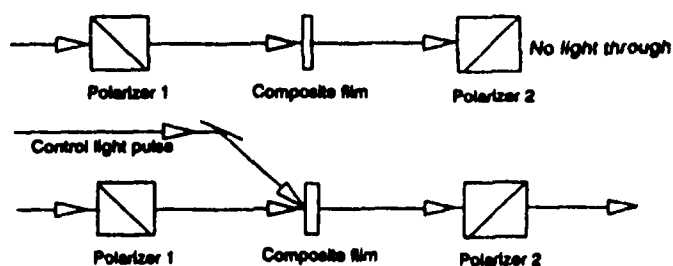


Figure 2

**AMPLIFICATION OF A BROADBAND OPTICAL SIGNAL
IN
AN ORGANIC LIQUID-CORE HOLLOW FIBER
USING
STIMULATED KERR SCATTERING**

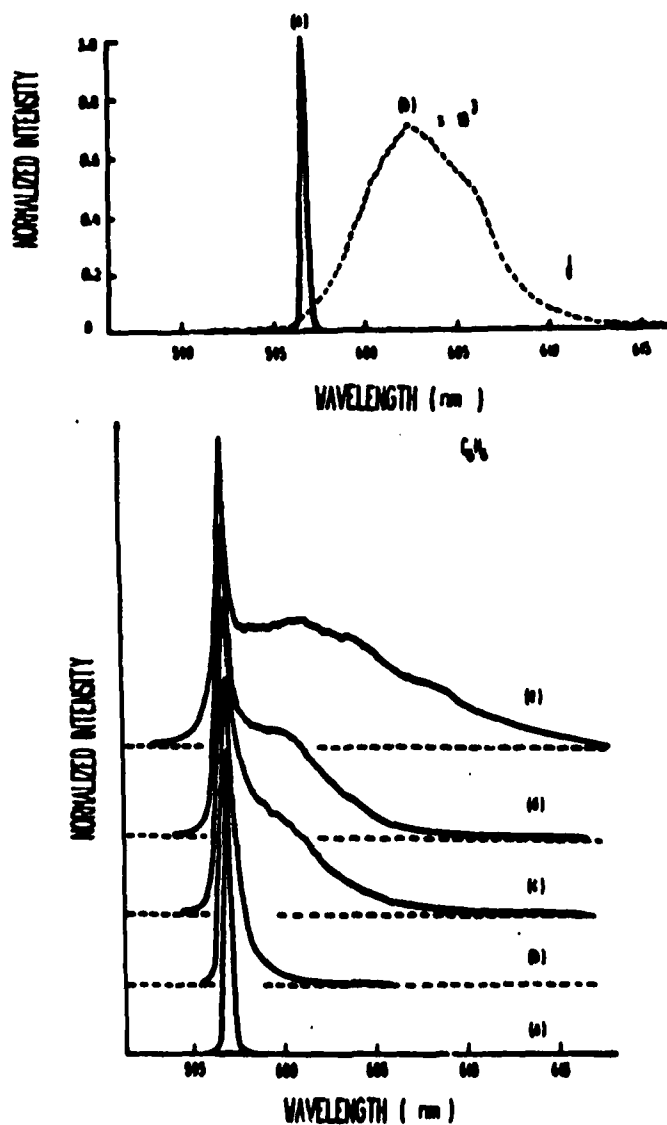


Figure 3

SECOND HARMONIC GENERATION PROPERTIES OF SOME COORDINATION COMPOUNDS BASED ON PENTADIONATO- AND POLYENE LIGANDS

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INTRODUCTION

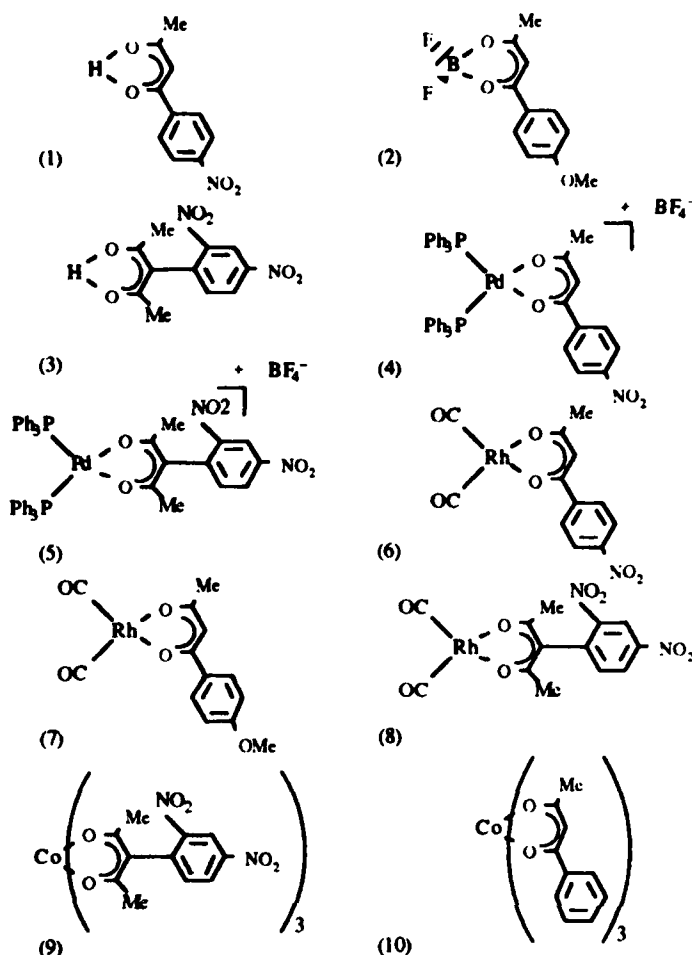
In recent years considerable success has been achieved in designing organic materials which display nonlinear optical properties^{1,2}. Furthermore, some attempts have been made to transfer these molecular design concepts to coordination and organometallic compounds.^{3,4} The results which have been achieved with substituted ferrocenes have been particularly promising.⁵

In this paper we describe the synthesis and characterization of substituted metal pentadionato-complexes which represented reasonable target systems for nonlinear optical systems. These complexes were chosen for the following reasons: (a) thermally stable pentadionato- complexes have been reported for the majority of metals; (b) the pseudo-aromatic nature of the metal pentadionato- ring can provide a range of derivatives via electrophilic substitution reactions and,^{6,7} (c) a wide range of ligands may be synthesized. Such complexes have been prepared and characterized by conventional analytical, spectroscopic and, in some cases, X-ray crystallographic techniques. Their nonlinear optical properties have been probed directly on powdered samples using a modification of the Kurtz powder second harmonic generation experiment and, less directly in solution, by solvatochromism measurements.⁸⁻¹⁰

Results and Discussion

Pentadionato- complexes with substituents at the 3 and 4 positions were synthesized using conventional techniques and some illustrative examples are shown in Scheme 1 as compounds (1) to (3).^{11,12} The coordination compounds (4) to (8) derived from these ligands, were synthesized by halide abstraction and ligand replacement reactions. The cobalt(III) pentadionato- complexes (9) and (10) were made directly from $\text{CoCO}_3 \cdot \text{H}_2\text{O}$, the ligand and hydrogen peroxide in aqueous solution.¹³ Compounds (4) to (8) have d^8 metals in square-planar environments and have been characterized by ^{31}P and ^1H n.m.r. spectroscopic studies. In addition the structures of (4) and (5) have been determined by single crystal X-ray structural determinations. These square planar complexes are yellow crystalline solids.¹⁴ The octahedral cobalt(III) complexes (9) and (10) are dark green crystalline solids and have been characterized by ^1H n.m.r. spectroscopy.

Pentadionato- complexes undergo electrophilic substitution reactions at the 3-position and this route has been used to synthesize the substituted octahedral complexes of cobalt(III) and rhodium(III) shown in Scheme 2.¹³ Compounds (12) to (14) have Cl , NO_2 and CHO substituents in the 3-position. All of the cobalt compounds are green, while the rhodium compound is yellow. These compounds have also been characterized by spectroscopic techniques, and have the physical properties stated in the original publications.

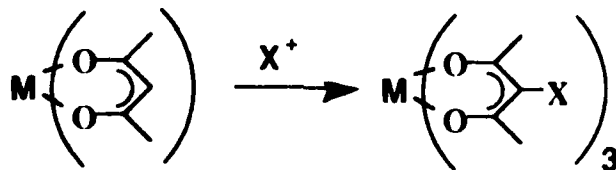


Scheme 1

The range of compounds illustrated in Schemes 1 and 2 demonstrate the ease with which a range of donor and acceptor groups may be introduced into pentadionato- coordination compounds. This is important if a number of such compounds are to be screened for SHG. All the compounds are air stable, and are not light sensitive.

Second Harmonic Generation (SHG) Properties

The SHG properties of the ligands and coordination compounds illustrated in Schemes 1 and 2 were measured using a modification of the Kurtz powder method and the results are presented in Table 1. Samples were ground, but not sieved, and exposed to incident light of 1064 nm.



Compound Number:

Group type:

	M=	X=
(11)	Co	H
(12)	Co	Cl
(13)	Co	NO ₂
(14)	Co	2 x H, 1 x CHO
(15)	Rh	H

Scheme 2

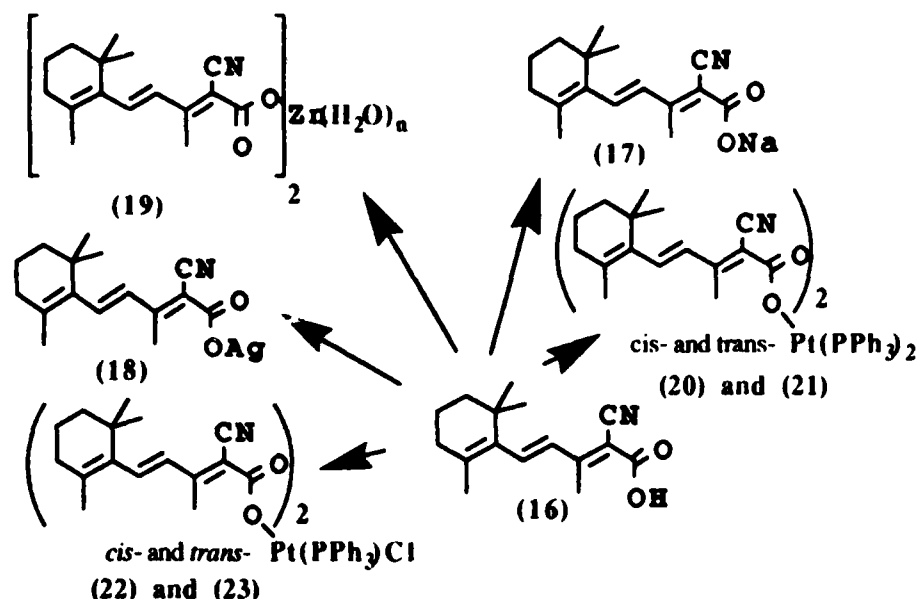
Table 1 Measured second harmonic signals at 1064 nm fundamental laser wavelength; all relative to urea, unless stated otherwise.

Compound	SHG	Colour
(1)	0.60	Yellow
(2)	0.70	Dark green
(3)	0.01	Pale yellow
(4)	0.22	Yellow
(5)	0.73	Yellow
(6)	0.00	Yellow
(7)	0.00	Orange
(8)	0.00	Orange-brown
(9)	0.00	Dark green
(10)	0.00	Dark green
(11)	detected	Dark green
(12)	detected > (11)	Green
(13)	detected > (12)	Dark green
(14)	0.00	Light green
(15)	0.00	Yellow
(16)	0.12	Yellow
(17)	not isolated	Yellow solution
(18)	0.01	Tan brown
(19)	detected	Pale yellow
(20+21)	0.02	Yellow
(22+23)	0.03	Off white

In part the small SHG effects may result from the crystallization of the compounds in centric space groups therefore not fulfilling the symmetry requirements for SHG. The single crystal structures of (4) and (5) have demonstrated that they crystallize in the centric space group $P\bar{1}$, although the ligands are quite asymmetric, either because the substituent is in the 4-position of the pentadionato- ligand or because of the asymmetric nitro- groups. The crystal structures have revealed that the phenyl group in (IV) is coplanar with the pentadionato- ring and therefore is fully conjugated with it. In contrast, the dinitrophenyl ring in (5) is perpendicular to the pentadionato- ring. Although the compounds crystallize in centric space groups they show significant, and reproducible residual SHG effects (see Table 1) of approximately 0.7 x urea. Such effects have been observed previously and attributed to co-crystallization of centric and noncentric modifications.^{15,16}

The solvatochromism of the pentadionato- ligands and their complexes (1) to (8) were also measured. All the compounds showed significant shifts of electronic transition state bands when the polarity of the solvent was changed. These results suggest that the excitations associated with these bands involve a reasonable change in dipole moment. The results support the above suggestion that the poor SHG properties observed for these compounds have their origin in the mode of crystallization rather than in the molecular properties.

Recent research is centred on the synthesis of coordination compounds derived from conjugated polyenes. In particular β -ionylidene cyanoacetic acid has been used to synthesize the coordination compounds illustrated in Scheme 3. The properties of this interesting class of compound are currently being measured.



Scheme 3

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OVERVIEW

MULTIFUNCTIONAL LADDER POLYMERS

by

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Devices based upon the nonlinear optical activity of materials inherently require multi-functional materials. For example, in addition to optical nonlinearity, materials routinely must exhibit good mechanical properties, outstanding thermal stability, reasonable electrical and thermal conductivity, excellent optical transparency, etc. Because of unique packaging requirements materials must be amenable to being processed into specific forms; special processing requirements in turn place extreme solubility requirements on materials.

Outstanding progress has been made in developing multi-functional materials for nonlinear optical activity applications. The inherent insolubility of electro-active materials has been essentially completely overcome by (1) monomer and polymer derivatization, (2) precursor polymer synthesis routes, and (3) copolymer synthesis techniques. Solutions of desired concentrations and viscosities are prepared for spin casting, Langmuir-Blodgett, and crystal growth techniques. Moreover, a variety of liquid crystalline properties such as nematic and smectic phases can be systematically investigated although the full potential of these materials is only just beginning to be explored. An amazing accomplishment in molecular engineering is represented by the combination of organic polymerization and sol-gel processing technologies to produce NLO glasses with improved transparency. This accomplishment is clearly an outgrowth of the OGAMM program. NLO materials (ladder polymers and metallated polymers derived from POL, PTL, PQL, BBL type structures, phthalocyanines, tetrazaannulenes, i.e., metallated macrocycles) have been developed which exhibit thermal stability to temperatures in excess of 1300 K. Electrical conductivities can be frequently varied by more than twelve orders of magnitude in the range 10^{-12} to 10^6 ohm⁻¹ cm⁻¹. Some NLO polymers such as PBT, BBL, POL, PQL, PTL type structures exhibit tensile strengths exceeding

those of the best steels and, given the outstanding strength/weight ratios, are clearly candidates for aircraft materials.

Enormous advances have been made in improving optical nonlinearity in the past three years. For second order materials, electro-optic, r_{33} , coefficients of 50 pM/V (picometers/volt) have been realized and the problem of decay of optical activity due to structural relaxation has nearly been solved by molecular engineering (polymer cross-linking and glass transition temperature control). The next three years will almost certainly witness the commercial introduction of electro-optic modulators. Radar beam steering applications are a clear possibility. Third order optical nonlinearities of organic and organometallic materials have been increased orders of magnitudes to the point that they are competitive with the best inorganic materials, multi-quantum well heterostructures (e.g., $\chi^{(3)} \sim 10^{-6}$ esu, $\tau \sim 10^{-13}$ to 10^{-12} sec, $\chi^{(3)}/\alpha \sim 10^{-9}$ esu cm for metallated ladder and macrocyclic polymers). It should also be noted that both photo-enhanced transparency and photo-enhanced absorption can be realized for organic materials in spectral regions from the UV-visible to the near IR to the far IR. These responses can be realized over quite large spectral regions and the spectral range can be systematically tuned by variation of the chemical structure of the electro-active unit. We have used derivatization with electron donating or withdrawing substituents ($-\text{NH}_2$, $-\text{OCH}_3$, $-\text{NO}_2$, etc.) and have used metallation (with Ni, Pt, Pd, Ru, Rd, etc.) to effect spectral sensitivity shifts up to 500 nm as well as to enhance optical nonlinearity. In addition to realizing materials which exhibit large absorption changes (both + and - $\Delta\alpha$ values), systems exhibiting large positive index of refraction (Δn) changes have been prepared. This development is relevant to beam steering and limits applications. These dramatic improvements in nonlinear optical properties are particularly impressive in that they have been realized together with improvement in the necessary auxiliary properties discussed above.

PREPARATION AND CHARACTERIZATION OF NEW NONLINEAR OPTICAL MATERIALS

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ABSTRACT

Overcoming the intrinsic poor solubility of π -electron electroactive materials, so that sophisticated processing techniques such as spin casting and Langmuir-Blodgett methods can be employed to fabricate optical quality films, has been an important objective of this work. This objective has been achieved by a three fold approach based upon: (1) polymer derivatization with solubilizing substituents; (2) synthesis of soluble and processible precursor polymers and subsequent use of solid-state reaction chemistry to achieve desired final product polymers; and (3) copolymer synthesis techniques incorporating both electroactive and flexible chain segments. A second important objective of this work has been the realization of improved optical nonlinearity and improved optical transparency. Systematic derivatization has also been utilized to achieve this objective. In addition to derivatization with electron donating and withdrawing organic groups, metallation with metals such as nickel, platinum, etc. has been used to increase third order susceptibilities to 10^{-7} esu and material figures of merit ($\chi^{(3)}/\alpha\tau$) to 10^4 esu cm sec. Organic materials have thus equaled the best inorganic materials (i.e., quantum well heterostructures) as materials of choice for the development of new devices based upon nonlinear optical (NLO) activity. A specific example of the aforementioned control of processibility and optical characteristics by synthetic procedures is given in Fig. 1 which illustrates the incorporation of an electroactive (in this case, "ladder" oligomer) unit into a traditional polymer backbone. Fig. 2 illustrates that this same group can be incorporated as a pendant to a polymer backbone. Such synthetic control has been used to define local field effects by studying the same electroactive moiety in different ultrastructures and to define the role of intermolecular interactions in influencing optical nonlinearity by systematically varying the amount of electroactive material incorporated into the polymer matrix. In this latter regard, we have used such synthetic control, together with detailed investigation of the temporal response of the optical nonlinearity to define the contribution to optical nonlinearity from excitons.

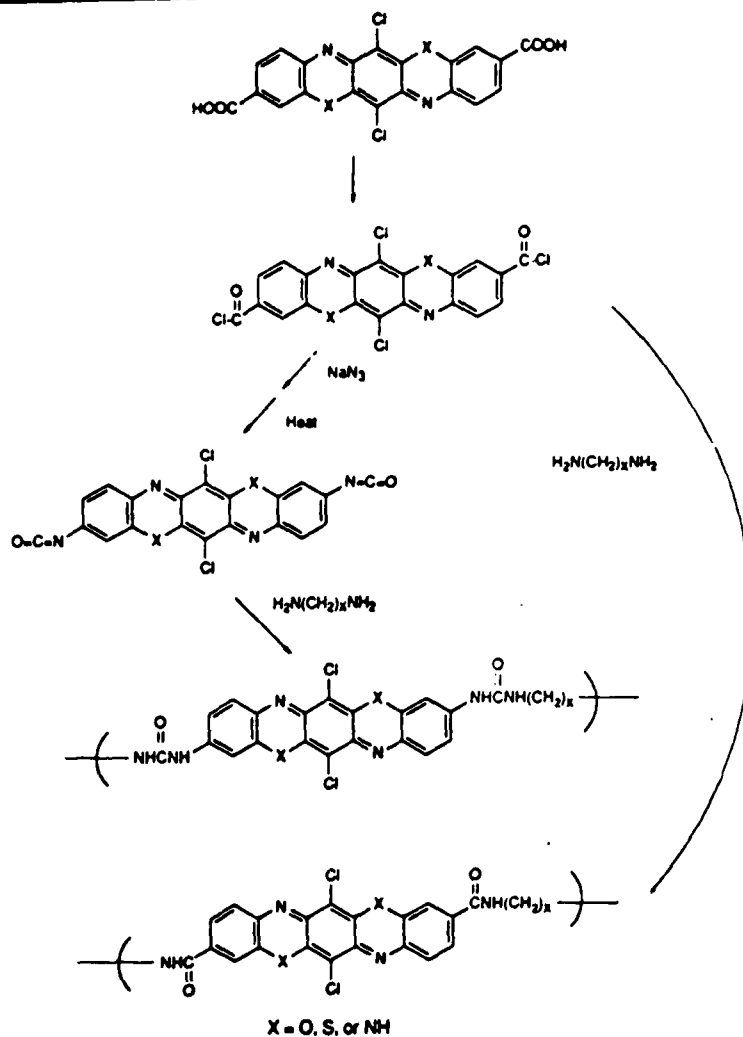


Fig. 1. Syntheses incorporating ladder units into polymer backbones.

