Highlights of the 42nd World Polymer Congress (Macro 2008)

Polymers at Frontiers of Science and Technology

The 42nd World Polymer Congress (MACRO 2008), sponsored by the International Union of Pure and Applied Chemistry (IUPAC) and organized by the Polymer Society, Taipei (together with the Chemical Society Located in Taipei, the National Tsing Hua University, and the Industrial Technology Research Institutes), was held at the Taipei International Conventional Center from June 29 to July 4, 2008. The aim of the biannually held WPC series is to bring polymer scientists and engineers from around the globe to address recent developments and urgent issues in polymer science. This 42nd WPC followed this general aim, for which the theme was set as "*Polymers at Frontiers of Science and Technology*" to fit in the current trends in the developments of polymer-related nano-, bio- and optoelectronic technologies.

The Taipei MACRO 2008 involved 11 plenary, 157 invited, 245 contributed oral, and 595 poster papers; these gave a total of 1008 papers contributed by more than 1189 participants from 41 countries, in which two-thirds of the papers were contributed by scientists oversea. Among the 11 plenary lectures, one was given by *Dr. Yuan T. Lee* (Nobel Laureate of Chemistry, 1986) on the general topic *''Awakening of Humanity in the 21st Century''* and another by *Prof. Robert Grubbs* (Nobel Laureate of Chemistry, 2005) on "*Macromolecular Molecules and Materials Using Olefin Metathesis*". There were 12 symposia, namely, (1) *Polymer Chemistry*, (2) *Polymer Physics*, (3) *Polymer Processing*, (4) *Nanostructured Polymeric Materials*, (5) *Advances in Bio-Related Polymers*, (6) *Polymers in Optics, Electronics, and Opto-electronics*, (7) *Environmentally Benign Polymers*, (8) *Polymer Membranes*, (9) *Polymer Composites and Blends*, (10) *Polymer Education*, (11) *Performance Materials* and (12) *Young Polymer Scientists*, in which the last two were arranged together with the IUPAC Polymer Division, along with DSM and Samsung Total Petrochemicals, respectively. Highlighted below are selected topics in areas of polymer physics and optoelectronics.

Polymers in Electronics, Optics, and Optoelectronics. Polymers for photovoltaic cells (PV) and flexible electronics were hot issues in Symposium 6 on *Polymers in Electronics, Optics, and Optoelectronics*. Polymer photovoltaic cells have unique advantages of light-weight, flexibility, low manufacturing cost, and large-scale production. They are considered as promising candidates for inexpensive renewable energy. Among the reported single layer polymer photovoltaic cells, the bulk heterojunction composite of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) has the highest power conversion efficiency (PCE) of 4–5%. For further enhancing the PCE, new materials with high carrier mobility and broad absorption, well-ordered morphology control and device structure optimization are equally important.

There were several exciting prsentations on polymer photovoltaic cells. Bau-Tsan Ko of Industrial Technology Research Institute reported a new copolymer of an acceptor and diphenylspiro-grafted poly(thiophene-phenylene-bithiophene) (Figure 1a)/PCBM based photovoltaic cells with the PCE of 4.4%, which was higher than the P3HT/PCBM using the same device fabrication. The spiro-locked, coplanar thiophene-phenylene-bithiophene moiety significantly

