Cross-cut Review
Polymer Science Research at the APS

SAC Review (1/25/2006)

Chair: P. Thiyagarajan (Thiyaga), ANL

Invited Experts

Professor Buckley Crist, Northwestern U

Professor John A. Rogers, UIUC

Professor Thomas A. Witten, U of C

Invited Speakers

Dr. Jin Wang, APS

Professor W. Burghardt, Northwestern U

Professor Sunil K. Sinha, UCSD

Professor Timothy Lodge, U. Minnesota

Professor Dale Schaeffer, U. Cincinnati

Dr. Roger Leach, DuPont

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  Chair, APS Partner User Council

Techniques/Beamlines for Polymer Science

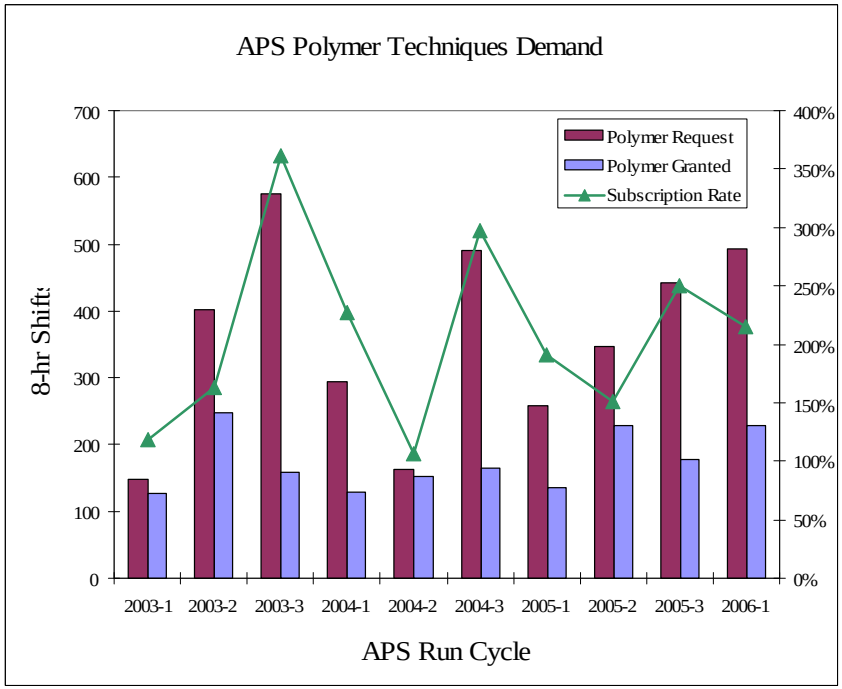
Bulk	
SAXS/ TR-SAXS	5-BM, 5-ID, 8-ID, 9-ID,12-BM, 12-ID, 15-ID
ASAXS/TR-SAXS	12-ID
SAXS/WAXS	5-ID, 15-ID
USAXS	33 ID
Films	
GISAXS	8-ID, 12-ID, 15-ID 6-ID
Reflectometry	1-BM, 8-ID, 12-BM,15-ID
Dynamics	
XPCS	8-ID