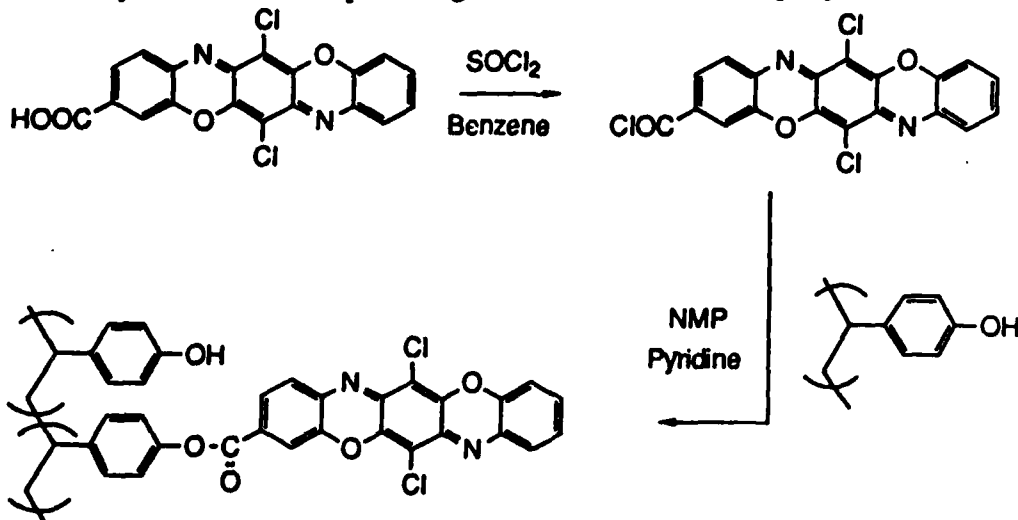


Fig. 2. Incorporation of a triphenodioxazine ladder unit as a pendant to a polystyrene backbone.

New synthetic procedures have also been developed to permit the realization of dramatically improved materials for second order NLO applications. The problem of loss of optical nonlinearity due to lattice relaxation following poling has been greatly reduced by

control of polymer glass transition temperature and by utilization of solid-state polymer crosslinking reactions. Polymers such as shown in Fig. 3 have facilitated retention of greater than 95% of nonlinear optical activity (e.g., second harmonic generation) for periods exceeding 1000 hours.

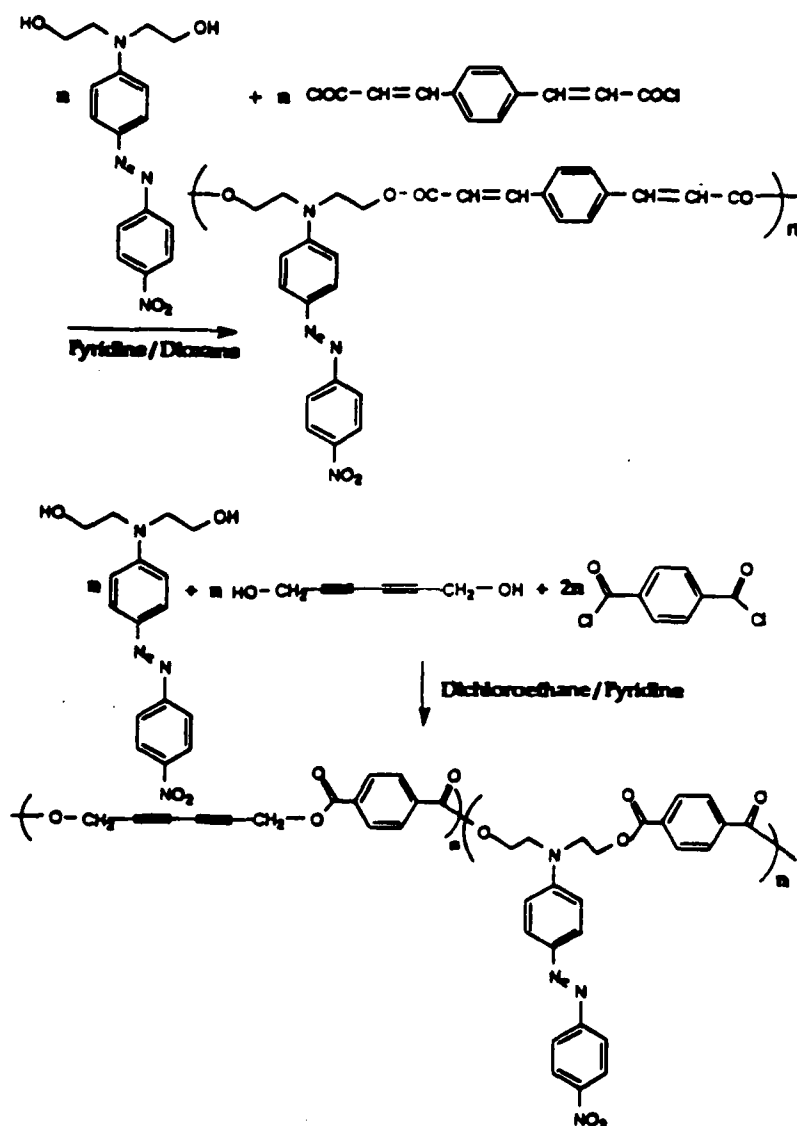


Fig. 3. Two examples of crosslinkable polymers developed in this work.

As with third order materials, copolymer synthesis techniques have permitted survey, under comparable local field conditions, of a variety of electroactive moieties including phenylpolyenes, thienylpolyenes, anthracenylpolyenes, stilbenes, carbocyanines, azo

dyes, tetraazaannulenes, phthalocyanines, squarylium heterocycles, and ladder polymers. Electro-optic coefficients on the order of 50 pm/V have been achieved. Metallation has been shown to be useful for improving optical nonlinearity and transparency. For second order materials, control of the frequency of absorption bands is an important route to achieving phase matching in second harmonic generation applications.

An additional objective of this research has been discovery and characterization of new mechanisms of optical nonlinearity unique to organic materials. Realizing the importance of simultaneously measuring the real (index of refraction change) and imaginary (absorption change) parts of the third order susceptibility, we developed a new instrumental method for achieving this objective. Our new interferometric degenerate four wave mixing (IDFWM) apparatus is shown in Fig. 4.

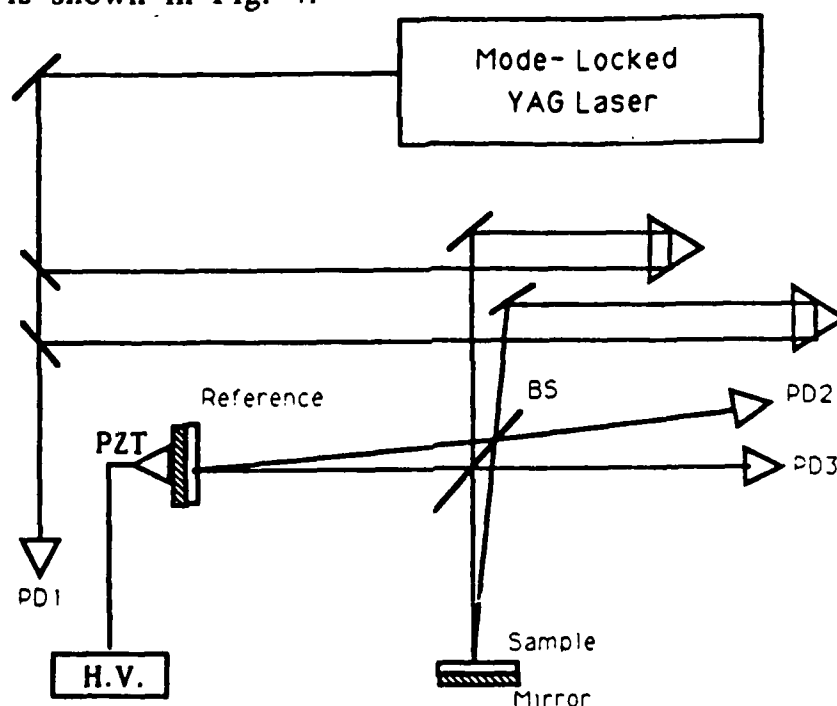


Fig. 4. Schematic representation of the double phase conjugate interferometer for IDFWM experiments.

Results obtained for a ladder polymer using this instrumentation are given in Fig. 5 and are compared with results of photo-induced absorption/bleaching experiments (solid line of Fig. 5). This work (when correlated with EPR and conductivity measurements) establishes, for the first time, the role of photo-generated bipolarons in enhancing optical nonlinearity. Note that bipolarons can lead to regions of photo-enhanced transparency and photo-enhanced absorption. Negative and positive optical nonlinearities are useful

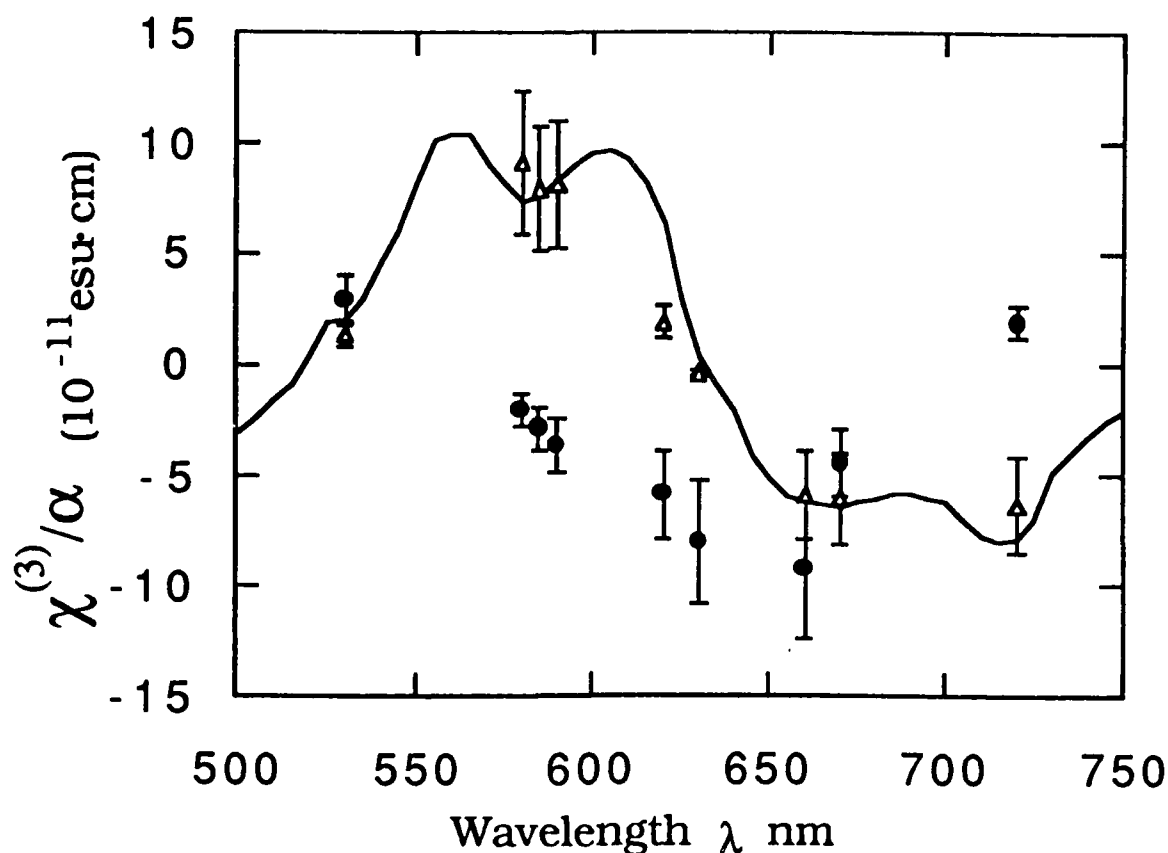


Fig. 5. Wavelength dependence for the real (solid circles) and imaginary (open triangles) parts of the third order susceptibility. The solid line is the photo-induced absorption /bleaching from pump-probe pulsed laser experiments.

for different device applications. Index of refraction changes (circles) are also uniquely identified including the sign of Δn which is important for device design. Our laboratory now permits, in addition to measurement of the magnitude and phase of the optical nonlinearity, investigation of the temporal, frequency, laser power, and spatial dependence of optical nonlinearity and has permitted discrimination of contributions to third order optical nonlinearity from photo-generated subgap species, excitons, multi-photon transitions, and coherent parametric mixing processes.

The basis for systematic improvement in both second and third order materials has been established by the development of new synthesis and characterization techniques. New metallated, including mixed valence, materials will be investigated in the coming year and optical nonlinearity of current materials will be further enhanced by derivatization.

OVERVIEW

GEL-SILICA MULTIFUNCTIONAL OPTICS GROUP

by

L. R. HENCH

University of Florida

There are three primary goals of this group of investigators:

1. To understand and control the ultrastructural interconnected porosity of Type VI optically transparent gel-silica matrices, and the associated defects and structural inhomogeneities in the solid network, thereby to produce a new generation of optical devices. This goal will be achieved by:

a. Studying the effects of water absorption processing including thermal history and chemical dopants on optical properties including scattering (Mie and Rayleigh) by T. King (University of Manchester) and J. West (University of Florida);

b. Interferometric studies by N. Phillips (University of Loughborough);

c. IR, NIR, Raman, UV SAXS, USAXS, SANS, NMR by C. C. Perry (Brunel University); and

d. Photocorrelation dynamic light scattering to determine the dimensions (nm scale) and stability of ultrastructure features by T. King (University of Manchester).

Quantum calculations of doped silica clusters using AMI and INDO methods will be used (J. West, University of Florida) to interpret the experimental results and design analytical experiments. All analysis will be done on the latest generation of Type VI porous gel-silica samples, now produced commercially by Geltech, Inc. These show high levels of optical homogeneity and low scattering. A new functional device, a transpiration-cooled UV window, is nearly operational (L. Hench, University of Florida).

2. Results from above will be used in designing experiments to achieve our second goal which is: "To understand and control organic-inorganic interfacial reactions in the porous gel-silica optical matrices". These studies will provide the basis for achieving multifunctional optical and electro-optical devices by combining the properties of optically active polymers with porous gel-silica optical matrices. Operational devices based on organic impregnated gel-silica are already close including: flash lamp pumped solid state dye lasers (T. King and J. West) and UV detector and wavelength shifter (L. Hench). The new DuPont photopolymer will be used in the gel-silica matrix by N. Phillips to achieve a number of passive optical devices such as diffractive and refractive optical arrays, GRIN lenses, and waveguides.

Active optical devices, such as a distributed feedback tunable laser, will also be produced by N. Phillips (University of Loughborough) using the photo-active polymer-gel silica matrix. Multifunctional prototype devices have been established that show fast fluorescent switching on the microsecond time scale using ferro-electric effects in low molar mass and polymer liquid crystals (H. J. Coles, University of Manchester). These materials are now being incorporated into the gel silica matrices. The matrices, because of their low u.v. absorption and small cavity size, should lead to even faster emissive displays than one currently available using alternate technology. In combination with the laser studies, it should also be possible to switch the dyes on and off in the cavity to give a novel Q switched dye laser. Switching in electromagnetic fields in the sol-gel liquid crystal has already been demonstrated.

3. Laser enhanced densification of gel-silica matrices leading to micro-optical arrays, GRIN lenses, waveguides, optical interconnects, light weight mirrors, and encapsulation of the devices arising from Goal 2, is the third thrust area of our group. Prototype waveguides have already been produced by T. King (University of Manchester). Optical arrays and GRIN lenses will be made by T. King (University of Manchester) and L. Hench and J. West (University of Florida) and tested in King's (University of Manchester) and N. Phillips' (University of Loughborough) labs. The CO₂ laser densified

structures will be characterized using the techniques listed in Goal 1 by C. C. Perry (Brunel University), J. K. West (University of Florida) and T. King (University of Manchester).

In addition to the above primary thrust areas, our group will have a number of additional collaborations in the OGAMM program, notably: characterization of the silicate gel matrices developed by J. D. Mackenzie (UCLA) and Yamane (Tokyo) for high temperature superconducting ceramics. Porous gel-gel matrices will also be provided by L. Hench (University of Florida) to J. D. Mackenzie (UCLA) for potential incorporation of non-linear optical inorganic dopants such as CdS and CuCl.

Organic impregnants with NLO or other optically active behavior coming from the University of Massachusetts effort (F. Karasz) with evaluation by P. Prasad (University of Buffalo) and from C. Williams (University of Southampton) and from C. Williams (University of Southampton) and L. Dalton (USC) will be incorporated into gel-silica matrices (L. Hench, University of Florida) for evaluation of the effects of steric isolation and adsorption on optical behavior.

GEL-SILICA MULTIFUNCTIONAL OPTICS GROUP

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The interdisciplinary group of investigators in this program is illustrated in Figure 1 together with their projects. There are three primary goals of this group of investigators:

1) Understand and control the ultrastructural interconnected porosity of Type VI optically transparent gel-silica matrices, and the associated defects and structural inhomogeneities in the solid network, thereby to produce a new generation of optical devices. This goal will be achieved by: studying the effects of water adsorption processing including thermal history and chemical dopants on optical properties including scattering (Mie and Rayleigh) by T. King (Manchester) and J. West (Florida); interferometric studies by N. Phillips (Loughborough); IR, NIR Raman, UV, SAXS, USAXS, SANS, NMR by C. C. Perry (Brunel); photocorrelation dynamic light scattering to determine the dimensions (nm scale) and stability of ultrastructure features by T. King (University of Manchester). Quantum calculations of doped silica clusters using AM1 and INDO methods will be used (J. West, University of Florida) to interpret the experimental results and design analytical experiments. All analysis will be done on the latest generation of Type VI porous gel-silica samples, now produced commercially by Geltech, Inc., which show high levels of optical homogeneity and low scattering. A new functional device, a transpiration cooled UV window, is nearly operational (L. Hench, University of Florida).

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using the techniques listed in Goal #1 by C. C. Perry (Brunel), J. K. West (University of Florida) and T. King (University of Manchester).

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Table 1
TYPE VI GEL-SILICA
INTERINSTITUTIONAL CHARACTERIZATION STUDY
September 5-7, 1990

Sample Configuration:

rectangular optical elements (2 x 1 x 0.5 cm)
circular cross section rods (10 cm x 0.5 cm dia.)