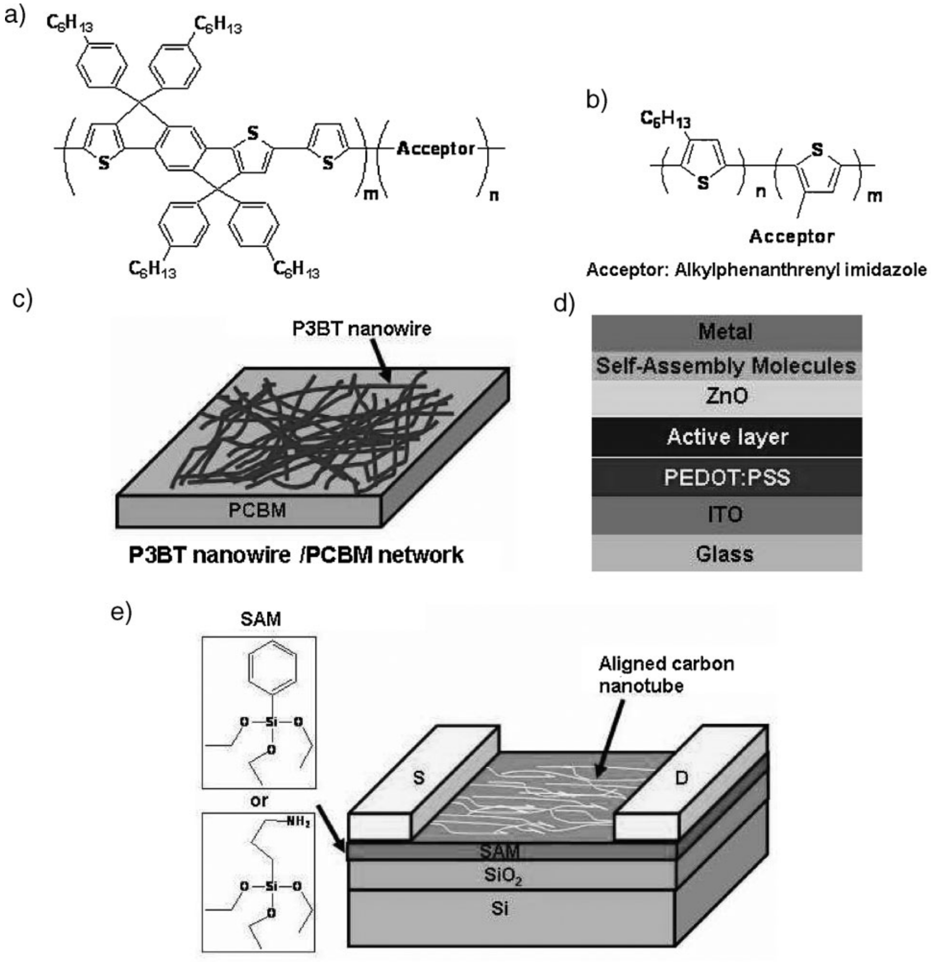

Figure 1.

(a, b) Novel donor-acceptor copolymers (Ko et al. and Wei et al., respectively), (c) polymer nanowire/PCBM composites for photovoltaic applications (Jenekhe et al.), (d) interfacial engineering via organic SAM/metal oxide modification for various organic electronics (Jen et al.), and (e) self-sorted/aligned SWCNT for OFETs (Bao et al.).

enhanced the light absorption and charge transport, leading to the high PCE. Kung-Hua Wei of National Chiao Tung University developed a novel poly(3-hexylthiophene) derivative by incorporating the alkylphenanthrenyl imidazole moiety (Figure 1b) within a high PCE of 4%. The sequential carrier transport from the thiophene to alkylphenanthrenyl imidazole and then to PCBM was believed to be responsible for such a high PCE. Sam Jenekhe from University of Washington demonstrated a nanowire approach that significantly enhanced the performance of poly(3-butylthiophene)/PCBM (structure 1c) based photovoltaic cells to the same PCE level of P3HT/PCBM. The interpenetrating two-phase morphology of the P3BT nanowire/PCBM provided superior hole transport than the corresponding phase-separated P3BT blend, hence the high PCE. Alex Jen, also from University of Washington, adopted carboxylic acid self-assembly monolayer (SAM)/ZnO approach (Figure 1d) to largely improve the device performance of light-emitting diodes, thin film transistors, and photovoltaic cells. The insertion of the SAM/ZnO layer between the active layer and cathode is believed to have assisted the formation of ohmic contact and hence improved device performance.

