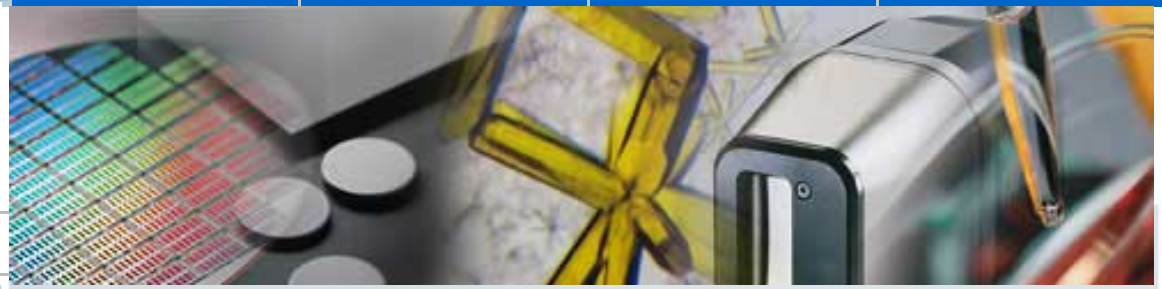

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A Simple XRD Setup to Track In Situ the Evolution of Structural Order in Polymer Liquid Crystals Exposed to Solvent Vapour
QIAN ZHANG, University of Montreal, C. Geraldine Bazuin

Bioalteration Textures Mineralized by Titanite in Fresh Basaltic Glass and Archean Greenstone Belts: Mineralogical Analysis of a Textural Biomarker
M.R.M. IZAWA, University of Western Ontario

catena-Poly[[(ethylene-1,2-diamine-κ2N,N`)-cadmium (II)]-μ-4-carboxyimidazole-5-carboxylato(2-)- κ4N1,O3: N4,O1]
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A simple XRD setup to track *in situ* the evolution of structural order in polymer liquid crystals exposed to solvent vapour

Qian Zhang* and C. Geraldine Bazuin

Département de chimie, Université de Montréal, C. P. 6128, succ. Centre-ville, Montréal (QC), Canada H3C 3J7

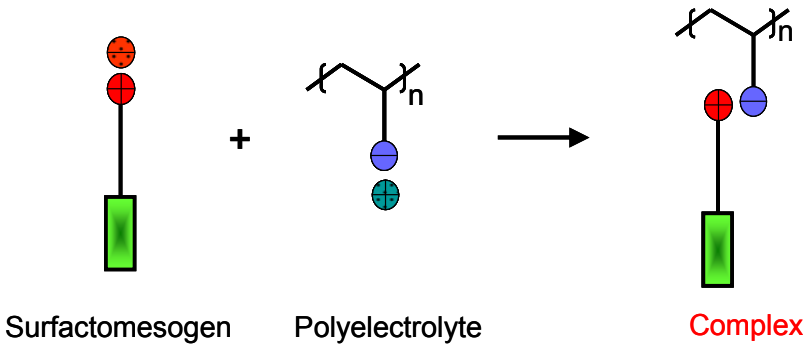
Introduction

Possessing the most delicate phases in the world, liquid crystals (LCs) – discovered more than a century ago – continue to fascinate scientists and engineers.[1] Their interest is further enhanced when the LC material is combined with nano-particles[2,3] or designed by self-assembly procedures[4] to obtain novel properties. X-ray diffraction (XRD) is undoubtedly the most important technique for gaining an understanding of LC structure.[5]

Our group has been engaged in the study of supramolecular LC materials, in particular based on the self-assembly of low molar mass mesogenic molecules with polymers through ionic bonds as illustrated in Scheme 1, for more than a decade.[6] This method of associating an ionically functionalized mesogen ("surfactomesogen") to an oppositely charged polyelectrolyte is attractive for its ease of synthesis in obtaining polymer liquid crystals (PLC). Additional functionality can be achieved by introducing functional moieties in the chemical structure; for example, using azo groups for photoresponsiveness.[7] Very recently, we discovered the first flexible spacer- and tail-free ionically bonded side-chain polymer that possesses LC order (as well as exceptionally high and stable photoinduced birefringence properties), simply assembled from commercially available methyl orange and methylated poly(4-vinyl pyridine).[8]