Sample Thermal History:

180 °C
700 °C
800 °C
899 °C
1000 °C

Nominal Pore Diameter:

2.4 nm

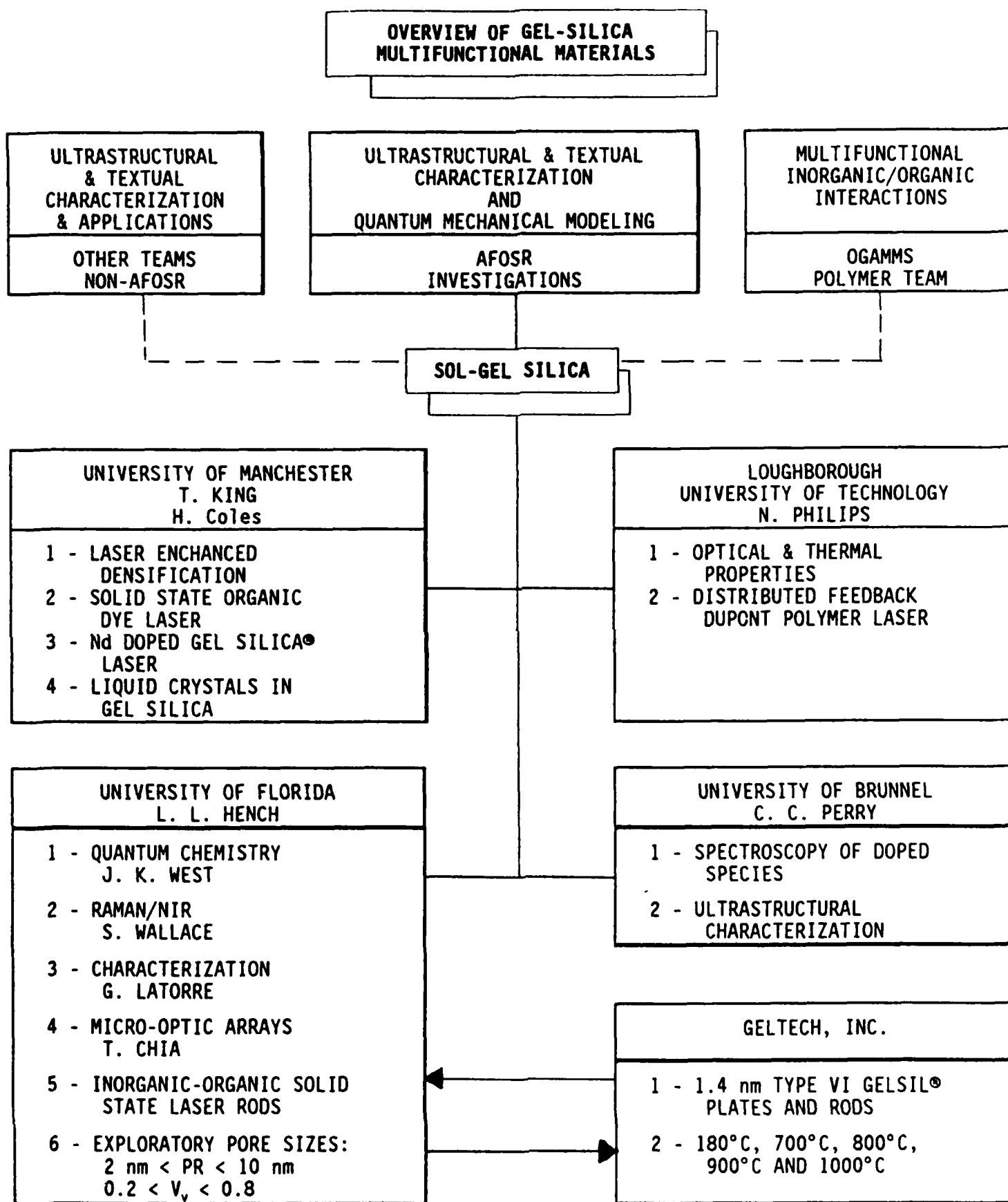
Nominal Surface Area:

400 to 750 m²/g

Table 2

Characterization Test	Institution
TGA, DMA, DSC, DTA	UF
Dilatometry	UF
Microhardness	UF
Nitrogen Adsorption Isotherm Analysis	UF
Neutron Activation	UF
Index of Refraction	UF, Loughbough U. of Tech.
Optical Dispersion	Subcontract
Surface Finish and Figure	UF
Dimensional Tolerance	UF, Loughbough U. of Tech.
Homogeneity (Zygo Interferometer)	UF
FTIR	UF, Brunel University
UV, VIS, NIR	UF, Brunel University
Vacuum UV	UF, Subcontract
AFM	Digital Instrument
Raman Spectroscopy	UF, Brunel University
Inorganic Doping	Brunel University
Organic Doping	University of Manchester University of Buffalo Loughborough University of Tech. UF
Positronium Decay	TCU
Neutron Scattering	University of Reading
Synchrotron Scattering	University of Montpellier
X-ray Small Angle Scattering	University of Sao Paolo
Pressure IR	University of Illinois
Vapor Stabilization	University of Wisconsin
Gas Permeability	UF
Liquid Diffusivities	UF
AC Impedance Spectroscopy	UF

Figure 1



MULTIFUNCTIONAL SOL-GEL SILICA OPTICS

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Sol-gel chemical processing of silica provides a new approach to the historical restrictions of silica optical components; i.e., 1) elimination of hand operations in manufacturing by net shape casting, and 2) development of multifunctional optics by producing ultraporous silica matrices that are optically transparent.

SOL-GEL PROCESSING

Recent publications have presented in detail the important features of sol-gel technology [1-3]. The use of sol-gel processing for producing monolithic silica optical components has also been previously described [1,2].

In order to make net shape multifunctional optics we use hydrolysis and polycondensation of alkoxide precursors followed by aging and drying under ambient atmospheres to form xerogels. In our process the alkoxide is tetramethylorthosilicate (TMOS) and the catalyst is either nitric acid or hydrofluoric acid, depending upon the average pore size desired after drying. Full density net shape precision optics termed Type V gel-silica, require all seven steps listed in Figure 1. Partially dense, controlled porosity Type VI gel-silica optics require the first six steps listed in Figure 1.

The ultraporous, optically transparent gel-silica, termed Type VI gel-silica [1], is uniquely suited for many multifunctional optical applications, as discussed by Hench et al. [1,4] and Nogues et al. [5]. It is possible to vary the pore size and volume fraction of porosity of the Type VI gel-silica by using HF as a catalyst in Step 1, as discussed by Parsell [6], Vasconcelos [7], and Elias [8]. Increasing the pore size of the network is important for a number of multifunctional optical applications, as shown below. However, the larger pores do degrade the UV cut-off to some extent, from 160nm to 235nm, probably due to Rayleigh scattering, as calculated by West and Elias [8]. The porous Type VI optics also have residual hydroxyls retained on the pore network with the concentration dependent on the maximum stabilization temperature. Since the larger pore network is more thermally stable, [7,8] the larger pore optics can be heated to higher stabilization temperatures to decrease the OH content and still retain a very large volume fraction of porosity. This increase in volume fraction of porosity and greater thermal stability of the 8.0 nm Type VI gel-silica offers a major advantage for the multifunctional optical applications discussed below.

TRANSPIRATION COOLED UV WINDOWS

Multifunctionality is highly desirable for optically transmitting windows in high speed rocket guidance systems due to severe operating conditions. The windows need to transmit light over a broad range of wavelengths, including the ultraviolet. Most importantly, the optical transmission must not be affected by very high ambient temperatures and impingement of very energetic gases. Reasonably good structural strength, thermal stability, and thermal shock resistance is also required for rocket windows.

A unique approach to achieving thermally resistant properties is to cool the window by passing gases through the window. Such a concept is possible with the ultraporous Type VI gel-silica monoliths.

The objective of the multifunctional optical component is to cool the window via transpiration of gases through the interconnecting pore structure while optical transmission is maintained.

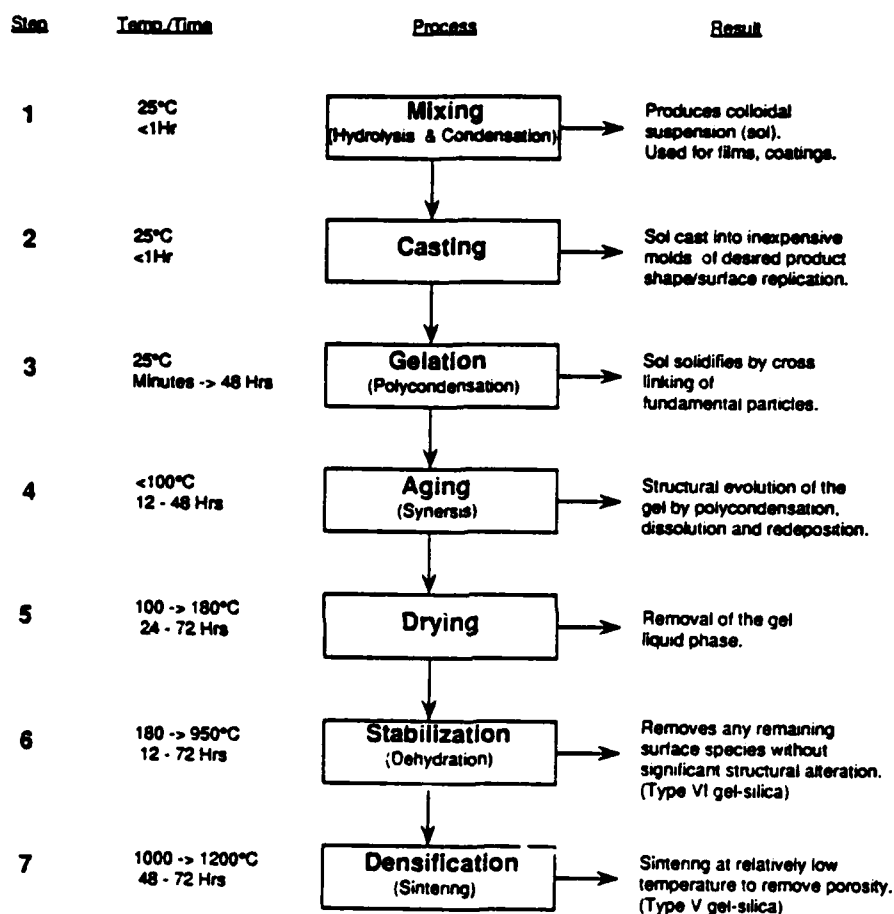


Fig. 1 Sol-Gel Processing Sequence for Multifunctional Optics

The first step in evaluation of the concept of a transpiration cooled window is to determine whether transpiration of gases is possible through a porous Type VI gel-silica medium. The second step, if transpiration is possible, is to characterize the transpiration rate as a function of pressure, pore radius, sample thickness, and type of gas. The third step is to determine whether UV transmission occurs through the Type VI porous gel-silica window at elevated temperatures and with gases impinging on it. Fourth, thermal shock characterization of the window is also needed.

A preliminary report of these multifunctional performance characteristics follows. A low pressure (< 700 psi) test chamber was designed and built to quantify the rate of gas transpiration through the porous optical windows. The results are shown in Figure 2 with the flow rates of helium through samples with pore radii

of 1.2nm and 8.0nm (processed to 180°C and 500°C stabilization temperatures) measured as a function of pressure. The flow rate of the He is considerable faster than nitrogen due to the difference in size and the diatomic nature of nitrogen; i.e., He = 0.36 nm, N₂ = 0.42 nm.

To determine the effect of elevated temperature upon the UV transmission of gel-silica, a high temperature test apparatus was constructed, Figure 3. This apparatus includes a UV light source, sample

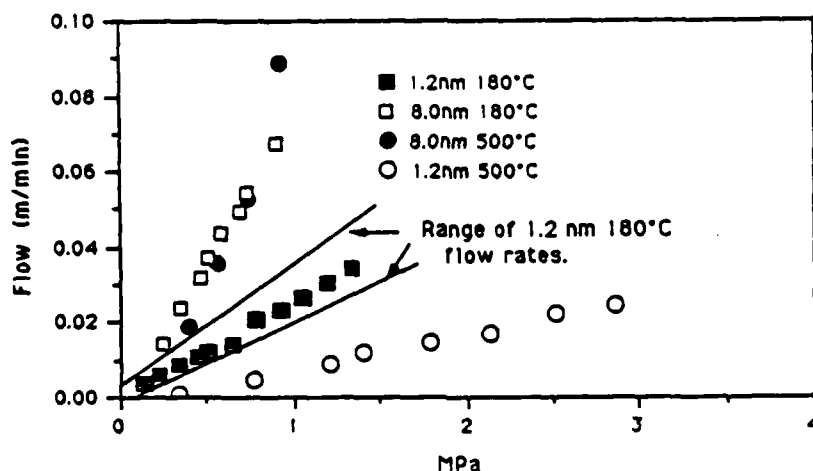


Fig. 2. Helium Transpiration Through 1.2nm and 8.0nm Porous Gel-Silica Windows.

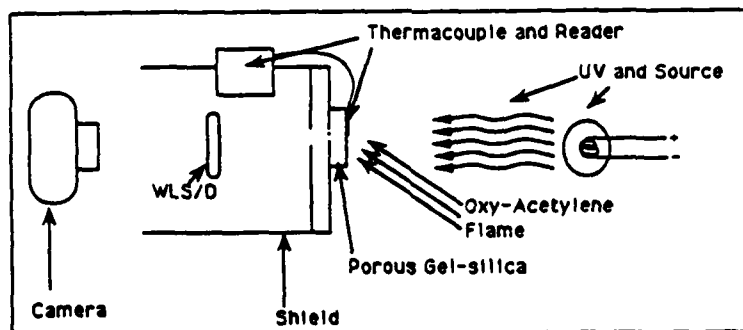


Fig. 3. Experimental Setup for UV Detection at Elevated Temperature.

holder with thermocouple, an oxygen-acetelyene torch heat source, and a multifunctional gel-silica optical component as a UV detector. This detector component is described in the next section. Fluorescent activity was observed in the detector at $T > 1000^\circ\text{C}$ due to the UV transmission of the window, absorption in the detector and emission at $\sim 600\text{nm}$ by the wavelength shifter. The upper limit of temperature performance of the gel-silica UV window under transpiration cooling is presently unknown but is probably much higher than can be measured in this experimental set-up. Tests are underway and results will be presented at the next OGAMM meeting.

FAST, RADIATION-HARD SCINTILLATING DETECTOR

The physical features of Type VIA porous gel-silica described above are attractive to use as matrices for doping or impregnation with fluors, non-linear optical polymers or compounds, wavelength shifters, or lasing dyes. The result is a hybrid multifunctional optical component.

Table I lists examples of some organic and inorganic compounds that have been successfully impregnated into several Type VI gel-silica samples [1].

Table I. Compounds Impregnated into Type VI Porous Gel-Silicas.

<u>Non-Linear Optical Polymers</u>	<u>Transition Metals</u>
-PBT [Phenylenebenzobisthiazole]	- Cu
-MNA [2-Methyl-4-Nitroaniline]	- Ni
	- Cr
<u>Organic Fluors</u>	- Ce
-B-PBD[2-4'-t-Butylphenyl]	- Ag
5-(4"-Biphenyl)-1,3,4-Oxadiazole]	- Fe
-P-TP [p-Terphenyl]	- Co
-P-QP [P-Quarterphenyl]	
<u>Wavelength Shifter</u>	<u>Rare-Earths (Lanthanides)</u>
-3-HF [Hydroxyflavone]	- Nd
	- Er
<u>Laser Dye</u>	
-Rhodamine 6G	

The Type VI gel-silicas with larger pore sizes described above make it possible to impregnate the component with higher molecular weight polymers. The same 800 °C treatment of a 1" diameter x 1/4" thick sample with 8.0nm pores produces an optical component that weighs 1.98 g, has a 18 HV microhardness, and has nearly 583 m² surface area with pores ~ 8.0 nm radius. This component can accept 2.36 cc of a dopant second phase in its 70-75 volume percent porosity. These differences are large and provide a wide range of textural features for use in tailoring multifunctional optics.

For example, consider the fast radiation hard scintillator developed by Nogues, et al.[5]. They utilized a Type VI gel-silica matrix with a 1.2nm average pore radius and 0.35 volume fraction porosity as a host matrix for organic fluors to produce a fast, radiation hard scintillation detector. The silica matrix provides high radiation resistance compared to the organic plastic scintillators [5] and the organic fluor provides fast scintillation response. Both properties are advantageous for high-speed counting necessary in high-energy physics applications. The primary fluors used by Nogues, B-PBD, P-TP & P-QP (Table I) have good radiation resistance and short decay times of a few nanoseconds, but the fluorescence spectra typically peaks at wavelengths below 400 nm, making it difficult to measure. To overcome this problem Nogues, et al. [5] used another fluor termed a wavelength shifter (WLF) (WLS) 3-HF (Table I) which absorbs the < 400 nm radiation of the primary fluor and re-emits in wavelengths of ~ 500-600 nm. These wavelengths are advantageous as they are less absorbing in glass than the shorter wavelengths and also result in higher quantum efficiency for silicon photodiodes. When analyzed for scintillation efficiency with α -, β -, and γ -ray sources, the light output was reported to be only 6-7 times lower than the much more highly developed

plastic scintillator [5]. The γ -radiation resistance of the silica matrix was many times greater than the organics. These are very encouraging results for the first generation of multifunctional optical components.

This same type detector with the 3-HF fluor dopant was supplied by Nogues for use as the WLS/detector shown in Figure 3 and was used for the high-temperature UV transmission test in the above mentioned transpiration study. A source emitting 365 nm radiation passes through the heated porous window being tested for transmission and is absorbed and re-emitted by the detector as visible green - yellow-green light from the WLS/detector. Thus, a qualitative and visual method for testing high temperature UV transmission through a porous silica matrix was achieved.

ACKNOWLEDGMENTS

The authors are grateful for the financial support of the Air Force Office of Scientific Research under contract #F49620-88-C-0073 and the encouragement of D. R. Ulrich throughout this research. A special thanks is extended to J. L. Nogues for the use of the wavelength shifter/detector.

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MOLECULAR ORBITAL CALCULATIONS ON WATER ADSORPTION ON A TETRASILOXANE RING USING THE AM1 SEMI-EMPIRICAL HAMILTONIAN

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ABSTRACT

AM1 Molecular Orbital Theory was used to model the adsorption of a water molecule onto a tetrasiloxane ring. This was done to improve upon the models previously reported using Intermediate Neglect of Differential Overlap (INDO). They were constructed to model the N/R transmission spectra for water adsorbed into the pores of a metal alkoxide derived silica gel monolith. The wavelength of the vibrational overtones were measured as a function of the adsorbed water content W ($\text{g H}_2\text{O/g SiO}_2$). One peak shifted from 1.39 to 1.420 μm as W increased by 0.14 g/g. The INDO MO theory showed that the O-H bond in the silanol hydrogen bonded to a H_2O molecule increased as expected. However, the INDO model also predicted that the O-H bond lengths in the water molecule should be lengthened. This would correspond to an increase in the wavelength of the 2v4 peak. The NIR did not show this effect. The improved accuracy of the AM1 Hamiltonian for hydrogen bonding problems showed that another structure is possible that shows bond length changes that correspond to the observed NIR spectra for both the 2v3 and 2v4 peaks. Raman data corresponding to the trisiloxane [D2] ring is also presented to justify the use of the tetrasiloxane ring as a stable structure during water adsorption.

INTRODUCTION

The sol-gel silica monoliths that were studied were made by acid catalysis of TMOS. They had a surface area of $750 \text{ m}^2/\text{g}$, a pore volume of 0.45 cc/g , an average pore radius of 12 $\text{\AA}$ and an average particle radius of 60 $\text{\AA}$. [1,3] The monoliths were heat treated to 800°C and then allowed to adsorb small amounts of water. The Near Infrared (NIR) spectra were then taken and the adsorbed water content measured [3].