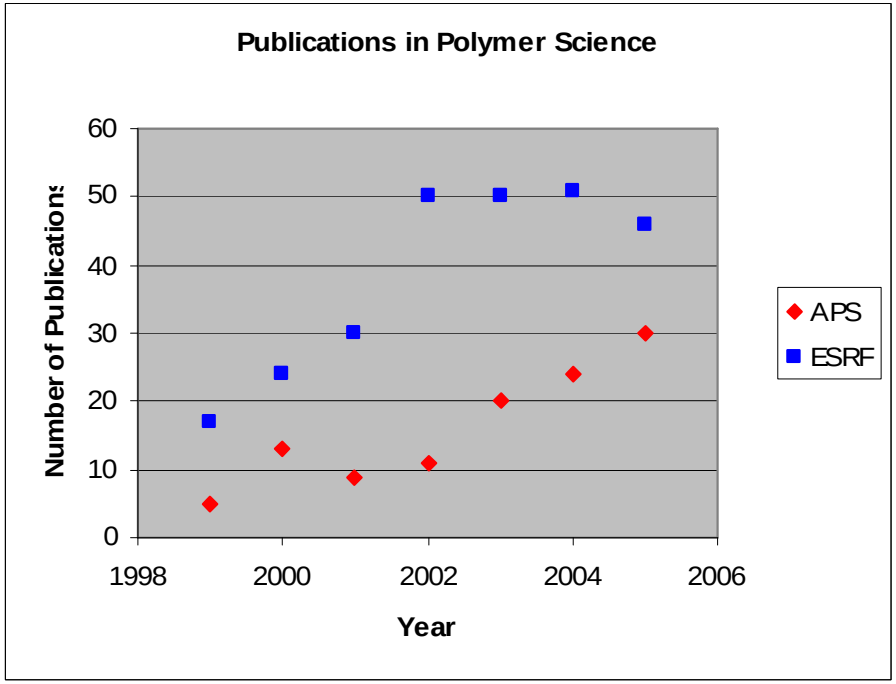
Imaging	
Tomography	2-BM, 13-BM, 5-BM-C
Phase Contrast Imaging	1-ID, 2-BM, 2-ID-B
Fluorescence	2-ID-B
USAXS Imaging	33-ID
Inelastic Scattering	
Nuclear Resonance Scattering	3-ID
Microprobes	
Microdiffraction	2-ID-D, 7-ID, 13-ID, 20-ID, 34-ID
High Pressure Studies	13-BM- 13-ID, 16-ID-B

Overview

- Facilities at the APS have been used by a broad range of academic and industrial users and have revealed important aspects of polymer materials.
- High impact publications and training of graduate students continue to increase.
- DND-CAT (5-ID and 5-BM) was developed about 10 years ago with polymer research as a priority. A key "general user" instrument is the simultaneous SAXS/WAXD instrument (5-ID) with tensile deformation capabilities. The CAT has placed an emphasis on mounting the necessary infrastructure to examine materials under the dynamic and nonequilibrium conditions that are most relevant for industrial processes and most pivotal for scientific advance.
- SAXS instruments at sectors 12-ID and 15-ID contributed strongly to the polymer science research at the APS.
- The USAXS instrument at sector 33-ID is a unique instrument that extended length scales to micron size enabling characterization of hierarchically structured polymer nanocomposites.
- The XPCS instrument at 8-ID has made unique contribution on the dynamics of polymers, both bulk and thin films using coherent X-rays. Infrastructure at this beam line is unique in the world.
- X-ray Tomography has been recently carried out at 2-BM on polymer foams and on industrial polymers at sector 5. X-ray based imaging when compared to the EM will enable *in situ* experiments.

User Demand and Publications





General User Proposals

Total: 112 (During 1999-2005)

Nature (1) , Science (1), PRL (15)
Macromolecules (18), Langmuir (8)

Training of Students

M.S. (9), Ph.D. (25)

Highlights of the Talks

Jin Wang:

- Dr. Wang's presentation showed several directions in which the APS capabilities are demonstrating unique value in probing polymeric materials.
- Years of development of XPCS have begun to bear fruit in addressing questions of active interest. Temporal relaxation of thermal fluctuations of polymeric vesicles as a function of wave vector demonstrated a clear-cut behavior supported by theory.
- An important development is the ability to probe structure at an interface. The GISAXS demonstrated here is an effective probe of both structure and motion, both along and normal to the interface. An intriguing anisotropic mobility of nanoparticles embedded in a polymer thin film was shown.
- Another demonstrated power of grazing incidence was the ability to reveal new forms of interfacial self-organization, notably in diblock copolymer domains and in grafted copolymer brushes.

Highlights of the Talks (Cont.)

Wes Burghardt:

- Prof. W. Burghardt presented a clear and riveting account of the interaction between flow and macroscopic orientation of macromolecules. The high flux of high energy X-rays was essential to overcome absorption problems in complex sample environments.
- His talk showed the power of flow to organize structure in polymers. This talk also demonstrated the value of sample under real processing conditions during scattering.
- Burghardt's flow research at the APS has lead to collaborations with at least a half dozen esteemed scientists from the US and Europe. A study with Lodge and Bates (Univ. Minnesota) on the recently discovered "microemulsion phase" in blends of block copolymers and homopolymers is a striking example of the synergism that derives from first class work at the APS.
- A promising future development in this direction may be to study flow in microchannels with microfocus beams.