An extremely impressive work was presented by Zhenan Bao from Stanford University in her PI-IUPAC Award-receiving lecture. Her research group has developed a novel self-sorting approach using spin-assembly and functionalized monolayer to sort and control alignment and density between the semiconducting and metallic single-wall carbon nanotubes (SWNT) (Figure 1e). The on/off ratio of the thin film transistor is as high as 9×10^5. Such new materials designs would be very important for flexible electronic device applications.

Structures, Dynamics and Thermodynamics of Polymer Solutions. Hashimoto *et al*. (Japan Atomic Energy Agency and Kyoto University) investigated the shear-Induced phase separation of entangled polymer solutions of ultra-high molecular weight polystyrene (UHMWPS) and polyethylene (UHMWPE) using small-angle light scattering, and optical microscopy for real-space imaging. The shear-induced phase separation, formation of string-like structures and a sharp transition of optical properties of the strings with shear from a weakly anisotropic state to a strongly anisotropic state were critically discussed (Figure 2a). In the case of the crystallizable solutions, the strong optical anisotropy is found to remain even after cessation of shear flow, which provides an important piece of information to understand formation of precursor structures of shish-kebab in shear-mediated polymer crystallization. Wu et al. (Chinese University of Hong Kong) showed for the first time the predicted discontinuous first-order transition in ultra-filtration of flexible linear polymer chains. The chain was found to be able to pass through a pore much smaller than its unperturbed radius only when the macroscopic flow rate exceeded a threshold value. They further revealed that the force to stretch a polymer coil in an athermal solvent was ca. 10 fN. Therefore, this ultra-filtration method allows one to measure how "soft" a polymer chain is and how strong the inter-chain interaction is when they are collapsed and entangled with each other. Hsiao *et al*. (National Tsing Hua University) presented the effect of chain stiffness on the conformation of polyelectrolyte in tetravalent salt solutions. The radius of gyration (R_g) of polyelectrolyte and ion distribution around polymer as a function of the charge ratio was investigated under different chain stiffness using the simulation scheme developed. Takano *et al*. (Nagoya University) revealed the inconsistence between the theoretical prediction and the experiments of the radius of gyration of cyclic polystyrene in a theta solvent and good solvent. The R_g's in both types of solvent were larger than those predicted theoretically. The second virial coefficient of cyclic polystyrene was also found to be larger than that of linear polystyrene due to higher repulsive force.

For the gel-forming systems, Hong *et al*. (National Taiwan University of Science and Technology) presented a new class of gel called "nucleation gel". They investigated the gel formation of poly(vinylidene fluoride) (PVDF) in salt solution through time-resolve small angle light scattering and identified that the gel formation mechanism was different from that of the chemically or physically crosslinking polymer gels and the jamming particles (Figure 2b). Shibayama et al. (The University of Tokyo) demonstrated the extraction of the partial structure factors of poly(N-isopropylacrylamide)-clay gels (NC gels) by using the contrast matching technique of SANS experiments. The partial structure factors thus obtained were used to elucidate the real-space conformation and structure of NC gels. Kim *et al*. presented an unusual sol-gel phase diagram of multi-arm poly(DL-lactic acid-co-glycolic acid-b-ethylene glycol) (PLGA-b-PEG) copolymer and poly((PEG-b-PLGA)A-co-AA) comb-like copolymer in aqueous solution (Figure 2c). The gel region of the copoly-