An isolated surface silanol (SiOHs) group produces an IR transmission peak, ν_1 , at 2.675 μm . ν_1 is due to the O-H stretching vibration of isolated SiOHs groups [2]. A H_2O molecule H-bonded to SiOHs groups produces an IR peak (ν_3) at 2.82 μm . ν_3 is due to the O-H stretching vibration of SiOHs groups H-bonded to H_2O molecules [2]. In the investigation by West and Wallace [3], the shift in the wavelength of the first vibrational overtone ($2\nu_3 = 1.39 \mu\text{m}$ at $W = 0.001 \text{ g/g}$) of ν_3 was measured as a function of the H_2O content W ($\text{g H}_2\text{O/g SiO}_2$) [3].

In the theoretical model, the adsorption of H_2O H-bonded onto a ring of 4 silica tetrahedra show a Si---Si diagonal expansion of 0.0873%. This model calculation used Intermediate Neglect of Differential Overlap (INDO) MO theory [4]. Dilatometry also indicated that expansion of porous sol-gel silica is due to water adsorption [6]. Finally, the same INDO MO structure was also used by West and Wallace [3] to examine the increase in the wavelength of the 2v3 IR peak. The summary of the model and the NIR observations for the adsorbed H_2O molecule, H-bonded to the hydroxylated siloxane sol-gel, and an isolated H_2O molecule are shown in Table I.

As a result of these studies, a more accurate H-bonding Molecular Orbital model was used to more closely match the NIR observations. The model chosen has the AM1 Hamiltonian optimized by Dewar, et.al.

[8,9]. This model calculates the binding energy of the H-bond much more accurately than INDO and has been calibrated using ab initio calculations by Burggraf, Davis, and Gordon [11].

Table I. Summary of the wavelengths, the observed IR peaks [2], their shifts [3] with 0.15 g/g of water adsorption, and INDO O-H bond length change.[3]

Wavelength (μm)	O-H Stretch Vibration	Observed Shift	INDO O-H Bond Change
1.460	2v4 of water H-bonded to silanols	None	4.04%
1.390	2v3 of silanols H-bonded to water	2.14%	4.22%
1.365	2v1 of isolated surface silanols	None	0.27%

THEORETICAL MODEL

The selection of a model structure has several competing problems. If one chooses a small cluster, i.e., 2 of 3 silica tetrahedra, then the cluster is probably not representative of bulk sol-gel silica but the computing time is short. On the other hand, larger clusters of 5, 6, or 7 silica tetrahedra require significant amounts of computer time even to calculate one geometry but may be more representative of the bulk material. The purpose of this study is to optimize the geometries of various clusters so that comparisons can be made between the various geometries. This requires many iterative calculations and significant utilization of computer time.

Rings of 3 silica tetrahedra are known as D2 defects [13] in Raman spectroscopy. These defects have been observed by Wallace [12] in the same porous sol-gel samples used in the NIR study by West and Wallace [3] and by Brinker and Scherer [13]. Wallace has shown that the [D2] concentration decreases as water is adsorbed into the gel. Figure 1 shows the reduction in [D2] concentration for Type VI sol-gel silica as water adsorption increases. Both large pore (90 Å) and small pore (12 Å) gels show the same

D₂ FRACTION FROM RAMAN SPECTRA

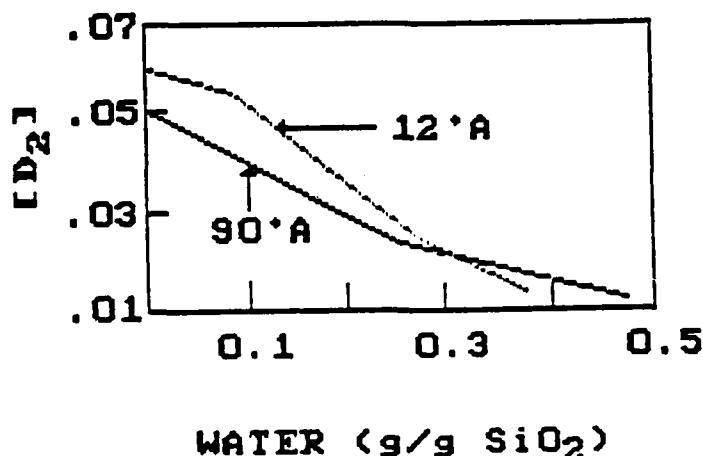


Fig. 1. D₂ Concentration as a Function of Water Content and for Pore Radii of 12 Å and 90 Å

relationship. Wallace also observes that the concentration of [D1] defects, tetrasiloxane rings, does not change as water is adsorbed into these gels. If then we are to model stable silica rings, we therefore must choose structures of at least 4 silica tetrahedra. Trial calculations were made on rings of 5 and 6 tetrahedra. The computing time was approximately doubled for each additional tetrahedra. Therefore, for these reasons the tetrasiloxane ring was chosen for this study.

The initial model was for a ring of 4 silica tetrahedra with each non-bridging oxygen terminated with a Hydrogen. This model as well as rings with the Hydrogen bonded water molecule were optimized geometrically using the highest level of precision offered by the program. Changes in the structure then could be compared. The absolute value of the bond lengths, bond angles, and enthalpies are slightly larger than the experimental values and this has been documented [11]. The changes between structures and the accuracy of the Hydrogen bond chemistry are the important features of this study.

RESULTS AND DISCUSSION

Several geometries were investigated using this model. The goal was to find a structure that qualitatively matched the NIR observations. The structure shown in Figure 2 was found to be the most energetically stable but most importantly it appears to predict bond length changes that correspond to the shifts in the NIR spectra. The heat of formation for the Hydrogen bond is also within the range of experimental values [8]. The heat of formation for the water adsorption in this model is -6.555 kcal where as the value found for the INDO structure was +45 kcal. Table 2 shows the results of this study for the tetrasiloxane ring with and without the adsorbed water and how this model qualitatively matches the NIR results.

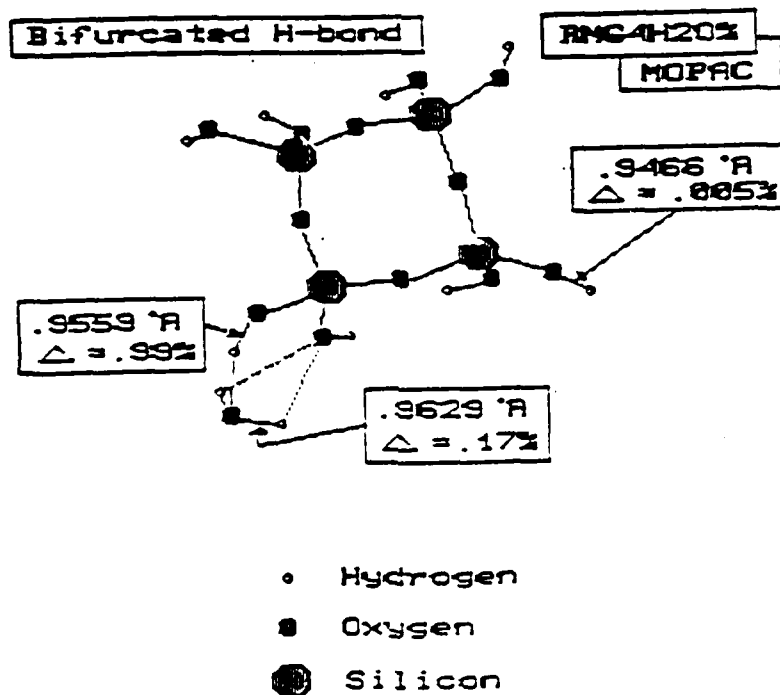


Fig 2 Cyclotetrasiloxane Ring with One Hydrogen-Bonded Water Molecule

Table 2: Results of the AM1 Model

O-H Stretch Vibration	AM1 Bond Without Water	AM1 Bond With Water	Percent Change	NIR Change %
2v4 (water)	0.96126 Å	0.962910 Å	0.17	None
2v3 (silanol)	0.94575 Å	0.955979 Å	0.99	2.14
2v1 (silanol)	0.94575 Å	0.946627 Å	0.005	None

Finally, this model also suggests a structure that requires two silanol to be bonded to one water molecule. This result also matches the experimental results of water adsorption data reported by Elmer, et al.[14]

CONCLUSIONS

The structures evaluated in this study do not represent unique solutions to the problem of sol-gel water adsorption. It simply represent one solution. This AM1 model seems to predict the changes necessary to account for the observations of the three NIR peaks, the H-bond chemistry, and the observed relationship of one water per two silanols. One interesting point is that such a small theoretical cluster may represent the surface reactions that can occur in porous Type VI sol-gel silica. This unique material gives an opportunity to observe surface chemistry that is not normally accessible in bulk silica.

ACKNOWLEDGEMENTS

This work was supported by the AFOSR and the SDIO/IST-AFOSR OGAMM research programs. The INDO [7] program was made available by the Quantum Theory Project (QTP) at the University of Florida. The AM1 program MOPAC 5.1 was made available through the Quantum Chemistry Program Exchange (QCPE) of Indiana University, Bloomington [10]. The computer facility is an AEON032, UNIX based system operated by the Advanced Materials Research Center, Gainesville, FL.

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STRUCTURAL STUDIES OF SOL-GEL DERIVED GELS AND GLASSES

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Research Objectives

To relate sol-gel microscopic structural chemistry and silica surface chemistry to the sol-gel process. Techniques used include, (1) electron microscopy, (2) FTIR and NIR transmittance and reflectance spectroscopies, (3) UV/ VIS spectroscopy, (4) nitrogen adsorption studies, (5) solid state NMR and (6) small angle neutron and X-ray scattering studies.

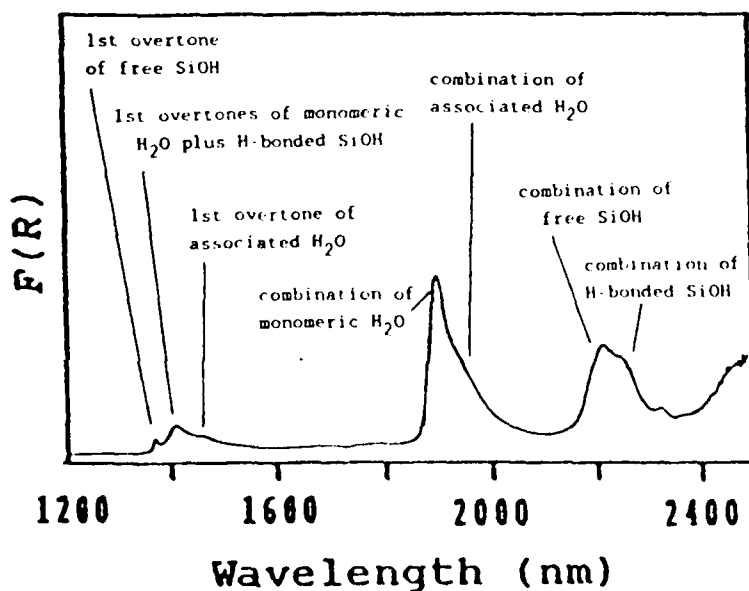
Research Accomplishments

An understanding of the effects of thermal treatment, the presence of adsorbed water and a range of inorganic compounds on pore surface speciation has been obtained. A model for the interaction of water with gel-glass surfaces has been proposed. Metal ions (neodymium and cobalt) have been used as a probe of pore chemistry (silanol functionality, hydration state, microporosity) in model studies for inorganic tunable lasers.

To date, silica monoliths with average pore dimensions of 24-28 Å at 190°C have been principally investigated. Preliminary data has also been obtained on mixed silica/ titania samples.

(1) Infrared Spectroscopic Studies

Fourier transform mid infrared (FTIR) and near infrared (NIR) spectroscopies have been performed on dehydrated and hydrated glass samples. Recent work has concentrated on the interpretation of data and has enabled new assignments to be made in the 900-2500 nm region to be made.



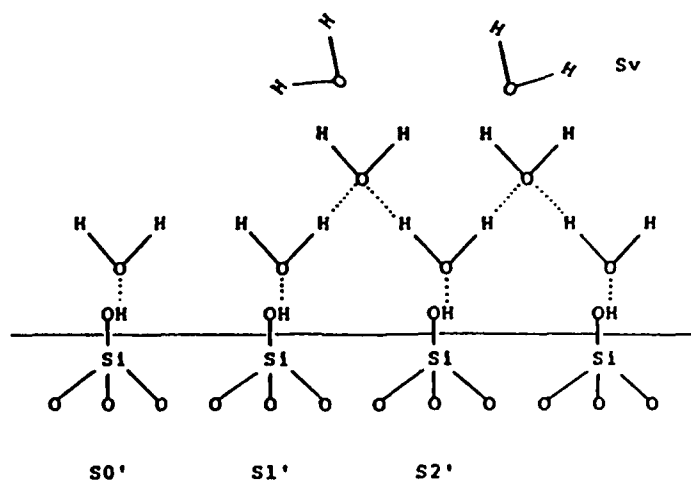
Assignments in the first overtone region (1200-2500nm) have been used to assess silanol levels and functionality and assignments in the second overtone region as a measure of water levels and extent of polymerisation. Two main aspects have been considered as follows:

(a) The Effects of Thermal Treatment on Structure

Effective dehydroxylation occurs above 700°C with consolidation of the bulk structure although residual silanol groups and water molecules remain within glasses treated above 1000°C. At all treatment temperatures, the bulk glass contained more hydrogen bonded silanol and water functions than the surface layers. At thermal treatment temperatures greater than this, these groups are effectively trapped within the glass matrix and are not subject to rehydration. The overtone bands for the silanol functionality (shift to lower effective bond energy and broadened) suggest that the silanol groups are highly perturbed on interaction with the glass network. At lower temperatures eg 900°C, resintered glasses also contain residual silanol groups which are not affected by external probe molecules, but these silanol groups show no evidence for interaction with the silica matrix. Control of resintering temperature has enabled both unperturbed and perturbed silanol functionalities to be viewed simultaneously.

(b) The Interaction of Adsorbed Water Molecules with the Glass Surface

A model describing the interaction of water with surface silanols during hydration of the gel phases at a range of treatment temperatures has been proposed. At least four kinds of water species can be identified including S_0 , S_1 , S_2 and S_v . S_0 and S_1 species exist after dehydration but the coexistence of S_0 , S_1 and S_2 species at the early stages of rehydration indicate that associated species are formed well before completion of the first water layer by monomerically adsorbed water molecules S_0 . Initially, the rate of development of the absorption band due to S_0 is greater than that for S_1 and S_2 but on further hydration, the order is reversed. S_v species only appear after the final stages of hydration and are thought to be responsible for the rotation-like features observed on the water combination band at about 1900 nm.

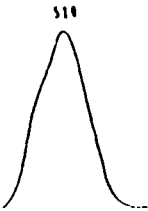
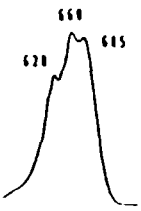


S_0' : monomerically adsorbed
 S_1' : partially H-bonded
 S_2' : fully H-bonded
 S_v : vapour molecule

The existence of water molecules and silanol functionalities in the fully densified glasses could have consequences for the durability and stability of the glass phases and hence to the engineering uses to which the glasses can be put.

(2) UV/VIS Spectroscopy

Metal ions (Nd^{3+} , Co^{2+}) have been used as a probe of pore chemistry (silanol functionality, hydration state, microporosity). The coordination of the metal ions depends upon the nature of the ligands, thermal history of the glass and the hydration state. Competition between water, surface silanols, a range of counter ions (nitrate, chloride, acetate) and controlled sintering in providing the primary coordination sphere for the metal ions has been explored.

Sample	Co doped P1 gel glass (made in $\text{CoCl}_2/\text{H}_2\text{O}$)		
Postdoping Treatment	before dehydration	dehydrated in vacuo at room temperature	sintered in vacuo at 900°C
VIS Absorption			
Colour	pink	blue	blue
Complex	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$[\text{CoCl}_4]^{2-}$	
Ligand	H_2O	Cl^-	SiOH or Si-O-Si
Symmetry	octahedral	tetrahedral	tetrahedral

(a) Coordination Chemistry of Cobalt

Studies have shown that ligand field effects predominate for cobalt in hydrated and dehydrated glasses, i.e. acetate > chloride > nitrate. The affinity of the counterions for silanol groups follows the trend, acetate > nitrate > chloride. Both metal ions and counterions can act as secondary centres for water adsorption where the trend is nitrate > acetate > chloride and depends upon interaction between the ions and silanol groups and the hydration state of the glass. Post sintering of the glasses at 900°C in vacuum (to prevent breakage and oxidation) leads to the metal ions being tetrahedrally coordinated within the matrix producing blue glasses which are unaffected by subsequent hydration.

(b) Coordination Chemistry of Neodymium

The Judd-Ofelt method is being applied for evaluation of the intensity parameters T_2 , T_4 , T_6 relevant to the f-f transitions which are found to vary with hydration state, counter ion and glass structure. Subsequent sintering of these samples in air results in incorporation of the metal ion within the glass

matrix although the fluorescence lifetimes of these materials, as measured by Dr King at Manchester are still too short for use in tunable lasers.

(3) Nitrogen Adsorption Measurements

The glasses under investigation are built up from meso and microporous regions and a novel method, developed at Brunel using a dynamic volumetric method to measure adsorption and desorption isotherms is being applied to the study of microporosity. Applications of the Horvath-Kawasaki method is giving information on pore size distributions of the micropores which have been analysed in relation to sample history. Immediately prior to densification, the mesopores present in the glass increase in size (approximately 50% above that at 180°C) but collapse to give a fully dense structure at 1100°C. Metal ion doping leads to decrease in micropore volume and the technique described above will yield some information on the specific geometry of the pores including those affected on post-metal ion doping.

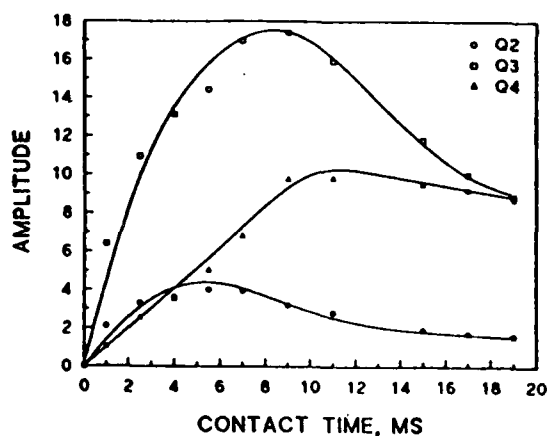
(4) Solid State NMR

^1H NMR has been used to measure relaxation behaviour (T_1 and $T_{1\rho}$) for a wide range of gel glass samples in order to assess domain sizes within the structure. No definitive results have as yet been obtained but data clearly show that sample history has a dramatic effect on the dimensions of molecular units within the structure. The running of complete 'matched' sample sets will enable this phenomena to be understood.

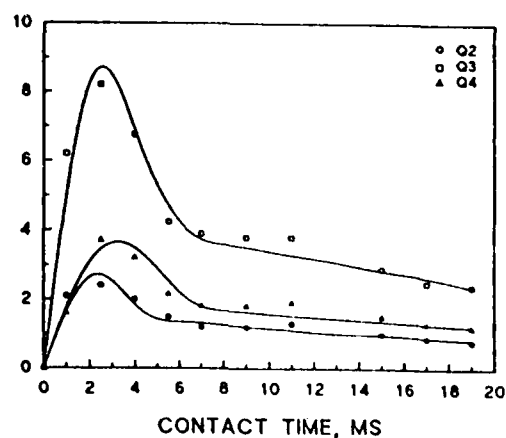
^{29}Si nmr on samples prepared under different environments has shown that the presence of oxygen (and presumably water) has dramatic effects on the speciation and relaxation behaviour of the glass samples. Quantification of this phenomenon is currently sought.