In the course of our investigations of surfactomesogen/polyelectrolyte complexes, we found that their LC characteristics are sensitive to solvents of various types and amounts, including residual quantities.[9] This phenomenon, common in liquid crystals (and forming the basis of lyotropic liquid crystals), is illustrative of their "delicate phase of matter" [1] and results from a

complex balance of interactions. It may be expected that the ionic bond in ionically complexed liquid crystals may be especially sensitive to residual amounts of polar solvents such as H_2O.[10, 11] To investigate more closely the effect of solvent on thermotropic liquid crystals, we devised a simple method to track the structural changes in LC materials during exposure to solvent vapours by *in situ* XRD. In this report, we will describe this setup, involving the use of a Bruker XRD system in automatic mode, and illustrate its application to a representative surfactomesogen/polyelectrolyte complex exposed to dimethyl formamide (DMF) vapour. This setup can be easily applied to conduct studies on the effects of solvent vapour on any LC (or other ordered) material.

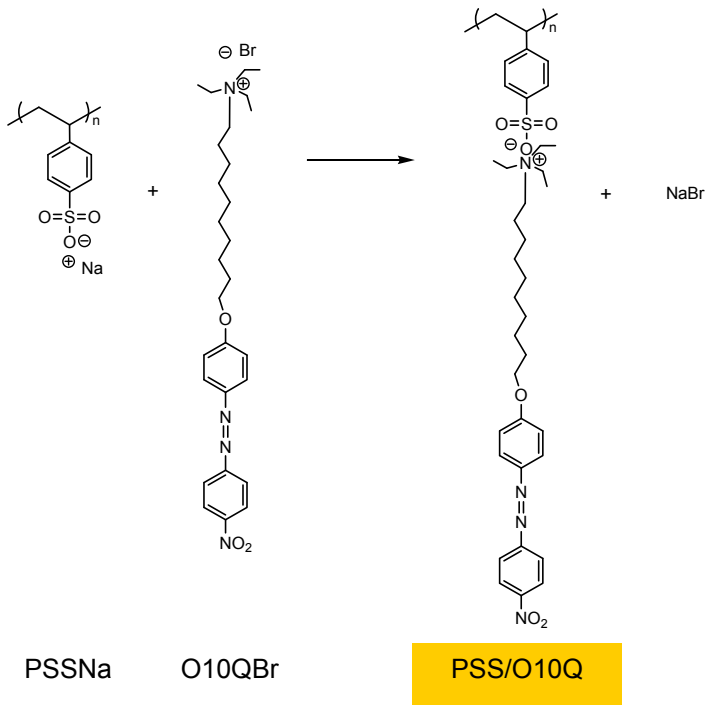


Scheme 1. Preparation of ionically bonded side-chain liquid crystal polymer complexes: the surfactomesogen and polyelectrolyte solutions are prepared separately, then mixed together, and purified of small counterions by precipitation and/or dialysis procedures.

Experimental Section

Preparation of complex. The complex investigated, PSS/O10Q, is composed of the sodium salt of poly(styrene sulfonate) (PSSNa) and the Br-neutralized azo-containing surfactomesogen, O10QBr, as shown in Scheme 2. PSS (Aldrich, Mw of 70,000) was dialysed against Milli-Q water before use. The surfactomesogen, O10QBr, was synthesized using a modified form of published procedures.[9,12,13] The dialysis bag (Spectrum/Por from VWR,

molecular cutoff 3500) was rinsed with water before use. Spectrograde DMSO (Aldrich) was used in the complexation procedure.

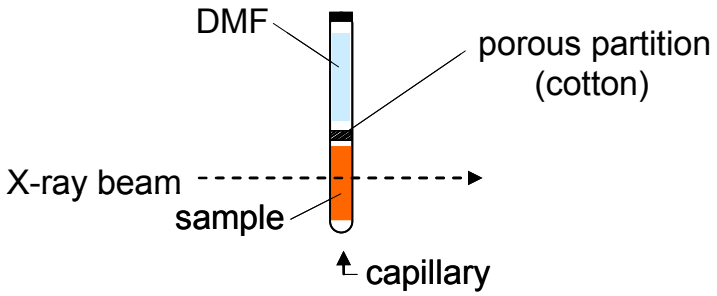


Scheme 2. Preparation of the complex, PSS/O10Q, from PSSNa and O10QBr.