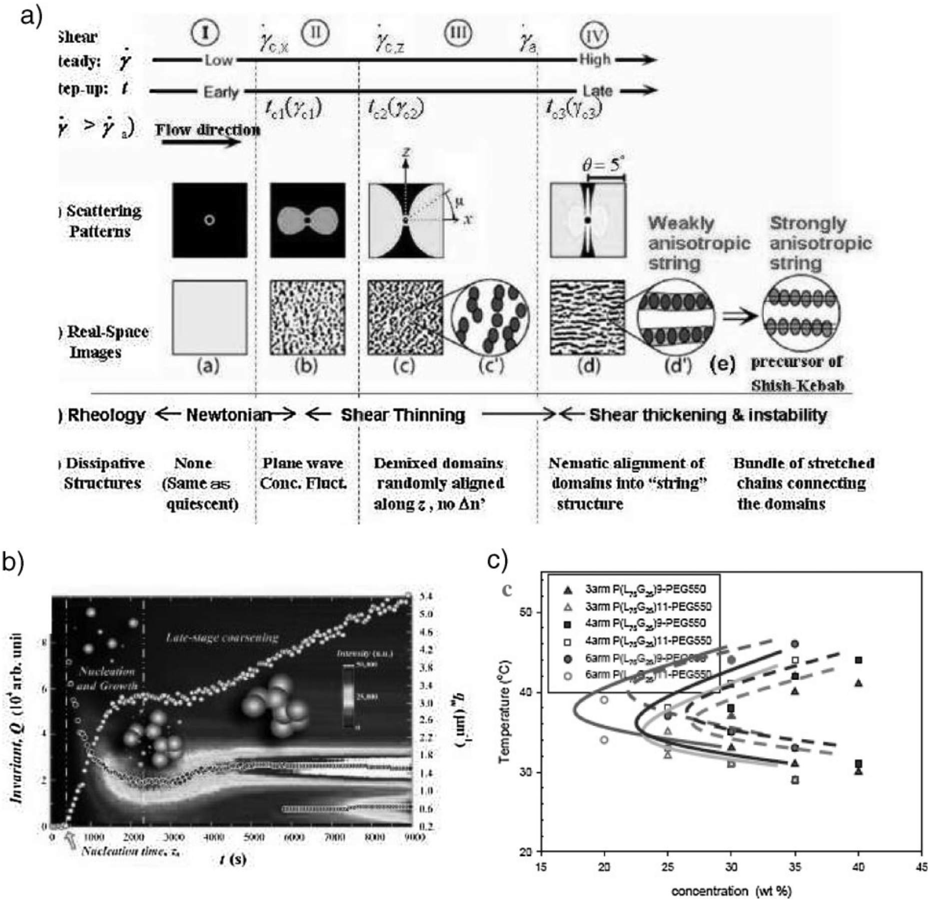

Figure 2.

(a) Shear-induced structure of UHMWPS and UHMWPE (Hashimoto et al.), (b) nucleation gels formed by PVDF in salt solution (Hong et al.), and (c) sol-gel phase diagram of multi-arm PLGA-b-PEG (Kim et al.).

mers was tunable by the pH of the solutions.

Polymers in the Solid State. Spiess et al. (Max-Planck-Institute) investigated the local chain mobility and chain diffusion in solid and molten polymers. In semicrystalline polymers such as polyethylene, local chain motions in the crystals, at the interface to the non-crystalline regions and the interchange between these two (chain diffusion) was of interest (Figure 3a). They showed that the NMR techniques can probe the chain dynamics on vastly different time and length scales. Allegra et al. (Politecnico di Milano) probed chain conformation in polyethylene (PE) solution crystallization. Neutron scattering results on mixtures of hydrogenated and deuteriated PE were found consistent with his ‘‘bundle’’ model. Using wide-angle (WAXS) and small-angle X-ray scattering (SAXS) and Raman spectroscopy which were measured in situ and simultaneously during the tensile deformation of specifically oriented polyethylene fiber, Tashiro et al. (Toyota Technological Institute) found that the *c*-axis of the crystal lattice, which was originally oriented in the direction perpendicular to the fiber direction, reoriented to the stretching direction discontinuously (Figure 3b). During this remarkable change in c-axial orientation