Crosspolarisation ^{29}Si solid state NMR
(N.B. $Q_4 = \text{Si}(\text{OSi})_4$; $Q_3 = \text{Si}(\text{OSi})_3\text{OH}$; $Q_2 = \text{Si}(\text{OSi})_2(\text{OH})_2$)

Prepared in air



Prepared in nitrogen



(5) Silica/ Titania Samples

Preliminary work on these samples has shown that increasing titania content, for a given temperature increases the hydrophilic character of the glass. For samples prepared at high temperatures, (1000°C) the presence of titania within the glass results in a complexity of surface and bulk functional species which are currently being identified using NIR spectroscopy.

Future Plans

Small angle neutron and X-ray scattering experiments in conjunction with Dr J.C. Dore of the University of Kent are planned to look at structure (aggregate) development as beam time becomes available.

Silica samples with larger pore dimensions will be investigated as and when they become available, both with respect to behaviour under thermal treatment regimes, but also for surface reactivity and pore structure development. Gel glasses impregnated with organic polymers will be studied and an assessment of catalytic behaviour for the selected metal doped samples is also envisaged.

Mixed silica/ titania samples will be analysed for surface chemistry functionalities and their behaviour under different environmental conditions will be explored.

Acknowledgements

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LASER DEVELOPMENTS IN SOL-GEL GLASS

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- 1. Laser enhanced densification of sol-gel glass**
- 2. Optical properties of sol-gel glass**
- 3. Tunable solid state glass lasers**

LASER ENHANCED DENSIFICATION OF SOL-GEL GLASS

Introduction

Work has continued in examining the parameters of laser densification, looking at variation of beam intensity, exposure times, sample types and irradiation conditions. Investigations have been made into densification behaviour in a controlled atmosphere compared with normal atmospheric conditions. Characterisation studies of laser densified regions have continued and, in particular, a method of measurement of refractive index by reflectivity has been developed to observe changes in refractive index with different degrees of densification.

Densification Studies

The objectives of this study have been to develop an understanding of the basic science of laser enhanced densification of sol-gel glass, and to use selected lasers to determine densification parameters and characteristics. Most of the work has used a continuous wave carbon dioxide laser with power output up to 17W. Successful laser densification of sol-gel glass has been demonstrated and the thresholds for permanent laser densification determined. Permanent laser written tracks have been produced on bulk sol-gel glass with refractive index increments of up to 0.1, and characterised by microhardness, Raman spectroscopy and surface refractometry.

Using a carbon dioxide laser with a beam power of 2.5W and a motorized translation stage (figure 1), densification of tracks with a laser beam diameter of $760\mu\text{m}$ was performed. These tracks can be detected by measuring the Vickers microhardness (figure 2). Compared with work already performed with a beam power of 17W, these studies were at relatively low powers and scanning speeds. It was found that in this low power, long exposure time regime, it was impossible to produce a densification effect that did not also produce laser damage on the surface of the sol-gel. Photomicrography of laser treated tracks did show, under interference, some evidence for the depressions expected with densification but were

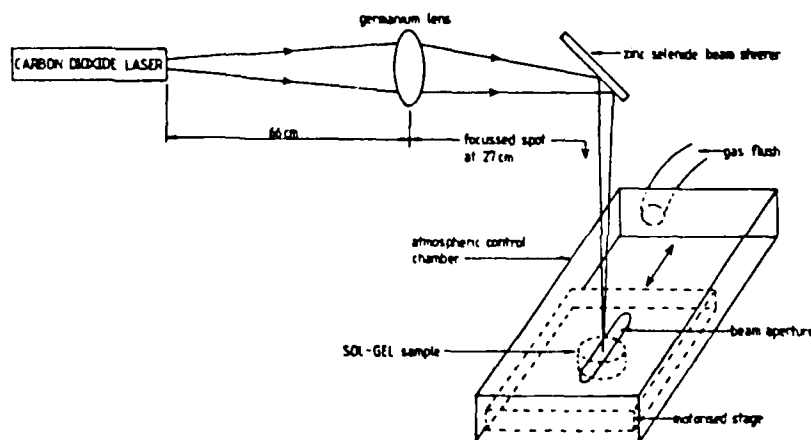
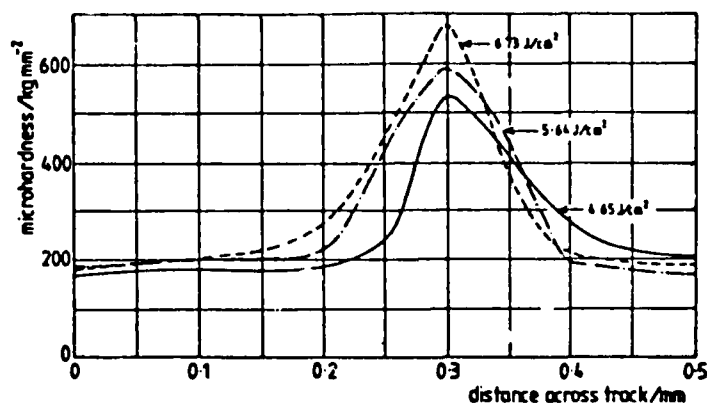
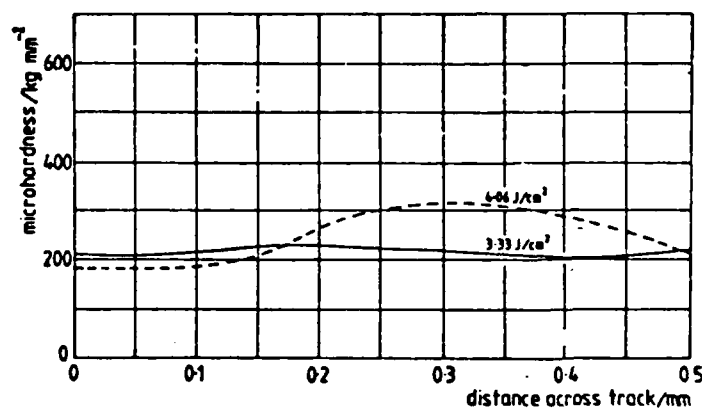


Figure 1.
Arrangement for densification of sol-gel samples



Microhardness profiles for different energies.



Microhardness profiles for different energies.

Figure 2.
Vickers microhardness profiles of densified sol-gel samples

on a millisecond time scale. Thus a smaller lateral heating effect was produced. Since at 2.5W it was not possible to separate densification and damage, and at 17W only a narrow energy range was found between densification and damage it is considered that the energy range between densification and damage will widen with laser beam power. A higher beam power will allow shorter exposure times and reduce lateral heating effects. The present carbon dioxide laser system available had a maximum output power of 17W.

Refractive Index Measurements

Measurements with the reflectivity refractometer as described previously have been made on sol-gel samples and standard Spec-B and BK-7 samples. For standard Spec-B and BK-7 a fluctuation of 0.2% from point to point on the surface was measured, to an accuracy of 0.2% with accepted values. For porous sol-gel, although measurements at each point on the surface had a statistical accuracy of 0.2-0.7%, fluctuations in measured values over many points were at the 5% level. Measured values averaged over a number of points were within statistical errors of the accepted refractive index for the porosity concerned. Bearing in mind the accuracy of measurements at each point we can conclude that there exist surface density fluctuations on a sub-millimeter scale which cause the spread in refractive index.

accompanied by cracking and crazing superimposed on the treated region. In marked contrast to previous studies carried out at higher laser powers and faster scanning speeds, damage in this case constituted micro cracks on the surface instead of the bloating seen previously. These micro cracks may be due to induced thermal stress from the heating effect of the laser beam. It can be concluded that the cracking is due to the relatively large lateral heating effect which occurs when the exposure time to the beam is long.

The thermal diffusivity time t_c for silica when exposed to $10.6\mu\text{m}$ radiation is approximately $30\mu\text{s}$. The exposure times with a beam power of 2.5W were typically tenths of a second and thus we should expect a large lateral heating effect. Experimentation at 17W beam power, where a densification effect was seen and laser damage was in the form of bloating, used exposure times

Measurements with a beam diameter of millimeters and focussed to a few microns were performed and found to give the same spread in values. These observations can be interpreted in terms of a fuller understanding of the optical properties of sol-gel glass, developed in this study, and described in the next section.

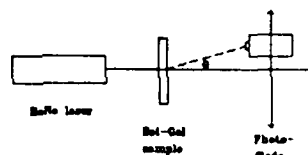
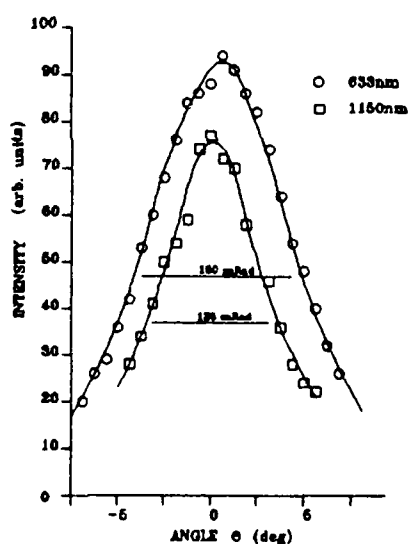
OPTICAL PROPERTIES OF SOL-GEL GLASS

Introduction

In order to produce a laser host of doped sol-gel glass it is essential that the intrinsic optical losses in the glass are minimised. This is of increasing importance as the pulse length is increased and the intensity of pump light, and hence the gain produced, is decreased. Absorption losses in sol-gel glass are known to be very small and the principle source of optical attenuation in the undensified glass is due to scatter. Experiments have been carried out to identify the physical processes responsible for this scatter and to find methods of reducing it to acceptable levels. These experiments involved the measurement of the angular distribution of the scattered light as well as inspection of sol-gel samples by optical microscopy. The use of water and ethylene glycol as index matching fluids has also been evaluated.

Results

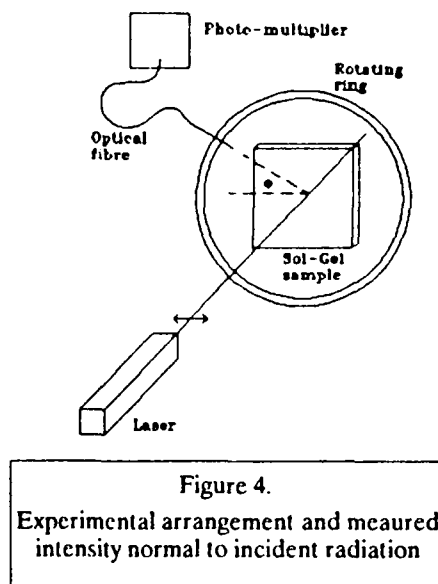
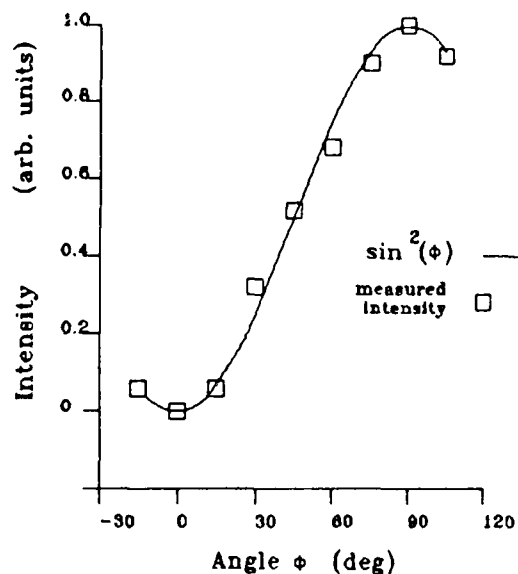
The small size of pores in sol-gel glass (1-10nm) is expected to lead to Rayleigh scattering of incident light which is characterised by the $\cos^2$ distribution of dipole radiation. The observed scatter however is sharply peaked in the forward direction, characteristic of Mie



scattering, with a 5mm thick dry sample giving rise to scatter into a cone angle of approximately 100mR (figure 3). This angle is independent of the temperature to which the sample is densified (over the range 700°C-1000°C) and linearly dependent on the thickness of the sample. Increasing the wavelength of the incident light from 633nm to 1.15 μ m leads to a reduction in the scattering angle by approximately 25%. The light scattered in a plane orthogonal to the wave vector of the incident light is much less intense but the angular distribution relative to the axis of polarization can be measured using a

Figure 3.
Experimental arrangement and measured intensity of forward scattering

photomultiplier and is found to follow a $\sin^2$ distribution (figure 4). The amount of scattered light as well as the scattering angle can be significantly reduced by filling the sol-gel pores with a suitable index matching fluid. Water and ethylene glycol are both effective, with ethylene glycol better matching the refractive index of fused silica, but water being retained better by the sol-gel glass.



Microscopic studies of the undensified glass clearly show domains within the bulk of the glass on a 10-50 μ m scale, and these domains are masked almost entirely by the inclusion in the porous glass of index matching fluid. Inspection of the samples between crossed polarisers exposes stress induced birefringence which can lead to refraction and dispersion of light.

Conclusion

These studies have identified three scales of the physical properties of undensified sol-gel glass which give rise to different optical effects.

1. nm scale: The individual pores give rise to Rayleigh scattering, although the magnitude of this effect will not preclude laser action.

2. μ m scale: The domains caused by inhomogeneities in the pore distribution lead to Mie scattering and diffraction in the forward direction. This can be a large effect which is significantly reduced by the use of index matching fluids and can be overcome in the preparation of the sample.

3. mm scale: Stress induced birefringence leads to refraction and dispersion of incident light. This can be removed by annealing of the sample.

TUNABLE SOLID STATE GLASS LASERS.

Introduction

A new type of laser based on a doped sol-gel glass host has recently emerged. The sol-gel glass can either be doped with inorganic ions in the fully densified state or with organic molecules in the partially densified state. Inorganically doped sol-gel holds certain advantages over traditional materials by providing a high purity medium, high power operation, low non-linear refractive index (n_2) and a constant and very low coefficient of thermal expansion.

Organically doped sol-gel provides an enhancement of the laser properties of organic dyes. This involves: molecular immobility / isolation which reduces collisional deactivation; greater heat dissipation (thermal conductivity of sol-gel = $1.3 \text{ Wm}^{-1}\text{k}^{-1}$ c.f. methanol $0.2 \text{ Wm}^{-1}\text{k}^{-1}$) which reduces thermal lensing and enables higher power densities to be attained; increased dye photostability and upper state lifetime; reduced dimerisation and thus reduced self quenching and absorption; and a greater dye concentration for a more compact and efficient cavity design. Finally, a departure from the traditional liquid state for the dye medium will lead to a more convenient and manageable glass state.

Results

1. Inorganic: Uniform Nd^{3+} ion distributions were produced by the use of an Al glass modifier. Characterisation of the doped glass was performed by TEM, SEM-EDAX and Raman spectroscopy. The Nd^{3+} fluorescence lifetimes and efficiencies have been measured and for deuterated samples are now found to be comparable to other laser glasses (figure 5), indicating that phonon quenching of the upper laser state by hydroxyls is no longer a problem. Therefore the Nd^{3+} exists in the host in a form suitable for laser action.

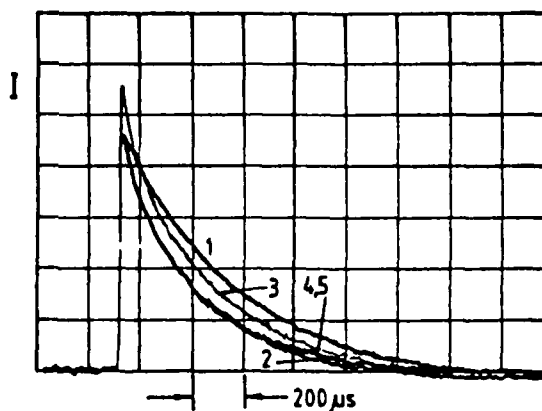


Figure 5.
Lifetimes of Nd^{3+} in laser glass (1,2) and in sol-gel glass (3,4,5)

2. Organic: Successful laser systems have been demonstrated with Rhodamine 6G doping of partially densified (850°C) sol-gel glass (figure 6). Laser action was observed both with excimer laser pumping and flashlamp pumped dye laser pumping with pulse durations of 10ns and $2\mu\text{s}$ respectively. The emission spectra and temporal profiles showing the spontaneous emission and laser output when pumped by the flashlamp pumped dye laser are shown in figure 7. In this case the doped sol-gel laser, for heavy duty pumping (0.2J/mm^2) had a lifetime of approximately 10 laser shots.

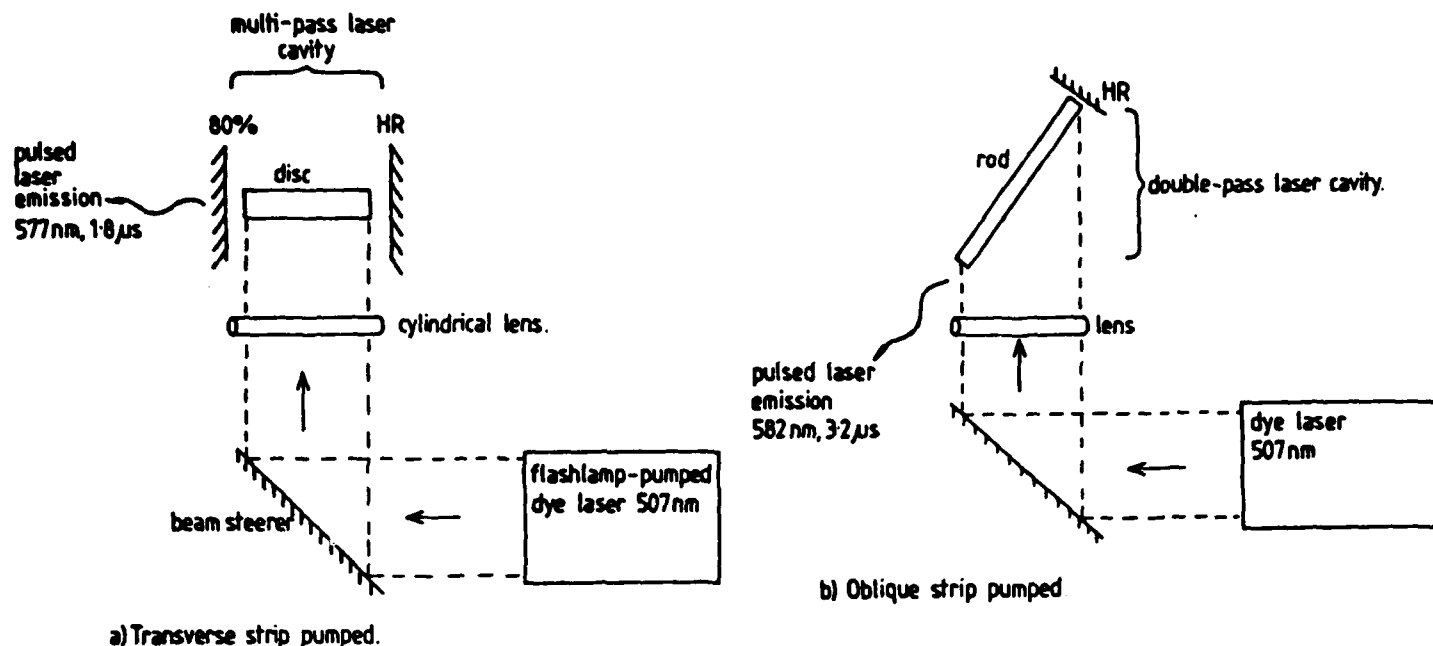


Figure 6.
Arrangements for laser pumping of organically doped sol-gel samples

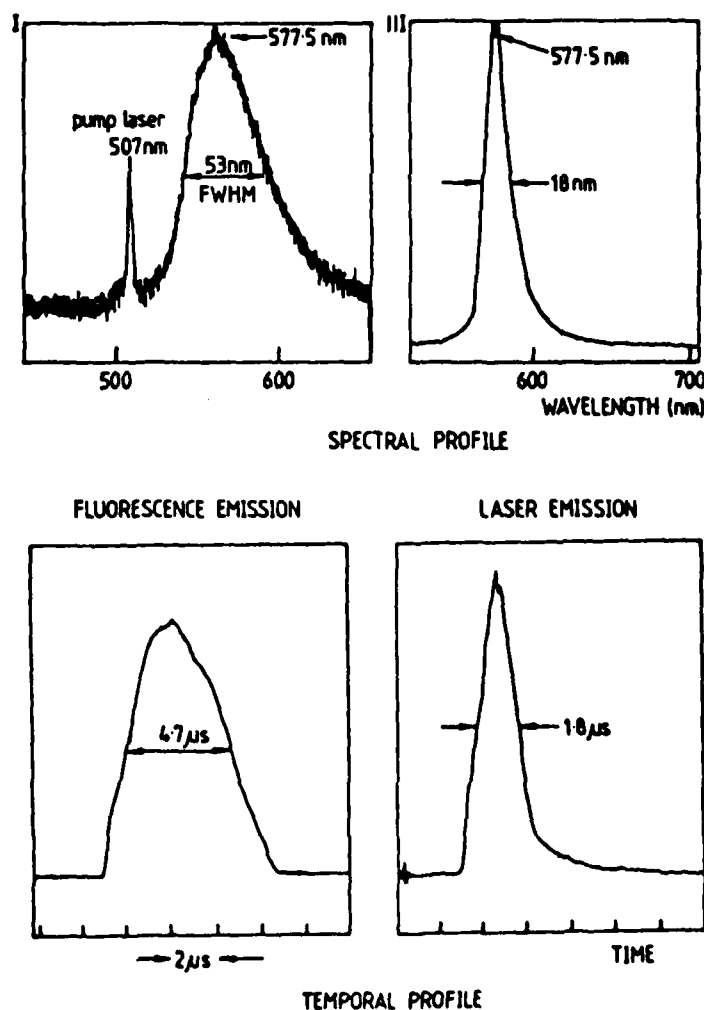


Figure 7.
Spectral and temporal profiles showing laser output from organically doped sol-gel sample.