To prepare the complex, 108.0 mg of PSSNa were added to 10 mL of deionized water followed by 26 mL of DMSO, and 310.3 mg of O10QBr were dissolved in 40 mL of DMSO, giving 5 mol % excess of O10Q relative to the PSS repeat unit. Both solutions were stirred in a 65°C oil bath for 15 min, following which the O10QBr solution was added dropwise to the PSSNa solution. The resulting transparent mixture was maintained at 65°C for 24 h to favour maximum complexation. The transparent solution was then dialyzed against deionized water until all DMSO, sodium bromide and excess O10QBr were completely removed (about 3 days), as verified by elemental and energy dispersive X-ray analyses, by ^{1}H NMR spectroscopy, and by conductivity measurements.[9] Finally, the product was freeze-dried, followed by further drying in vacuum at about 60°C.

XRD analysis and setup. X-ray diffraction (XRD) analysis was performed using a Bruker AXS Advance D8 Discover Diffractometer with GADDS (General Area Detector Diffraction System, equipped with Hi-Star area detector), using Cu Kα radiation (λ = 0.1542). The detector-to-sample distance was 9.8 cm. A home-made beamstop, permitting access to angles as low as 1.1° (2θ), was used. Calibration was effected using corundum (Bruker) and tricosane (Aldrich). The sample was mounted on a 2-position chi stage. Diffractograms of 30-min exposure times were acquired.

As illustrated in Scheme 3, the powder sample of PSS/O10Q was packed in the lower third to half of a 1.0-mm diameter glass capillary (Charles Supper), a small wad of cotton (VWR) was then inserted (leaving a small space to avoid contact with the sample), and spectrograde DMF (Aldrich) was added to the upper part of the capillary, after which its top was sealed with a flame. In this setup, DMF does not flow downward, but its vapour saturates the air space, with the cotton wad acting as a porous partition through which the DMF vapour diffuses to the sample.



Scheme 3. XRD sample capillary setup to track the *in situ* evolution of the LC structure of the sample exposed to DMF vapour.

A first diffractogram was taken immediately following preparation of the capillary, before the sample was affected by DMF (labelled 'Original' in Figure 1). Then, to increase the rate of diffusion of DMF vapour to the sample (since DMF has a high boiling point, and limited machine time was available), the capillary was immersed in a 60°C water bath. As soon as the top edge of

the sample was contacted by DMF vapour, which was visually obvious by a small colour change, the capillary was remounted immediately on the sample stage such that the X-ray beam passed through the part of sample contacted by DMF vapour, and an initial 30-min diffractogram (labelled "Initial contact" in Figure 1) was recorded to check how it compared with the "Original". XRD data collection was then set to automatic mode, where a diffractogram was recorded every 30 min for 14.5 h. The capillary was demounted, and, 4 days later, a final diffractogram was acquired. Bragg spacings, d, were calculated from the Bragg equation: $\lambda = 2d \cdot \sin\theta$.

Results and Discussion

The various diffractograms obtained, with a representative selection of those recorded in automatic mode, are shown in Figure 1A. The diffractogram labelled "Original", taken of the sample before contact with DMF, shows a broad halo centered at about 19^o and a weak diffraction peak at $2\theta = 4.2^o$ (corresponding to a Bragg spacing of 19.6 Å), with hints of additional peaks near 2^o and 8^o (2θ). Once DMF enters the sample ("Initial contact"), the peak at 4.2^o becomes much more intense and sharpened, and is clearly accompanied by three weaker peaks near 2^o, 6^o and 8^o. The Bragg spacings of these four peaks are 42.5, 20.7, 14.1 and 10.6 Å respectively, giving a ratio of 1:1/2:1/3:1/4. Thus, they can be interpreted as the 1^{st}, 2^{nd}, 3^{rd} and 4^{th} diffraction orders arising from a lamellar (smectic) structure having a periodicity (lamellar spacing), d, of 42.5 Å. This, along with the wide-angle halo and the fact that the lamellar spacing is comparable to the complexed side-chain length (ca. 40 Å), indicates that the liquid crystal order is of the single-layer smectic A type. It is significant that the odd diffraction orders are much weaker than the even orders, which is generally attributed to a pseudo-periodicity, d/2, arising from the electron density distribution profile across the lamellae.[14] A possible packing model taking this into account is shown in Scheme 4B, where the electron density is higher in both the backbone/ion pair subplane and in the aromatic subplane compared to the aliphatic subplanes.