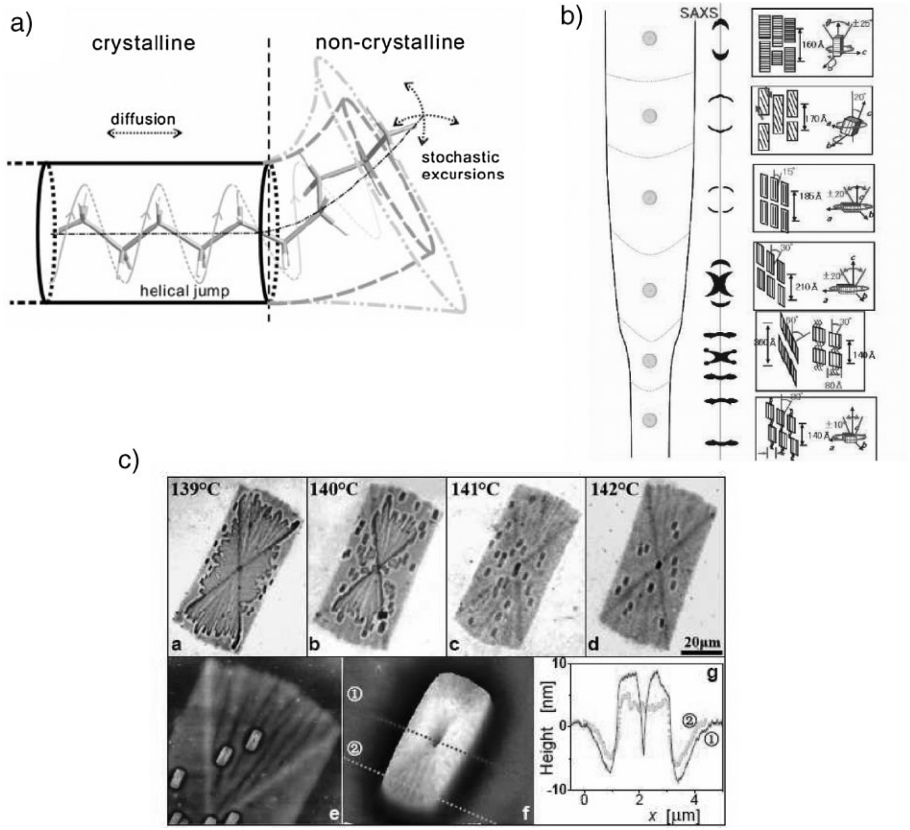

Figure 3.
(a) Local chain motions in the crystals, at the interface to the non-crystalline regions and the interchange between these two (chain diffusion) investigated by NMR (Spiess et al.); (b) reorientation phenomenon of crystal lattice and the stacked lamellar structural change in the cold drawing process of polyethylene fiber (Tashiro et al.); (c) self-seeding from molten poly(ferrocenyl dimethyl silane) single crystal (Reiter et al.).

of the crystal lattice, the higher-order structure or the lamellar stacking structure did not change very much. Once after the *c*-axial reorientation was settled, then a remarkable structural change started to occur. That is to say, the drastic slippage of lamellae occurred as known form the change in SAXS 4-lobe scattering patterns. After this structural change the higher-order structure changed again and suddenly to the so-called fibrillar structure, where the *c*-axis was highly oriented. Takenaka et al. (Kyoto University) investigated the density fluctuations in crystalline polymer under uniaxial stretch in the length scale of sub-micrometer to micrometer using 2-D ultra-small-angle X-ray scattering. Before uniaxial stretch, they found the isotropic density fluctuations obeying the mass fractal with the fractal dimension of 2.6. After stretching, the isotropic scattering pattern was transformed into the butterfly pattern. The butterfly patterns were caused by the heterogeneous deformation, where the lamellar structures and fibrils were deformed with almost affine deformation while the amorphous region between the fibrils was not deformed as much. Thierry et al. (Institut Charles Sadron) discussed the impacts of the crucial parameters for efficient nucleation agents, including compatibility, epitaxial growth and gel formation, on polymer crystallization. Dasmahapatra et al. (National Chemical Laboratory, India) reported a dynamic Monte Carlo simulation study on the effect of additive on the crystallization of homopolymers. The simulation showed a systematic decrease in the chain diffusion, crystallinity and crystallite size with increasing the strength of the interaction between additive and monomer, but the change of specific heat shows a non-monotonic behavior with the interaction near the phase transition. They attributed this behavior to the interplay between monomer-additive interaction and parallel bond packing interaction, which is responsible for crystallization. Lotz (Institut Charles Sadron) presented a comprehensive overview on the powerful means that crystallographic and structural investigations provide to infer and evaluate the local processes at a play in polymer crystallization. The crystallographic aspects deal with the conformation of the stems and their organization in the unit cell. The structural aspects involve features that are maintained over long stretches of the crystallization process and determine the crystal morphology, such as the single crystal shape or the sense of lamellar twist.