These results suggest that direct flashlamp pumping of organically doped sol-gel rods is possible. An optical cavity and close coupled ceramic pumping chamber have been constructed and tested with an inferior 'Vycor' porous glass rod doped with Rhodamine 6G. Although no laser action was observed, this can be explained by the large amount of scattering which occurs in Vycor, and recent samples of sol-gel rods show great promise with their improved optical and mechanical properties approaching that of best quality laser glass.

Conclusions

Laser action has been observed in organically doped sol-gel glass pumped both by an excimer laser to give short duration 10ns pulses, and a flashlamp pumped dye laser giving long duration 2 μ s output. Results indicate that, with recent improvements in the preparation of the sol-gel samples, direct flashlamp pumping of both organically and inorganically doped sol-gel glass rods should be realised in the near future.

SOL-GEL IMAGING TECHNOLOGY

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INTRODUCTION

Our interest in gel-silica monoliths was triggered by the observation of abnormal performance of etalons, made of such material, which when placed in the cavity of an argon-ion laser exhibited unusual levels of conversion efficiency (single line — single mode). Detailed studies of later samples of material have indicated a complex set of truths without revealing some single clear performance maker for these materials.

We decided to investigate the optical and thermal expansion properties of gel-silica etalons using our own home-built test so that accurate measurements of refractive index changes and thermal expansion could be made.

It transpires that the measurement of transmissive etalon-like properties is relatively simple and in fact allows a ready relationship of the product of optical path and the index of refraction, nd , to environmental temperature. The extraction of n as a function of temperature from this product is of extreme importance both in commercial as well as AFOSR applications.

If such an etalon is placed in an oven and its transmission or reflection is monitored then the typical transmittance behavior is observed as predicted by classical theory.

We note that the transmittance of a simple etalon is of the form τ , where the

$$\tau = \frac{I_t}{I_i} = \frac{1}{\left[1 + F \sin^2 \left(\frac{\delta}{2} \right) \right]} \quad (1)$$

where δ is the double path phase shift and F is a factor depending on the reflectance of the etalon surface. Since $\delta \propto nd$, changes of the temperature of the etalon cause a change of phase shift which can be observed directly via the transmittance. We note however that we cannot characterize the structure fully since n and d are inextricable. Thus incrementally, we have

$$\Delta \delta = n \Delta d + d \Delta n \quad (2)$$

and Δd and Δn need to be determined independently.

A major area of interest of our program has been the determination of these two increments as a temperature increment is applied. We have opted for optical interferometry using the most modern methods available to us.

Our second major area of interest is in the incorporation of the DuPont imaging polymer into porous silica matrices. This work encompasses two main application areas. The first of these relates to the generation of reflective or transmissive optical elements which can invoke the best properties of both the porous silica and the polymer.

Finally, by incorporation of fluorescent dyes such as Rhodamine 6G into the polymer we expect to create a range of distributed feedback laser devices which can then be incorporated into the matrix of the porous gel-silica.

An examination of the properties demanded for a single mode distributed feedback laser shows a key feature to be the need for a slightly inhomogeneous laser medium. We believe that such a property is certain to be endemic in such mixed material devices and may have interesting consequences.

The observations to date of intra cavity etalons made from gel-silica indicate that a major difficulty exists in the achievement of the optical homogeneity comparable to that of the high temperature prepared silicas.

Inhomogeneity of refractive index of intra cavity samples can produce severe problems of ray deviation within the cavity hence partially de-stabilizing the optical pattern with a resultant loss of output.

PROGRESS IN THE STUDY OF THERMALLY INDUCED OPTICAL CHANGES IN GEL-SILICA ETALONS AND GENERAL OPTICAL MONOLITHS

We have built a sensitive interferometer for the measurement of expansion of gel-silica monoliths. The outlines of the experimental scheme is shown in Figure 1.

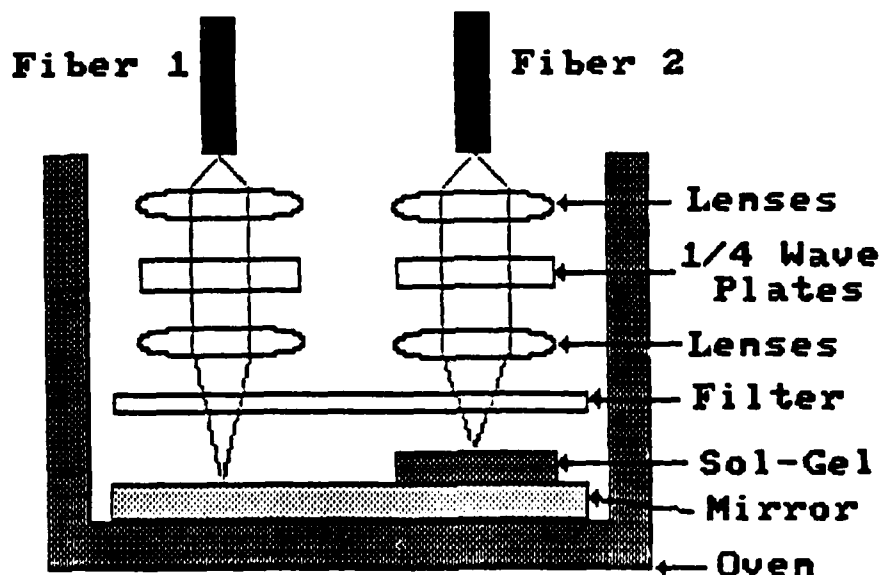


Fig. 1. Layout of Optical Fiber Based Dilatometer

Optical fibers 1 and 2 are fed to a remote sensing head from the interferometer. Having passed down the polarization preserving fibers, the beams are immediately collimated. We have found this collimator to be an essential ingredient of the optical system since it endows flexibility of return of the light back into the fiber.

After collimation, the fiber beam is focused on to the reference substrate (for fiber 1) and the sample (for fiber 2). The beams are however circularly polarized before focusing and on return, their polarization is turned through $\pi/2$ with respect to the beam exiting from the fiber at the sensing end.

We have found enormous advantages in using the focusing system as distinct from say attempting to reflect the collimated exit beam from the fiber back into the system. A degree of angular flexibility in the attitude of the samples results and hence slightly unflat as-cast samples be accommodated.

When the beams return up the respective fibers they are combined and two exit interference patterns can be observed.

The observation of a pattern which is sinusoidal in form suffers from the difficulty that when the observation is made at a peak or a trough, there is no differential sensitivity. A neat way around this problem is to observe the intensity at the centers of say two bullseye patterns in phase quadrature. Two detectors in the interferometer feed their signals into the control computer where their respective intensities are registered and then divided.

Thus, if we observe an intensity pattern of the form $I_m \sin \delta$ where δ is a phase shift and I_m is the amplitude factor and simultaneously observe the quadrature signal $I_m \cos \delta$, the ratio is $\tan \delta$ and is independent of I_m (e.g. laser fluctuations). As δ varies, the function $\tan \delta$ has an observation slope so long as δ is not too close to 0.

The computer is then instructed to print-out $\tan^{-1}$ of the ratio and δ and hence the expansion of the sample is directly read out.

We note that the maximum derivative of $\sin x$ or $\cos x$ is ± 1 and that this is exceeded when x reaches $\pi/4$ in the case of $\tan x$. This shows that quadrature phase detection systems are endowed with considerably more sensitivity.

A detailed analysis of the conformity of gel-silica to the predictions of the Lorentz-Lorenz theory of refraction will be made. It is hoped to compare the intrinsically amorphous gel-silica and titania-silica complexes with conventional high temperature prepared silica.

NOVEL DEVELOPMENTS IN DISTRIBUTED FEEDBACK LASERS

The conclusion drawn from our analysis of sol-gel derived silica for use in the important intra cavity situation in the ion laser has given clear indication of problems of ultimate homogeneity. We suspect that thick monoliths are likely to be problematical in this context although novel properties such as those first discovered by Hench and Phillips in 1987 may justify further searches.

The phase of gel-silica prior to total densification exhibits interconnected pores which can occupy a significant fraction of the volume of the matrix.

We have for some time been involved with imaging experiments with the DuPont photopolymer. This material actually comes in several forms.

One form of the material is appropriate to the formation of low frequency transmissive elements such as diffraction gratings. In Figure 2, we see the formative experiment for a diffraction grating in the DuPont material.

Irradiation of the monomeric form of the polymer creates a spatially modulated refractive index field as shown in Figure 3. The regions exposed to the antinodes of the pattern become partially polymerized. This results in diffusion of monomer into those regions where depletion concentration takes place.

Such a diffusion mechanisms results in a build up of refractive index in the antinodal zones. The final index field is then non-uniform with a spatially periodic structure as in Figure 4.

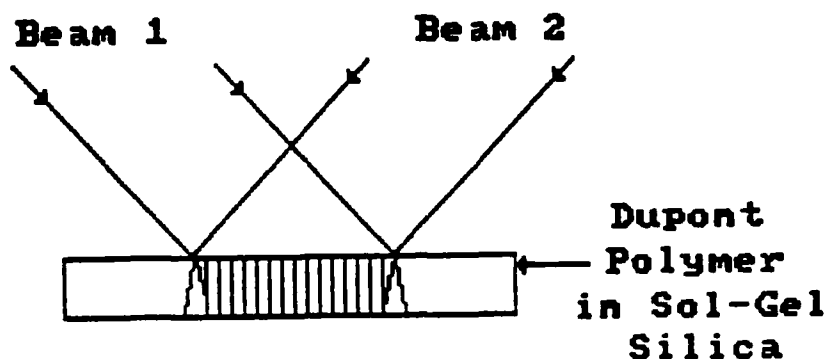


Fig. 2. Fringes of Interference are Created by Two Beams of Coherent Light.

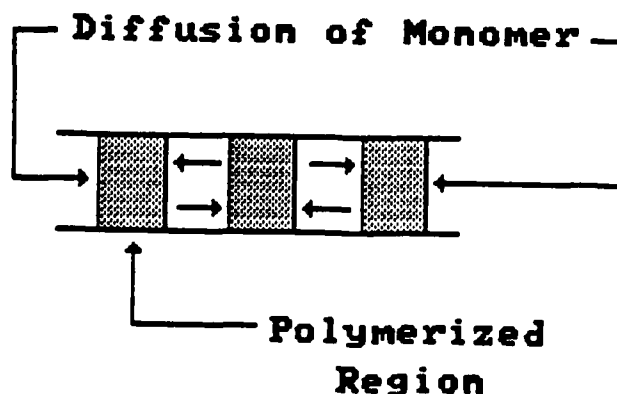
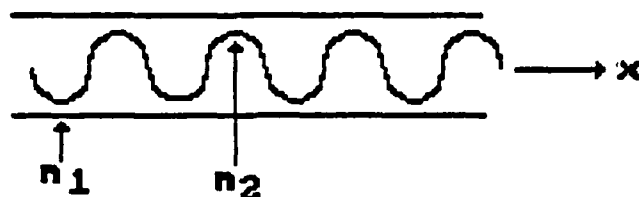


Fig. 3. Process of Monomeric Migration in the Exposed Sample

$n(x)$ = Index of Refraction



$$\Delta n = n_2 - n_1$$

$0.01 < \Delta n < 0.07$ for the Polymer

Fig. 4. Resultant Index Modulation in the Composite Sol-Gel Silica/Polymer.

Materials such as these are very convenient since they need no further processing. For this reason, they can be embedded in the pores of porous gel-silica where they also perform the role of index-matching, thus eliminating the scatter caused by the pores.

Thick optical elements can be contemplated using such technology. Passive devices created by such means are implicitly interesting. For example very thick holograms are simple concept.

We are generalizing the possibilities to include a study of including in the polymeric structures laser dyes such a Rhodamine 6G. The possibility of providing sensitization of the polymeric process with such dyes and hence the creation of a spatially periodic pattern of index is an attractive proposition.

Let us now look at one of the ultimate possibilities:

Firstly, we fabricate a grating in a polymer R6G composite.

The spatial period is chosen to match part of the fluorescence spectrum of the R6G say in the range at 600 nm. We have then fabricated a fluorescent structure with periodic index variation with potential for use as a distributed feedback dye laser.

A distributed feedback laser returns the light in the cavity not just with end mirrors on the resonator but by partial and distributed feedback in the gain medium. Such distribution of feedback can be achieved if one arranges the spatial modulation of the index to resonate with the lasing light.

SUMMARY

We have summarized our work to date in important areas of application for gel-silica. The new interferometer will enable accurate in-house measurements for n and d to be performed in relation to etalons and as-cast gel-silica samples. A basic understanding of the relevance of the Lorentz-Lorenz relationship to gel silica will then be possible.

Agreements are now in place to enable the experiments on the DuPont polymer in relation to distributed feedback lasers. A further agreement between DuPont and Geltech enables the joint use of the polymer and porous silica samples in a range of passive and active optical devices.

ACKNOWLEDGEMENTS

We greatly appreciate the background efforts of Dr. Don Ulrich of AFOSR who has kept the money flowing and offered touching enthusiasm for our modest effort. We also thank Professor Larry Hensch for his unstinting support and encouragement.

OVERVIEW

HIGH T_c CERAMIC SUPERCONDUCTORS AND INORGANIC NLO MATERIALS

by

J. D. MACKENZIE

University of California, Los Angeles

In order to provide a broader coverage and a better balance in the overall OGAMM program, an international collaborative research effort was initiated in 1987 on high T_c ceramic superconductors with J. D. Mackenzie as the team leader. The original goal was to fabricate the superconductors via the sol-gel technique. The team consisted of J. Livage (University of Paris), A. D. Wright (Reading University) and J. D. Mackenzie (UCLA). Dr. Livage's task was to study the structures and reaction mechanisms in the sol-gel liquid solutions. J. D. Mackenzie's charge was to investigate the formation of the superconducting ceramics from the gels. It soon became evident that whereas the sol-gel method was especially adaptable to thin films, bulk superconductors from the bismuth system were better prepared by a glass-ceramic method. The task of A. D. Wright of Reading University, UK, was to study by X-ray and neutron diffraction the transformation of the amorphous gel as well as the glass to the crystalline superconductors. Significant progress has been made in the Livage laboratory on solution chemistry, leading to the use of metal hydroxides to form gels. Work at UCLA has resulted in the fabrication of dense superconducting ceramic tapes and fibers. Recently, Professor D. C. Bradley, F.R.S., of London University has been recruited to join the team. Professor Bradley is the recognized "Father of Alkoxide Chemistry". His task will be the preparation of new and superior alkoxide precursors. They will permit the formation of thin film superconductors of enhanced properties via the sol-gel route. The immediate goal of the glass-ceramic approach is to fabricate large quantities of tapes and fibers for industrial evaluation.

Semiconductor crystallites such as CdS, with dimensions less than about 10 nm, when embedded in an inert transparent matrix such as a silicate glass, are so-called "quantum dot" materials. They can have very high third order

nonlinear coefficients at room temperature. In 1989, a new task was initiated to prepare these new nanocomposites via the sol-gel route because of the possibility of better process control at lower temperatures. Professor M. Yamane of the Tokyo Institute of Technology was invited to collaborate with J. D. Mackenzie in this work. In the past year, these new nanocomposites have been made via two variants of the sol-gel method. In particular, the "ORMOSIL" approach, with the copolymerization of inorganic and organic precursors has led to the fabrication of fairly large discs (inches in diameter) of good optical and mechanical properties. Crystallites of CdS of less than 10 nm in dimension were grown in the ormosil matrix. During the coming year, such samples will be sent to Professor Prasad of the University of Buffalo for evaluation while improved process control will be studied at UCLA. The performance of these inorganic NLO materials will be compared to those silica-organic composites made by Dr. T. King and Professor Hench and with the polymeric NLO materials prepared by others of the OGAMM program. New precursors prepared by Professor D. C. Bradley will be tested for the ormosils and Professor Livage will be investigating the reaction mechanisms of these new solutions. The basic studies of Hench and West in Florida on the densification of silica gels will be correlated with the formation of ormosils. "Gel-Sil" samples from the Hench group will be evaluated as hosts for CdS crystallites. It is expected that such interactions will be extremely beneficial to the overall progress in the entire OGAMM program on organic, inorganic and organic-inorganic advanced materials.

Progress Report, 1989-1990

Semiconductor Quantum Dot Materials

Principal Investigator: Professor John D. Mackenzie, UCLA

Ph. D. Student: Chia-Yen Li

Collaborator: Professor Masayuki Yamane, Tokyo Institute of Technology

1. Background

Semiconductors like CdS and CdSe are known to have very high values of third order non-linear coefficients ($\chi^{(3)}$) at $T < 20^\circ\text{K}$. The very low temperatures needed are not attractive for applications. Theoretically, if the crystal size is reduced to much less than $100\text{\AA}$, of the order of the dimensions of a phonon, quantum confinement occurs. Very high $\chi^{(3)}$ now achievable at room temperatures. Commercial colored glasses containing CdS and CdSe, long used as red and yellow filters, were found to have CdS and CdSe crystallites of about $100\text{\AA}$. Their $\chi^{(3)}$ values were found to be 10^{-8} - 10^{-10} esu at 20°C . Because these glass filters are made by glass fusion methods at high temperatures and because the mechanisms of crystallite formation are not understood and hence control is difficult, other methods to prepare such "Semiconductor quantum dot materials" have become desirable research projects. This program involves the preparation of such nanocomposites by the sol-gel method. Cuprous chloride microcrystals have also been studied since they also give high $\chi^{(3)}$.

The sol-gel process to prepare semiconductor-doped glasses is superior to the conventional melt-quench method, since the size and the amount of semiconductor dopant can be controlled easily. The sol-gel method can also give glasses with new compositions, high purity and good homogeneity at temperatures significantly lower than those required by the melting method. The semiconductor microcrystallites formed in the melting method are created by complex crystal

growth during heat treatment, while those formed via the sol-gel process are by chemical reactions at low temperature. For all optical elements, low temperatures are preferable to high temperatures.