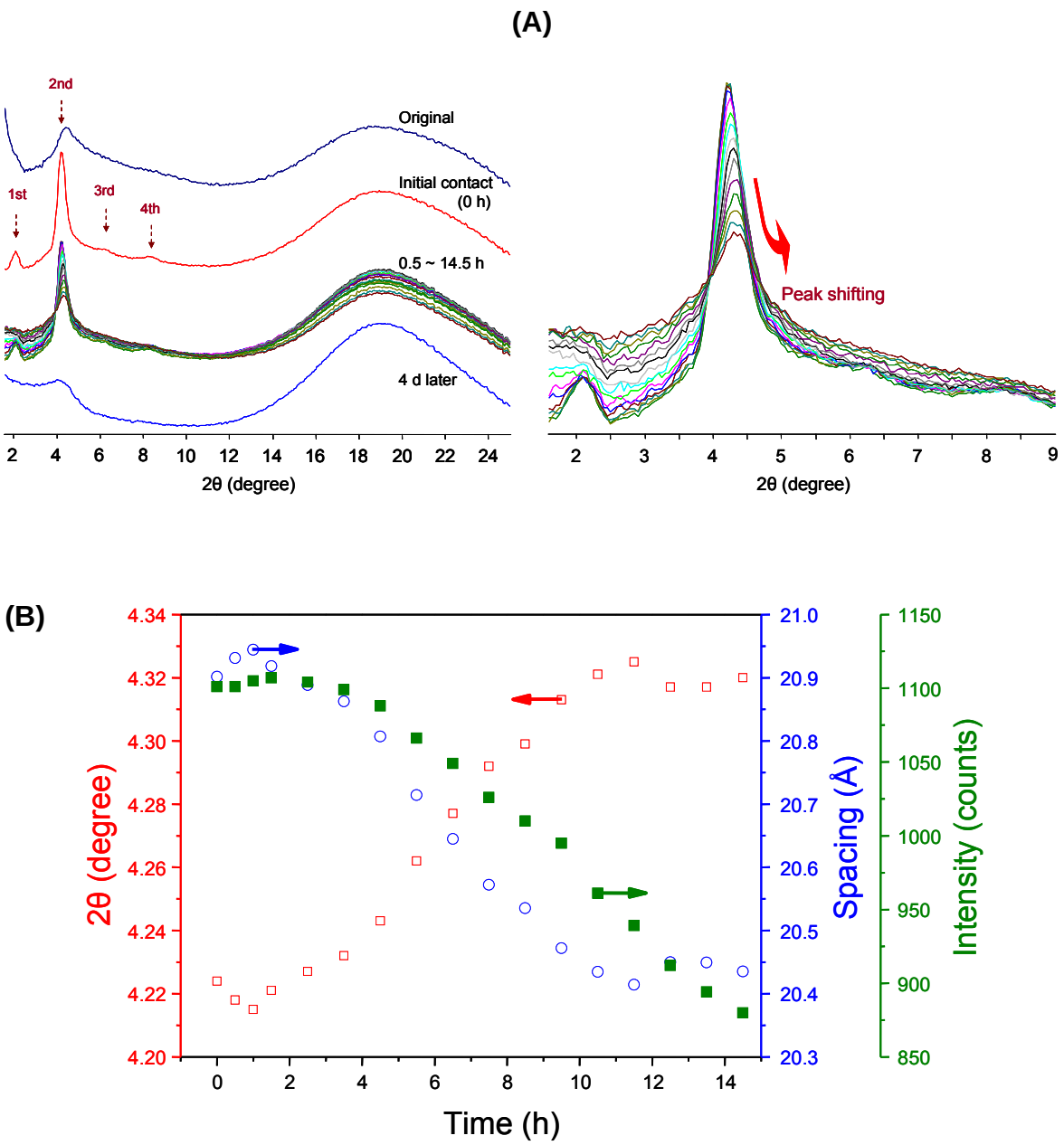
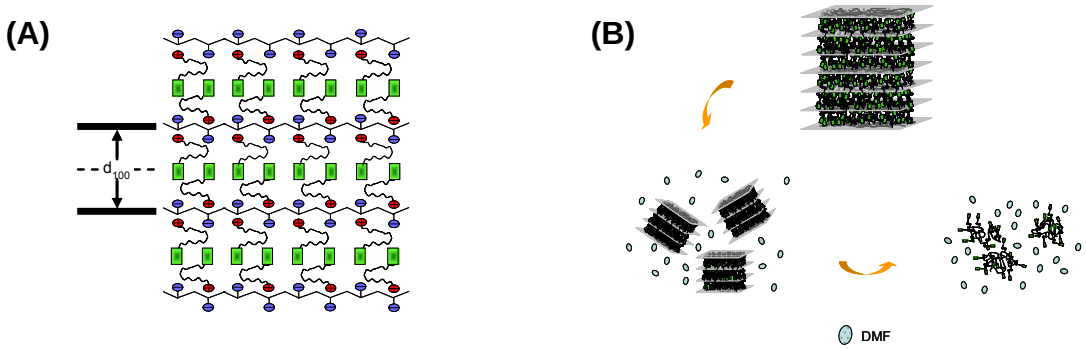