Crystallization processes in block copolymers has been an important subject for understanding the crystallization behavior of chain molecules in confined space. Müller et al. (Universidad Simon Bolivar) investigated the crystallization behavior of polyethylene-containing diblock copolymers. A glassy PS block, rubbery PLDA or PEO blocks, semicrystalline PLLA block and miscible PEP block were used to assess the influence of the degree of confinement and miscibility on the crystallization kinetics of polyethylene. It was demonstrated that the confinement effects and topological restrictions caused by the vitreous PS block were stronger than those imposed by the PLDA or PEO rubbery blocks or the semicrystalline PLLA block. Reiter et al. (ICSI-UHA-CNRS) demonstrated that self-seeding may serve as a feasible approach to obtain at molecular scale information on the initial order within a polymer crystal and how order within such crystals varied in the course of time. They reported the experimental results of self-seeding, i.e. re-growing crystals from molten poly(ferrocenyl dimethyl silane) single crystal, as a function of self-seeding temperature and time (Figure 3c). The average number density of identical regenerated crystals was found to decrease exponentially with increasing self-seeding temperature but did not depend much on self-seeding time. The orientation angle of the re-grown crystals had a very narrow distribution around the direction of the seeding crystal which only widened slightly with an increase in self-seeding temperature and self-seeding time. This orientation and distribution of the baby crystals can be affected by thickening of lamellae during and after crystal growth as well as by processes which the seeds undergo during the self-seeding step. The origin of correlated self-seeded crystals was attributed to regions of differing degrees of chain folding within polymer single crystals. Strobl et al. (University of Freiburg) reported the pathway followed in the growth of polymer crystallites by indicating the existence of an intermediate phase of mesomorphic character. They pointed out that it is possible to set up a nanophase diagram dealing with the transitions between melt, mesomorphic layers and lamellar crystallites. Su et al. (National Tsing Hua University) reported a cold crystallization mechanism involving the formation of nanograins for poly(9,9-di-*n*-octyl-2,7-fluorene) (PFO). Their simultaneous SAXS/WAXS/DSC results revealed formation, growth and coalescence of PFO ellipsoidal nanograins from prolate into oblate shapes. Thermal effects of the crystallization process started early in the nucleation but WAXS-identifiable crystallinity was observed only in the coalescence stage. Ho et al. (National Tsing Hua University) introduced a chiral Schiff-based rod-coil amphiphiles to study the variation of helical twisting power with the alkoxy chain length. They elucidated that the formation of twisted superstructure and banded spherulites was attributed to the chiral effect on the self-assembly. The self-assembled morphologies could be tuned by varying the alkoxy chain length to form platelet-like textures and helical twists.

Polymer at Surfaces and Interfaces. The physics of polymers at surface and interfaces is an important subject receiving widespread attention, as there are many advanced applications involving polymer thin films, bio-interfaces, etc. Tran et al. (ESPCI) used responsive polymer brushes to realize smart surfaces with switchable/adaptative/responsive properties. For polyelectrolyte and polyampholyte brushes, chain stretching or collapse was highly dependent on the pH value. It was found that the weakly dense polyampholyte brushes were the most efficient pH-responsive systems in terms of deformation amplitude (Figure 4a). Netz et al. (Technical University of Münich) showed that the friction coefficient of bound polymer was very low on hydrophobic substrates due to the presence of the vacuum layer between substrate and water. This layer acted like a lubricating agent and allowed a polymer to glide on the substrate. Conversely, the friction forces on hydrophilic substrates were large. Potemkin et al. (University of Ulm) reported the conformations, flexibility and orientational correlations of strongly adsorbed comb-like polymers. They also proposed a model that can be useful for making a molecular motor based on the adsorbed combs. Kramer et al. (University of California, Santa Babara) produced 2-D single crystal block copolymer film with a perfectly ordered domain structure by thermal annealing or solvent annealing method (Figure 4b).