Research Objectives

- (a) Prepare glass-semiconductor nanocomposites with high $\chi^{(3)}$ at room temperature.
- (b) Develop an understanding of how fabrication processes affect the final size, size distribution, composition and crystal structure of semiconducting microcrystallites.
- (c) Determine experimentally the relation between non-linear optical properties and nanostructure of quantum dots in semiconductor-oxide nanocomposites.
- (d) Understand the interplay between quantum confinement effects arising from the nanostructure of the semiconductor clusters and the structure of matrices.

2. Research Progress

(A). Fabrication of semiconductor-oxide nanocomposites by the sol-gel process

Various methods of obtaining semiconductor-oxide nanocomposites have been studied. Two different matrix systems were investigated to prepare these nanocomposites. In the first multicomponent silicate glass system, the sols containing Cd^{2+} were prepared by adding aqueous solution of Cd salt and sodium acetate to the methanol solutions of partially hydrolyzed mixture of tetramethylorthosilicate and boron ethoxide. Gelation of the sols was accomplished by ultrasonic agitation. The obtained gels were heat-treated at around 430°C to decompose the remaining organics and, subsequently, expose to a H_2S stream to sulfidize CdO in the heat-treated gel. The CdS-doped porous glasses were fully densified at a temperature as low as 550°C .

The second type of matrix used was organically modified silica (Ormosils). Part of the bridging oxygen bonds in ormosils were replaced by alkyl groups by adding 10 wt.% of

polydimethylsiloxane into a tetraethylorthosilicate alcohol solution. The resulting ormosils were highly transparent. The organic groups present decrease the risk of fracture on drying. Both cadmium sulfide and cuprous chloride have been doped in these ormosils. Cadmium sulfide can be formed by the same method as mentioned above. In the later case, CdS microcrystallites were formed by the reaction of Cd salts and sulfur containing compounds, such as thiourea and thioacetamide. By utilizing colloidal technology, the semiconducting microcrystallites can be formed in the sols prior to gellation. Cuprous chloride were formed in the ormosils by heat treatment. During the heat treatment, nucleation and growth of semiconducting microcrystallites occurred as a result of a diffusive phase decomposition of the supersaturated solid solution. Fig.1 shows the CdS and CuCl semiconductor-oxide nanocomposites prepared by the methods described above.

(B). Structural characterization of the semiconductor-oxide nanocomposites

Formation of semiconducting microcrystallites was observed by a color change of the composites. Exposing the CdO-doped ormosils to H_2S gas changed the transparent sample from colorless to yellow. The colouration was dependent on both the heat treatment and the time of exposure.

Fig. 2 shows the X-ray diffraction (XRD) patterns of ormosils heated to $380^\circ C$ for 24 h (a), reacted with H_2S gas for 8 h (b) and 72 h (c) at room temperature. The ormosils heated at $380^\circ C$ for 24 h only shows the typical amorphous pattern, whereas the XRD patterns of ormosils reacted with H_2S gas have several broad peaks on the amorphous background of matrices. The precipitated crystallites are identified as hexagonal wurtzite CdS crystals. The particle sizes estimated by the Scherrer equation are $35\text{\AA}$ for sample (b) and $60\text{\AA}$ for sample (c). Transmission electron micrograph and electron diffraction pattern of fracture surface are shown in Fig.3. Both Fig. 3 and Fig. 2 are from the same sample. Cadmium sulfide clusters show faint images in the micrograph with the same average size as estimated by XRD pattern. Selected area diffraction pattern (SAD) shows these clusters having a hexagonal wurtzite structure.

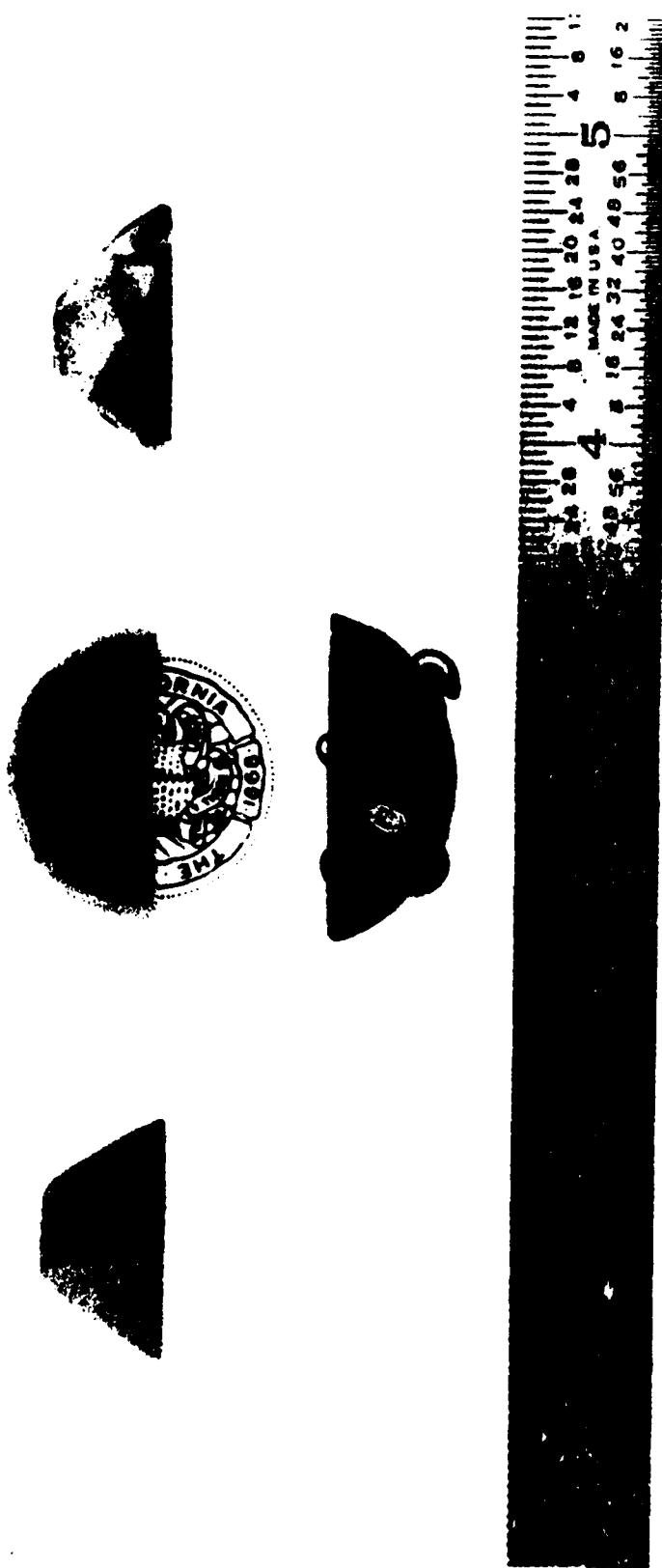


Figure 1 Transparent semiconductor-doped ormosils prepared by the sol-gel process.

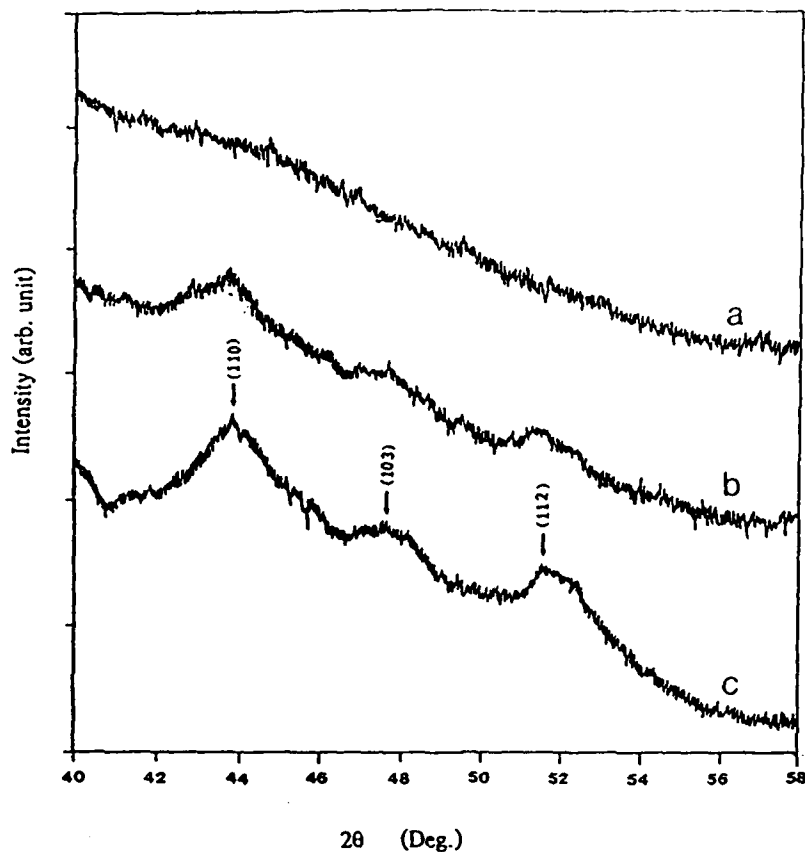


Figure 2 X-ray diffraction patterns of ormosils heated for 24 h at 380°C (a), reacted with H₂S gas for 8 h at room temperature (b) and 72 h (c). The numbers in (c) are the indices of hexagonal CdS crystal.

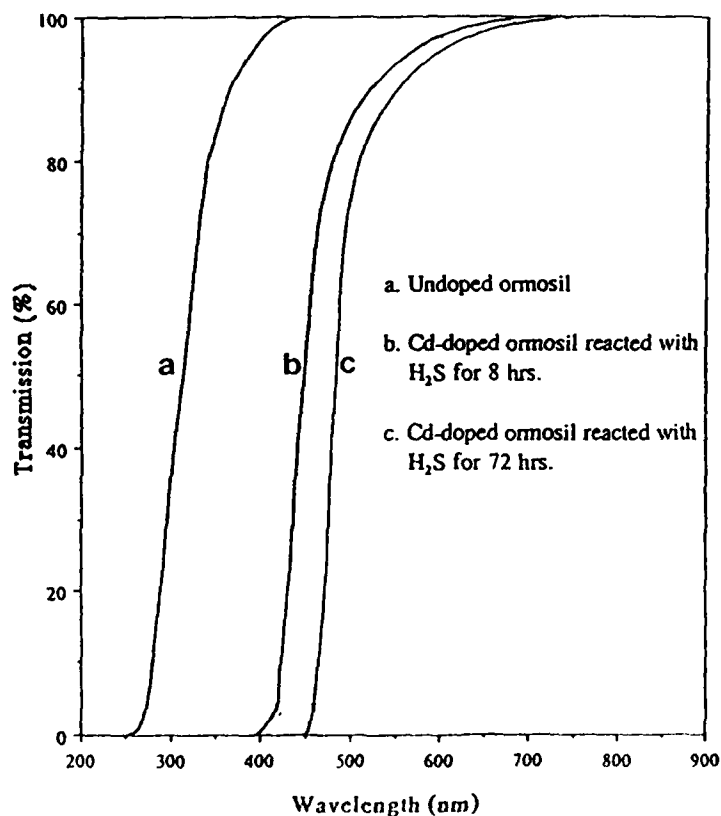


Figure 4 Optical transmission spectra of CdS-doped ormosils. The blue shift of curve b by 0.25eV compared to c is a consequence of the quantum confinement effect due to smaller particle size.



Figure 3 Transmission electron micrograph and (inset) electron diffraction pattern of ormosils reacted with H_2S for 72 h. CdS crystallites are seen as dark spheres with average size of 60 Å. The electron diffraction pattern shows that CdS crystals have a hexagonal wurtzite structure.

(C). Optical spectra

Fig. 4 shows the transmission spectra of ormosils heated for 24 h at 380°C (a), exposed to H₂S gas for 8 h (b) and 72 h (c) at room temperature. It is apparent that the absorption edge of (b) is blue shifted by 0.25eV compared to (c). The blue shift is attributed to the quantum size effect of the carrier confinement.

3. Future Plans

(a) Investigate the mechanism of semiconducting microcrystallite formation. Results will be used to optimize the present processes in order to control the final size, size distribution and composition of the microcrystallites in the nanocomposites.

(b) Conduct structural characterization measurements by thermal analysis, X-ray diffraction, and electron microscopy to determine composition, average size, size distribution and crystal structure of the semiconducting microcrystallites as well as nanostructure of matrices prepared by sol-gel methods. High resolution electron microscopy (HREM) can provide much more detailed information compared to normal TEM because these clusters are of nanometer in size. We have submitted a proposal to HREM Facility, Arizona State University to collaborate with Prof. Leroy Eyring to investigate our samples.

(c) Conduct linear and non-linear optical measurements of quantum-confined semiconductor glass composites in collaboration with professor P. Prasad of the University of Buffalo. Measurements of the frequency and intensity dependence of the absorption, luminescence, third-order optical susceptibility ($\chi^{(3)}$), and non-linear index will be conducted on these semiconductor-oxide nanocomposites.

Progress Report, 1989-1990

Fabrication of High Temperature Ceramic Superconductors

Principal Investigator: Professor John D. Mackenzie, UCLA

Research Associate: Haixing Zheng

Ph.D Student: Yi Hu

1. Background

The discovery of high temperature superconducting ceramics with T_c above liquid nitrogen temperature (77 K) is expected to open an era of high technology. The unique properties of zero resistance and perfect diamagnetism of superconductors can lead to wide applications: (1) high-field magnets for high energy physics, nucleated fusion, magnetic-resonance imaging (MRI), (2) SQUID used in biomagnetism and gravity-wave detectors, (3) Josephson junction for electronics, and so on. All these applications require either continuous fibers or wires and thin films. Numerous efforts have been made to fabricate these high T_c superconductors into fibers or wires. The promising techniques include extrusion, deposition-on-supporting wires, oxidization of metallic alloys, sol-gel and the glass ceramic process. Superconducting tapes, wires and fibers prepared by these techniques have superconducting transition temperature ranging from 80 K to 110 K. However all the materials made so far have low critical current density: $10^2 - 10^3$ A/cm² at 77K and zero magnetic field. The main causes are believed to be porosity, random microstructure and impure grain boundary.

The glass-ceramic process involves the controlled crystallization of glasses. A glass is first shaped from its molten or plastic state to produce articles of the required form. It is well-known that practically any shape can be readily formed from a glass. The sample is next subjected to a controlled heat-treatment cycle which brings about nucleation and crystallization of various phases so that the final product is a dense polycrystalline ceramic. Therefore the glass ceramic process

offers several unique advantages for preparation of high Tc Bi-Ca-Sr-Cu-O superconductors: (1) ease of fabrication into any specific form; (2) preparation of dense superconducting ceramics free of porosity; and (3) control of microstructure through the control of crystallization.

Soon after the discovery of the Bi-Ca-Sr-Cu-O superconductor system in 1988, glass formation was obtained by us in this system. Glasses were then used as the precursors for processing the superconductors [1,2]. We demonstrated that pore-free superconducting glass ceramics with high mechanical strengths could be made [1]. By making use of well established glass ceramic technique, different shapes of superconducting sample such as rods, rings, and short fibers were fabricated [3,4]. This bismuth system has at least three crystalline phases. We have investigated the formation mechanism of the 110 K phase ($\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$) and the 75 K phase ($\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_y$) in order to produce a pure 110 K phase. We succeeded in producing a glass ceramic with zero resistance above 100 K. [5]

Although a great deal of work have been done on the glass ceramic processing of superconductors in 1988 - 1989, systematic work such as glass formation, structure, properties, crystallization mechanism, phase purity, preferred orientation, etc. are needed in order to obtain the optimum conditions to produce continuous flexible superconducting fibers which can meet all application requirements, e.g. high Tc (110 K), high critical current density ($> 10^4 \text{ A/cm}^2$ at 77 K), good chemical durability and high strength.

2. Research Progress

PbO doping in the Bi-Ca-Sr-Cu-O system enhances the formation of the 110 K phase and lowers Tg. Therefore a systematic investigation on glass formation has been done on Pb doped Bi-Ca-Sr-Cu-O glasses [6].

It is known that Cu^{2+} ions can be reduced to Cu^+ ions at high temperature. It is expected therefore that Bi-Ca-Sr-Cu-O glasses which are quenched from high temperature will contain not only Cu^{2+} but also Cu^+ ions. Both wet chemical analysis and TGA show the existence of Cu^{2+} and Cu^+ ions. The higher the melting temperature, the larger the $\text{Cu}^+/\text{Cu}_{\text{total}}$ ratio (>0.5). The

presence of large amount of Cu^+ ions retards the devitrification of the Bi-Ca-Sr-Cu-O glasses [7]. Thus increasing the $\text{Cu}^+/\text{Cu}_{\text{total}}$ ratio would minimize devitrification and hence enhance the drawing of continuous Bi-Ca-Sr-Cu-O glass fibers. In addition to melting at higher temperature (e.g. 1200°C), we have found that doping vanadium oxides also helped. Glass preforms prepared by using these two methods were quite devitrification-resistant. Continuous Bi-Ca-Sr-Cu-O glass fibers have now been successfully drawn and then converted into superconducting fibers by using the equipment shown in Fig.1. The resultant fibers were quite flexible [8].

The mechanisms of formation of the $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_y$ (2122) phase and the $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ (2223) phase have been investigated. As shown in Fig.2, $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_y$ first yields a (2122) phase at 650°C , with gradually conversion into the (2223) phase:

$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_y$ glasses ----->

$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_y + (\text{Ca,Cu})\text{O}$ ----->

$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_y$ glass ceramics

The Bi-Ca-Sr-Cu-O superconducting crystals are platelet like mica. We have discovered that there glass-ceramics are machinable. The superconducting ceramics can be drilled, and fine threads cut by common steel tool without cracking (Fig.3).

These glass ceramics generally have a random microstructure. In order to align the superconducting crystals, the application of uniaxial pressure during the crystallization of the glasses was attempted. These technique yielded the desired preferred-orientation of (2122) crystals as shown in Fig.3.

Almost pure (2223) crystals, the 110 K phase have now been prepared, and showed zero electrical resistance at 108 K.