Figure 1. XRD diffractograms of the PSS/O10Q complex exposed to DMF vapour. (A) Left: Full range of angles detected, with small angle diffraction peak orders indicated; Right: Enlargement of the lower angle region of selected diffractograms collected in automatic mode. (B) Variation of the 2θ position, corresponding Bragg spacing d (must be multiplied by 2 to obtain the structural periodicity d_{100}), and intensity of the second-order peak as a function of time of exposure to DMF relative to the "Initial contact" diffractogram (times given are for the beginning of the 30-min recording period for each diffractogram; data from every other diffractogram only are shown after the first four points).



Scheme 4. (A) Possible packing model for the single-layer smectic A structure of the complex. (B) Possible mechanism of destruction of the smectic A structure by addition of DMF.

In comparing the "Original" and "Initial contact" diffractograms, smectic A packing also appears present in the original sample, but much more weakly. This suggests that DMF initially acts to permit solvent annealing or that it intersperses itself within the LC structure to permit more efficient and long-range packing or to enhance electron contrast for diffraction. As DMF continues to diffuse into the sample, the smectic packing gradually deteriorates and is hardly apparent four days later, suggesting that any residual smectic packing at this point is short-range.

Figure 1B shows the evolution in intensity, 2θ position, and corresponding Bragg spacing of the most intense low angle peak (second order, $d = d_{100}/2$) during the *in situ* tracking of DMF absorption. The intensity appears to have reached its maximum within the first two hours following initial DMF contact, and then it decreases gradually, suggesting that the smectic packing is gradually undermined as DMF diffuses into the LC structure. In parallel, the peak shifts to slightly higher angles (lower Bragg spacings) during the first 10 hours of DMF exposure, and then is constant. The total shift is small (ca. 0.5 Å in d), but it is contrary to what is expected from solvent swelling which should lead to increasing lamellar spacings (and as observed when comparing the 'Original' and 'Initial contact' diffractograms: 39.2 vs. 41.4 Å for $2d = d_{100}$).

A possible mechanism to rationalize the data is illustrated in Scheme 4B. Following a small amount of swelling to optimize the LC packing, after which no further swelling occurs, the large LC domains gradually break up into smaller ones and only nanoaggregates of smectic

layers are left after 4 days, thus accounting for the continuous broadening and weakening of the diffraction peaks. It is less clear why the lamellae appear to shrink slightly in this process, but possibly the breakup allows somewhat greater disorder among the alkyl chains, as occurs in smectic A systems exposed to increasing temperature.

In conclusion, the setup described in this paper has been shown to allow successful *in situ* tracking of the influence of solvent vapour on the LC packing structure, and thus allows new insights. The method could be even more powerful if the concentration of the solvent were also tracked by an appropriate measurement technique, in parallel with the XRD tracking. A feasible candidate might be FTIR (Fourier Transform Infrared) spectroscopy with IR fiber optics. A coupled XRD-FTIR system, working in automatic mode, would enable efficient quantitative *in situ* tracking of the evolution of structural order during solvent absorption.