Physical Techniques in Polymer Characterization. Several new techniques have been reported in this symposium. Berek et al. (Slovak Academy of Sciences) presented a novel isocratic, fast, robust and user-friendly method of separation of constituents of complex polymer systems. The method is called ‘‘liquid chromatography under limiting conditions of enthalpic interactions’’. The procedures combined exclusion with either adsorption or enthalpic partition or phase separation retention mechanism in a column filled with porous column packing. Zigon et al. (National Institute of Chemistry, Slovenia) demonstrated how size exclusion chromatography coupled to a light scattering photometer as a detector is useful as a complementary tool for the characterization of complex polymers. The success was demonstrated for various polymer systems including plyurethanes, hyperbranched polyesters and bodegradable polymers. Chang et al. (Pohang University of Science and Technology) reported the interaction chromatography technique for the analysis of branched polymers as this method can separate branched polymers with good sensitivity to molecular weight but not chain size. Far more detailed information is able to be obtained if the interaction chromatography is combined with SEC and multiple detections. Jeng et al. (National Synchrotron Radiation Research Center,

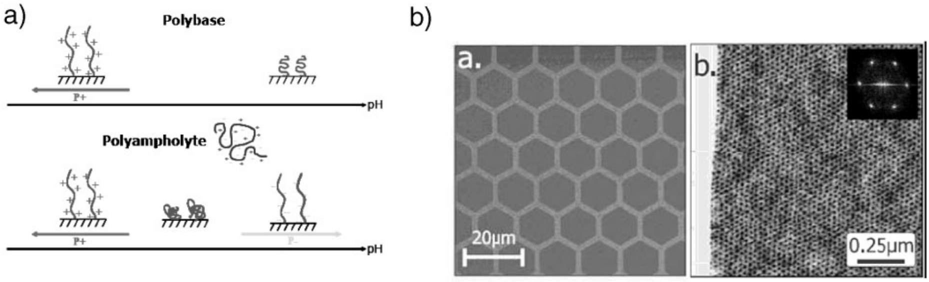

Figure 4.
(a) Responsive polymer brushes smart surfaces with switchable-adaptative-responsive properties (Tran et al.); (b) 2-D single crystal block copolymer film with a perfectly ordered domain structure produced by thermal or solvent annealing methods (Kramer et al.).

Taiwan) presented a dedicated SAXS beamline installed at the NSRRC, Taiwan, and its applications for various studies of polymers and soft matter. For the time-resolved experiments, the high-flux X-ray is expected to provide the capability of dynamic studies of 10–100 ms time resolution. This instrument is also capable of conducting anomalous SAXS experiments for multi-element systems including bimetallic catalysts, semiconductor quantum dots, or copolymer/nanoparticle composites and GI-SAXS experiments for liquid surfaces or solid substances with polymer- or biomolecule-adsorbed layers.

There were also interesting papers in other symposia that attracted extensive attention. On the fundamental side, transmission electron microscopic tomography results of Hasegawa et al. (Kyoto University) provided conclusive evidence for the presence of a gyroid *double-diamond* mesophase (which was once thought erroneously assigned) in block copolymers. At the opposite extreme of practical applications, Stepto et al. (University of Manchester) demonstrated feasibility and characteristics of processing moist starch via common polymer processing techniques such as injection molding. This should bear significance in biodegradable packaging and disposable containers.

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