In summary then, we have been successful in fabricating continuous glass ceramic superconducting fibers which are almost pure (2223) crystals with zero resistance at 108 K

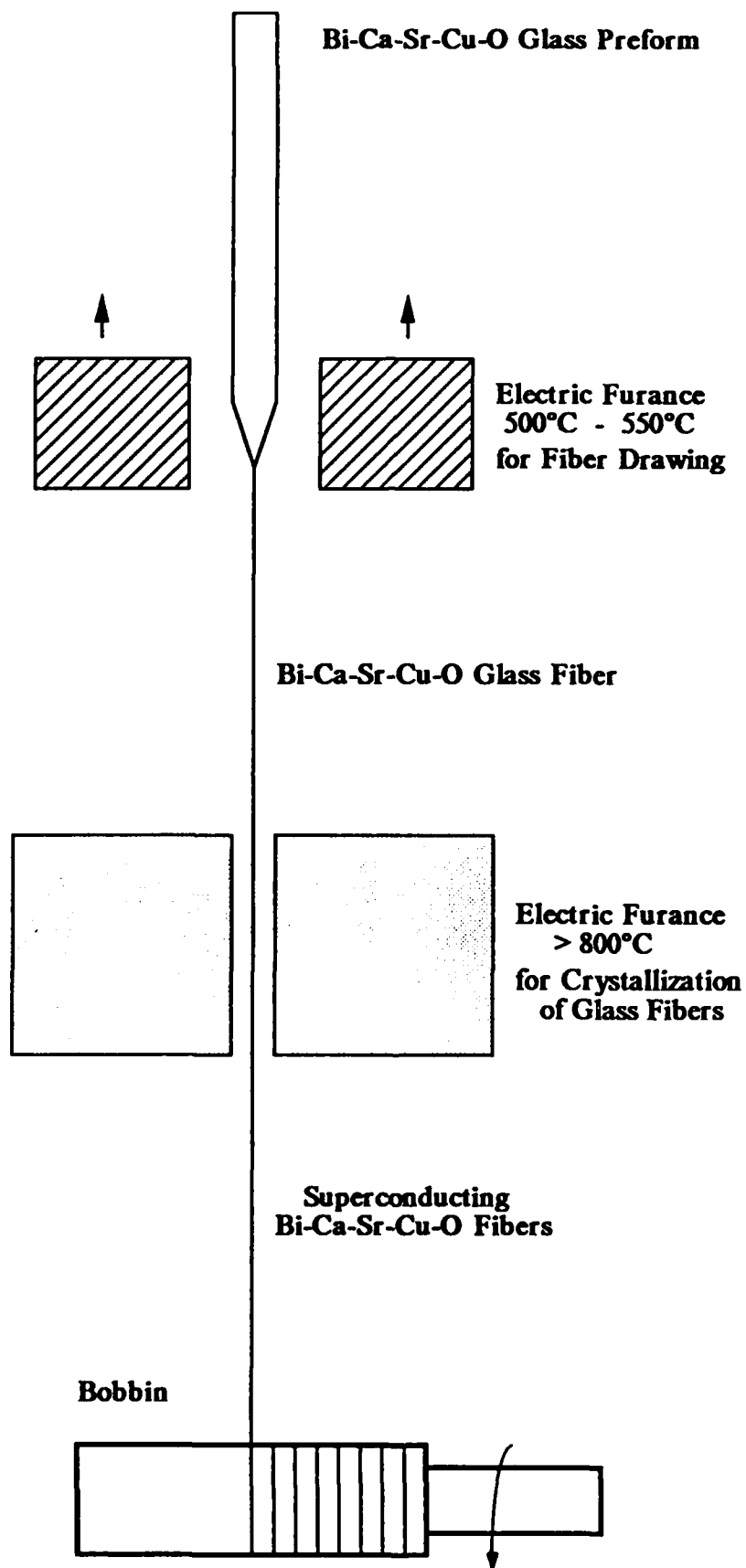


Fig.1

Superconductor From Glass Crystallization

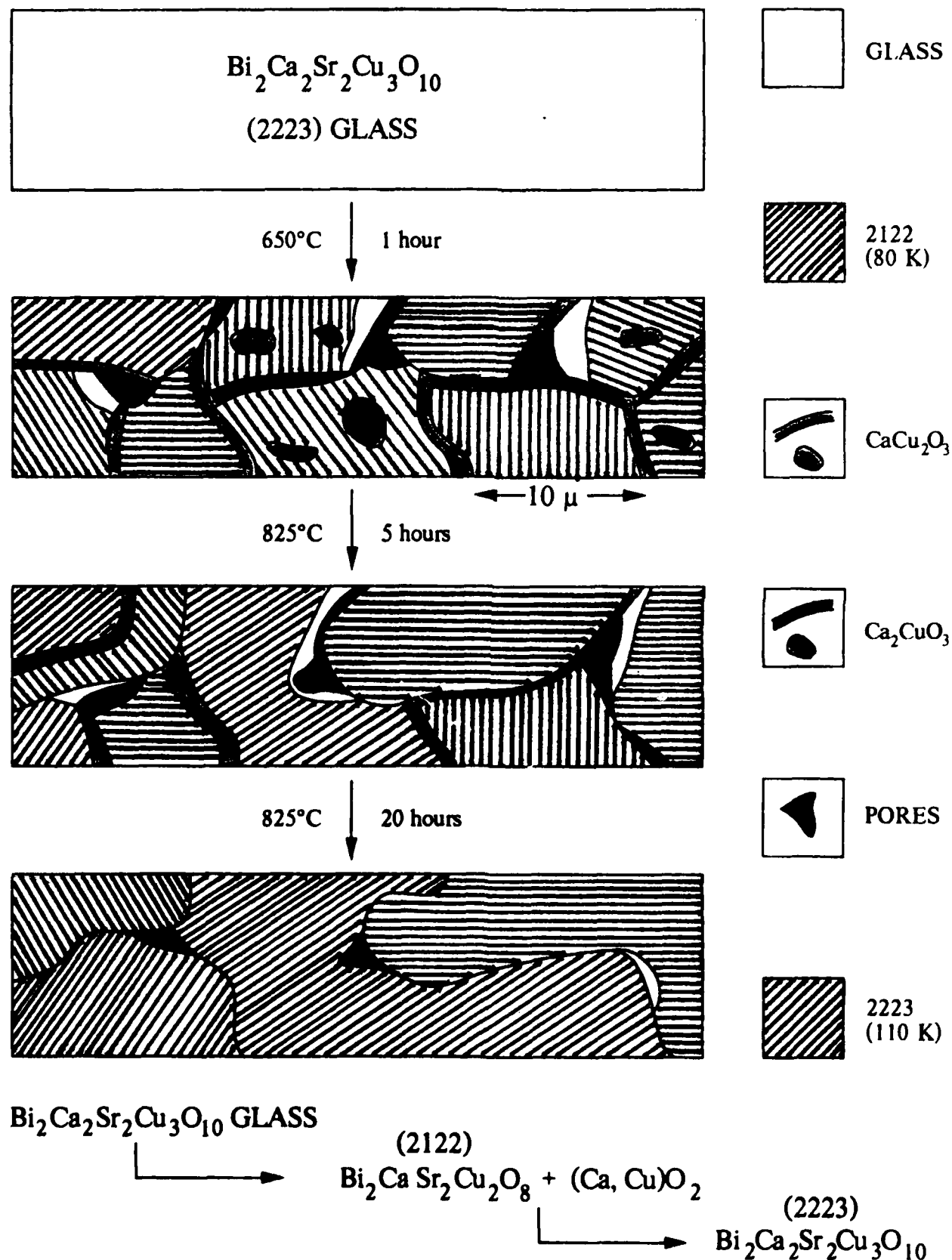


Fig. 2

Pressure Induced Preferred-Orientation



Machinable Superconducting Bi-Ca-Sr-Cu-O Glass Ceramics

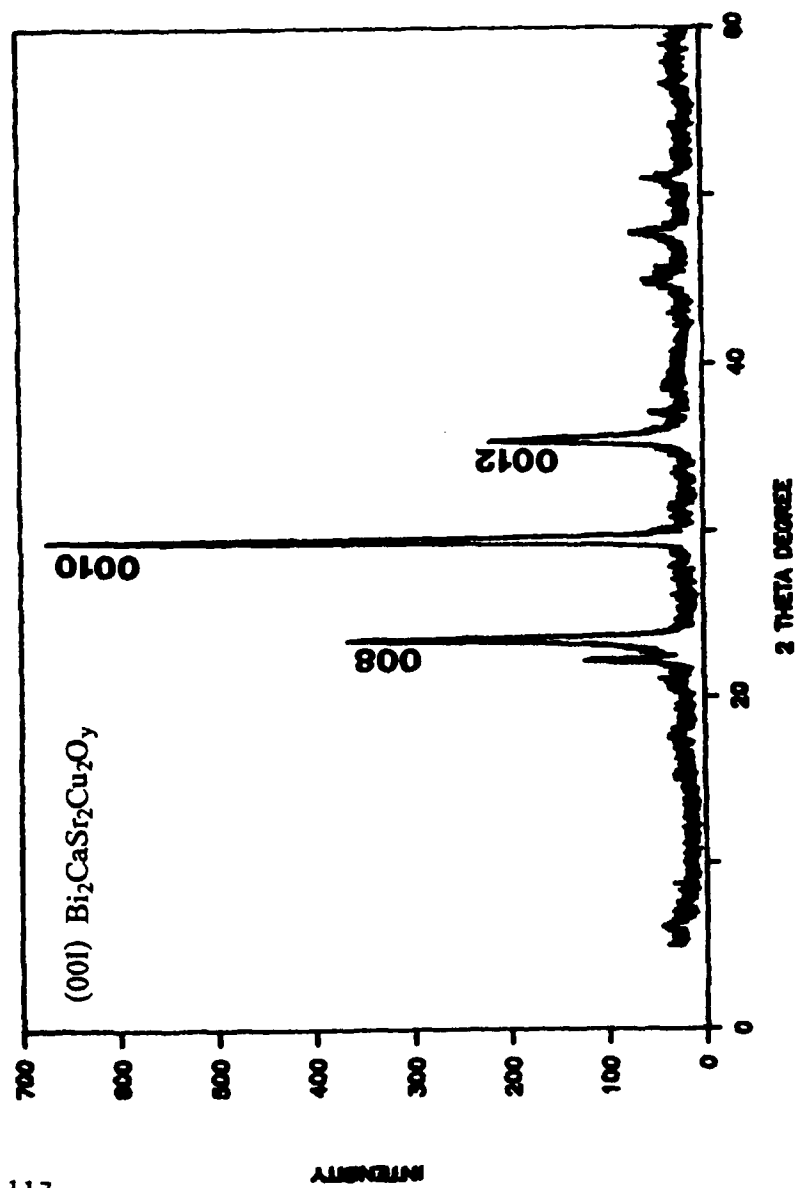
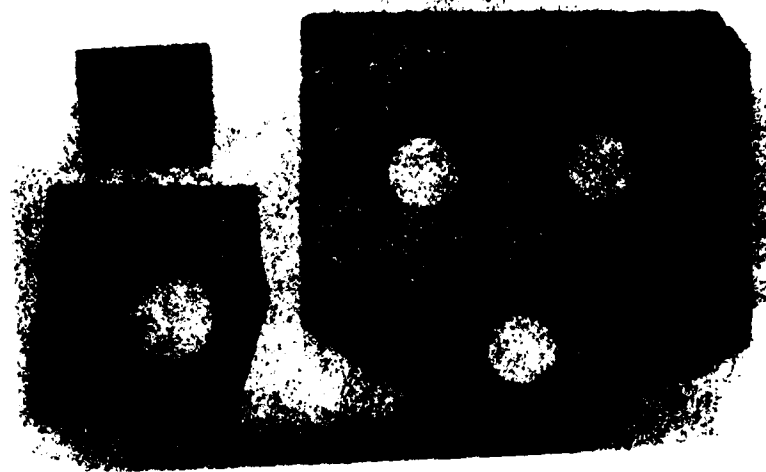


Fig. 3

3. Future Plans

- a. Further effort on the minimization of crystallization of the glass preforms during fiber drawing in order to produce kilometers of the fibers.
- b. Investigation of the formation of (2122) and (2223) phases in the fibers to prepare the glass ceramic fibers with T_c up to 108 K and with high mechanical strength.
- c. Develop novel techniques to align the crystals for highest critical current density.
- d. Collaborate with Professor J. Livage (France) on structural transformation and with Professor D.C. Bradley (U.K.) or precursors for preparing fibers via solution route.
- e. Study the relation between microstructure and mechanical strength
- f. Investigate the chemical durability.

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Sol-Gel Solutions for Superconductors and other Advanced Ceramics

by J. Livage
University of Paris, France

Despite their high T_c , superconducting ceramics cannot find applications because of their low critical currents. This drawback is due to the short superconducting coherence length, a few Å, which is much smaller than the usual size of inhomogeneities arising from grain boundaries. As a result conventional solid state processing has failed to produce ceramics of sufficient homogeneity.

The sol-gel method is especially adaptable to the deposition of homogeneous thin films. The intimate mixing of solution precursors at a molecular level provides a better homogeneity and lowers the synthesis temperature of multicomponent super-conducting ceramics. However experiments on $\text{YBa}_2\text{Cu}_3\text{O}_7$ have shown that phase separation occurs during the thermal treatment. Oxides and carbonates then react in the solid state and one of the main advantage of the sol-gel process is lost.

This project addresses the solution chemistry of molecular precursors for multicomponent ceramics. The aim is to favour the co-polymerization of different molecular precursors in order to be able to form a mixed oxide network at lower temperatures. A basic analysis of the solution chemistry of these precursors was undertaken in order to be able to optimise the chemical process.

1. Solution chemistry.

Sol-gel chemistry is based on the polymerization of metal cations in aqueous or organic solutions. Most scientific work was performed on silica based systems and very few is known about other metal oxides such as yttrium, copper or barium. It was therefore necessary to extend the present knowledge to transition metal oxides.

The structural evolution of condensed species during the formation of the oxide network needs to be fully understood before a real mastery of the sol-gel process can be reached. Our contribution brings both theoretical and experimental results.

A major advance for the theoretical understanding of these reactions was obtained with the so-called "Partial Charge Model" developed in our group (1). This model is based on electronegativity data and allows to predict the chemical nature of molecular precursors and how they react toward hydrolysis, condensation and complexation.

A wide range of spectroscopic techniques (X-ray absorption, multinuclear NMR, infra-red absorption, ESR, small angle scattering) was used in order to characterize all chemical species which are formed during the course of

inorganic polymerization reactions. One of the main result was to show that molecular precursors can be chemically designed in order to control their molecular structure, chemical reactivity and fonctionnality. Monodispersed colloidal particles can be synthesized by adding chelating ligands such as acetylacetone while long chain polymers are formed with bridging groups such as acetates(2).

2. Sol-gel solutions for superconducting thin films.

Different solution routes have been investigated in order to optimize the process for making high T_c superconducting thin films.

The simplest technique is based on the coprecipitation of oxalates. Decomposition of the organics then leads to a mixture of oxides and carbonates so that the reaction temperature remains rather high. A chemical control of the condensation process with acetates leads to gels rather than precipitates. These gels are suitable for making thick films (3). However the reaction temperature remains high so that contamination from the substrate leads to large superconducting transitions. Organic precursors must actually be avoided because they lead to the formation of barium carbonate that reacts very slowly so that the superconducting phase can only been obtained at high temperature. Carbon free precursors have therefore been used in the following procedures.

Superconducting films have been deposited by spraying aqueous nitrate solutions onto a substrate (MgO). This method was succesfully applied to the following phases ; $YBa_2Cu_3O_7$, $Bi_2(Sr,Ca)_3Cu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_8$. Nicely oriented superconducting films have been obtained that exhibit good metallic properties above the transition temperature.

Major advance was obtained by using the hydroxide route. Hydroxides are first coprecipitated from an aqueous solution. They are then decomposed below $600^\circ C$ giving rise to highly reactive oxides. The superconducting $YBa_2Cu_3O_{7-x}$ phase is then obtained at $850^\circ C$, about $150^\circ C$ lower than via the usual solid state route and in less than 20mn as shown in Figure 1. Contamination from the substrate is then negligible(4). Good electrical and magnetic properties have been obtained (Figure 2).

An interesting modification of this procedure was developped by using OH exchange resins instead of adding a base. Colloidal copper and yttrium hydroxides are then obtained free from foreign ions coming from the base. Deposition of these hydroxides onto a substrate leads to $YBa_2Cu_3O_7$ ceramic films at rather low temperature.

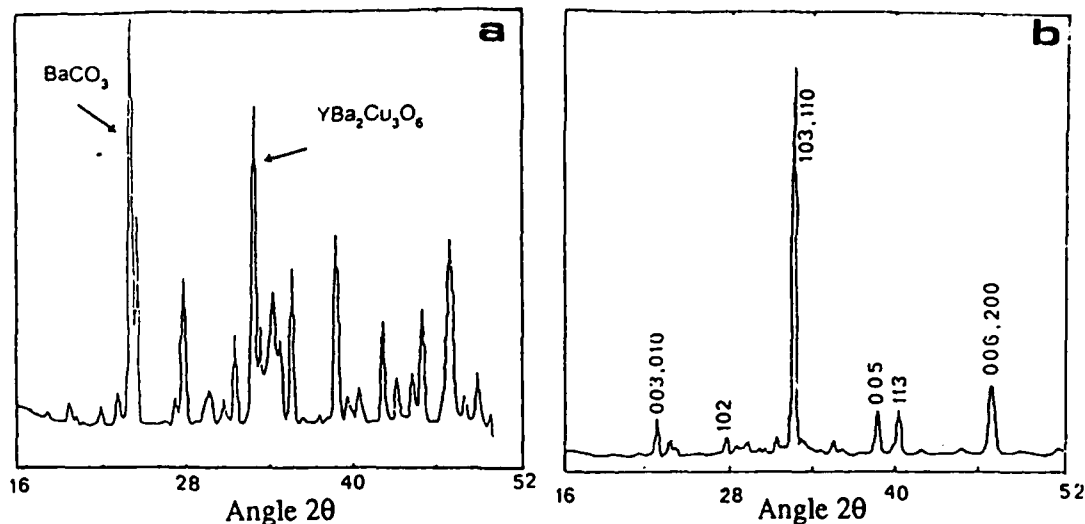


Figure 1: X-ray pattern of superconducting powders obtained after heat treatment at 850°C for 20 mn:

- a) From a mixture containing carboxylates: the phase is impure
- b) From hydroxides: the pure superconducting phase is obtained.

3. Towards the sol-gel synthesis of other advanced ceramics.

The major advances in sol-gel chemistry gained during this work on superconductors can now be extended to other multicomponent ceramics. Promising preliminary results have already been obtained.

PZT ferro-electric ceramics $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ have been synthesized from metal-organic precursors in the presence of chemical modifiers. As storage devices these films work because of the hysteresis in the polarization curve under an applied voltage. Preliminary results give films with permanent polarization of 7 microcoulombs/cm² compared to the best reported value 10. For such ceramics, the sol-gel process appears as very competitive compared to evaporation processes.

Optically active thin films have also been made by incorporating organic or inorganic dyes into a gel matrix. Such results have already been reported with silica based gels. However our expertise in the sol-gel chemistry of transition metal oxides allows us to develop NLO devices with a wide range of optically transparent oxide gels such as TiO_2 , ZrO_2 or Al_2O_3 so that the refraction index can be adjusted to the desired application.

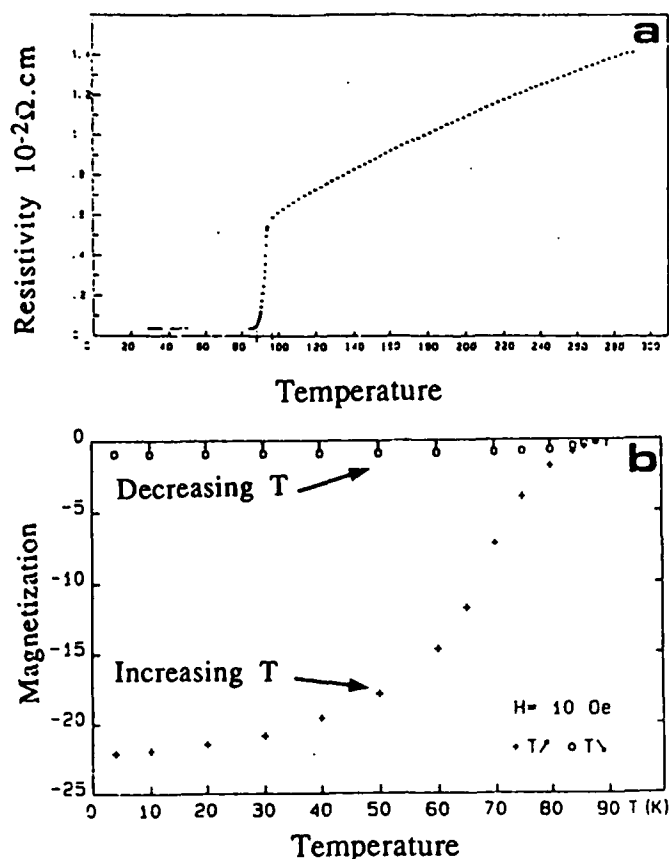


Figure 2: Physical properties of a superconducting material synthesized at 850°C.

a - Electrical resistivity

b - Magnetic behaviour of a ceramic below room temperature. The good shielding properties (measured by increasing temperature) proves the quality of the phase. The low Meissner effect (measured with decreasing temperature) indicates flux pinning and expected good critical currents.

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