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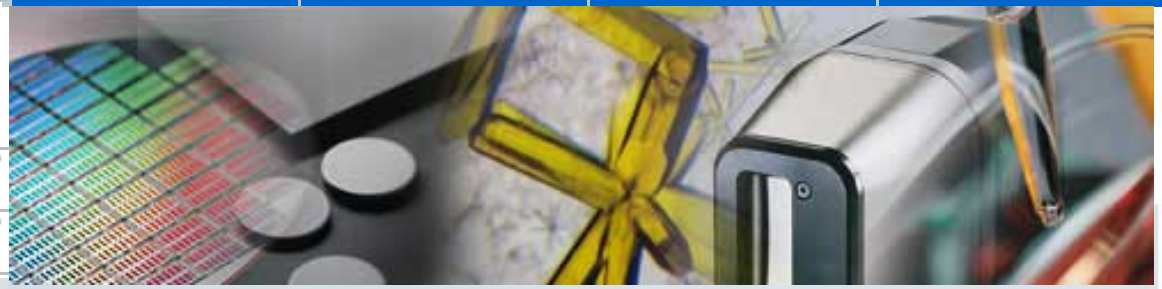

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NEWS

Bruker AXS Awards $6000 X-ray Diffraction Scholarship at Materials Research Society Fall Meeting in Boston

During the 2007 Materials Research Society Fall Meeting now taking place at the Hynes Convention Center in Boston, Bruker AXS, a leading global provider of advanced X-ray solutions for life and advanced materials sciences, announced the recipient of its 2007 Excellence in X-ray Diffraction (XRD) scholarship – based on unique experiments performed by university students. Recognizing academic achievement in advanced XRD, Bruker AXS yesterday presented its $6,000 scholarship for the most unique application in the field of materials research.

This year, the annual Bruker AXS XRD $6,000 scholarship has gone to Ph. D. student Michelene E. Miller at Alfred University for her research paper "Novel Processing of Microporous Glass-Ceramics for Gas Separation." She is advised by Dr. Scott T. Misture, Professor of Materials Science at the New York State College of Ceramics at Alfred University in Alfred, NY. "Using high temperature XRD, we determined that nickel-doped cordierite glass-ceramics are candidates for application as permeability-controlled microporous membranes to separate out carbon dioxide and hydrogen gases in fossil fuel power plants, both reducing greenhouse gas emissions and generating hydrogen," explains Miller.

Professor Misture's group studies the dynamic behavior of oxide ceramics and glasses related to energy conversion devices. Projects generally rely on detailed in-situ characterization using X-rays and neutrons to understand the relationships between structure and properties. Their recent work has focused on the effects of atmosphere and humidity on structure, phase stability, and conductivity at high temperature.

Their current research focuses on materials for solid oxide fuel cells and hydrogen production. Funded by the NSF, DOE, EPA, and other agencies, their work centers on solid oxide fuel cells and photocatalysts.

This year's runner-up is Ph.D. student Qian Zhang from the University of Montreal. His research paper is entitled, "A simple XRD setup to track in situ the evolution of structural order in polymer liquid crystals exposed to solvent vapour." Qian Zhang's research concentrates on physical and optical studies of azo-surfactomesogen/polyelectrolyte complexes. He is advised by Professor C. Geraldine Bazuin of the University of Montreal's Department of Chemistry. Professor Bazuin's research concentrates on the development of novel supramolecular and nanostructured polymeric materials. "Our particular areas of interest include liquid crystalline materials, block copolymers, blends, ionomers, nanopatterns on surfaces, ultrathin films, and applications in optoelectronics and gene delivery," indicates Professor Bazuin.

The scholarship winner and runner-up have been selected by an independent panel of judges: Dr. Tom Blanton from Eastman Kodak; Dr. Jim Kaduk from Innovene and current Board Chairman of the International Centre for Diffraction Data; Dr. Pam Whitfield from National Research Council Canada; Dr. Jim Britten from McMaster University; and Dr. Nattamai Bhuvanesh, Department of Chemistry at Texas A&M University.

"We are quite pleased again this year to provide a Bruker XRD scholarship to another extraordinary student," says Uwe Preckwinkel, Bruker AXS XRD Sales and Marketing Manager. "Both Bruker AXS and the judges are most impressed by the quality of the XRD experiments all these future X-ray scientists have performed, and the valuable scientific results they have obtained," adds Dr. Frank Burgaezy, Executive Vice President of Bruker AXS in charge of the company's global XRD and XRF business.

Bruker AXS scientists are available at the Company's MRS Fall Meeting booth (Number 300) to discuss the award and all the student research findings. Bruker AXS has published the various papers on a CD now being

distributed to the press, MRS Meeting attendees, other scientists, and research libraries worldwide.

The MRS Fall Meeting is providing a unique opportunity to present innovative products and services to over 5,000 attendees from all sectors of the global materials science and engineering communities. For more information, please visit www.mrs.org.

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