Highlights of the Talks (Cont.)

Sunil Sinha:

- Prof. S. Sinha presented fascinating new results for thin polymer films (thickness on the order of the characteristic chain dimension Rg) on silicon substrates. SAXS intensity measured with different incident grazing angles (GISAXS) permits separation of scattering from the surface (polymer-air interface) and from the interior of the film.
- The dynamics of capillary waves on the liquid polymer surface were delineated with the novel application of XPCS obtained with grazing incidence. Thickness effects are striking; relaxation times for films with t= 4.Rg are described by (bulk) viscosity, while ultra-thin films (t= Rg) resembled static surfaces. These are stunning results.

Highlights of the Talks (Cont.)

Timothy Lodge:

Prof. T. Lodge's talk reminded us about the power of the APS facility to probe the rich class of self-assembled structures made by block copolymers. In recent years this class has expanded dramatically by using polymers with three immiscible blocks. The emerging structures are precisely periodic, but complicated. Scattering at APS can reveal more than ten diffraction orders, thus showing both the quality of lattice order and the value of the intense APS beam. In concert with electron microscopy and theoretical modeling, these diffraction patterns definitively identified intricate structures of great potential value. Notable was a structure consisting of two interpenetrating networks having the same shape but contrasting composition. Lodge showed how scattering could reveal the kinematics of a transformation from one form of lattice order to another. Scattering proves useful in characterizing structure of micellar solutions of multiblock polymers as well, complementing direct microscopic observation.

Highlights of the Talks (Cont.)

Roger Leach:

- **DuPont relies heavily on X-ray analysis to determine relationships between chemistry, processing and structural properties.**
  - EXAFS and XAS studies of a copper based polyolefin catalyst. Of note here was that the resulting data formed a key part of the IP that DuPont filed on this system
  - In situ SAXS of polyester-ether block copolymer (thermoplastic elastomer) revealed the structural behavior of the polymer during deformation. These properties were correlated to the mechanical response and to the strain hardening observed in these materials.
  - SAXS and calculations on the behavior of polyvinylbutyral (butacite) in the plastic deformation regime seem to support a model for deformation in which crazing forms wide, flat fibrils with much different morphologies (and, therefore, physical toughness) than those observed in more conventional polymers.
  - In situ study of crystallization and chain alignment in nylon fibers generated by melt spinning at different speeds. For these studies, an elaborate spinner, with speeds of up to 4000 meters/minute, was built next to the beam line to allow for in situ probing at different stages of the process.

- **The APS management for industrial research:**
  - (1) Eliminate or reduce impediments to access caused by the current proposal based mechanism for beam time.
  - (2) Continue to enhance the unique capabilities of the APS (e.g. microtomography, microbeam, dynamic, in situ measurements, flexibility in mode of usage, grazing incidence SAXS).
  - (3) Make the facilities more ‘user friendly’ in terms of analysis software and user training.

Highlights of the Talks (Cont.)

Dale Schaeffer:

- Schaeffer stressed the healthy complementarity between the unbiased sampling of scattering and the rich but anecdotal imagery provided by microscopy. He also stressed the value of USAXS measurements to provide a comprehensive view of many forms of structure over a wide range of length scales.

My Perspective

- Planned Dedicated beam lines at APS
- Hiring of polymer scientists at APS
- Growth of CNM
- IPNS scientists' polymer science at APS
- MSD plans for soft matter science
- Workshop on X-ray imaging (APS user meeting, Lecture at ANL School?)

Summary and Recommendations

- APS is well suited for polymer research with a vibrant user program and large potential for growth.
- The development of GISAXS and XPCS are genuinely exciting as they opened up fascinating new avenues for the study of polymer thin films and surfaces.
- The Bonse-Hart instrument (USAXS) at 33-ID has the potential for characterizing second phases with dimensions approaching 1 micron. Better schemes and models for interpreting USAXS patterns would make that technique more powerful.
- Imaging with USAXS should be pursued.
- Develop large fast read out position- sensitive detectors for fast time-resolved SAXS, GISAXS and XPCS experiments.
- Microfluidics should be included in the flow studies, logically at sector 5.
- Tomography (sector 5 and elsewhere) should be utilized more.
- Provide easier and faster access to the industrial research and increase their base.
- More (unforeseen) developments will likely come - keep up the good work!