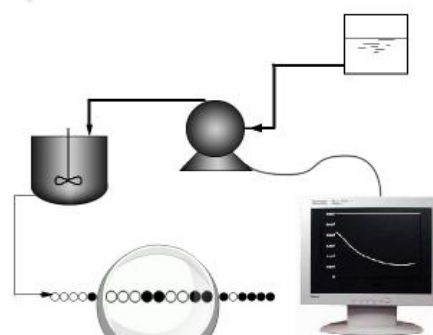
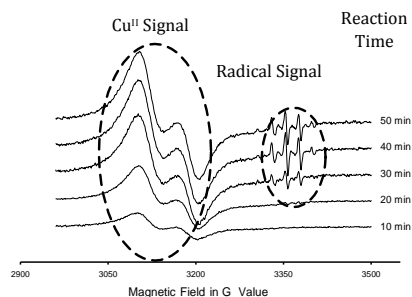


EXPLANATION OF THE CONTRIBUTIONS

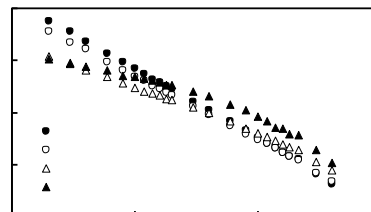
1/ **Controlled/living radical polymerization:** Atom transfer radical polymerization (ATRP) was developed by Dr. Matyjaszewski of Carnegie-Mellon in 1995. ATRP allows unprecedented control over polymer chain microstructure such as molecular weight, composition and architecture. The cumulative number of publications (journal papers and patents) on ATRP has reached about 14,000 by the end of 2010. Dr. Matyjaszewski is predicted by Thomson Reuters Scientific to win a Nobel Prize in Chemistry for “his development of ATRP and other methods living polymerization”. My group started ATRP research in 1997 and was probably the first reaction engineering group in the world involved in the area. The group’s contributions included:

- Direct observation of radical species in ATRP: A free radical mechanism was proposed for ATRP from the very beginning: $PBr + Cu^I Br / L \leftrightarrow P^{\cdot} + Cu^{II} Br_2 / L$. However, its radical nature was questioned and debated because of lacking direct evidence. Radical species was termed as the “missing gem”. In 2000, we hypothesized that the reason for not being able to detect radical was its too low concentration. Adding crosslinker that induced diffusion-controlled radical deactivation and thus moved the equilibrium to the right side, we finally found the “missing gem” in an electron spin resonance study (*Macromolecules* 2001, 34, 1612-1618).
- ATRP catalyst supporting and continuous reactor technology: Early ATRP recipes required an impractical level of about 1wt% catalyst loading, that is, 1:1 ratio of catalyst to initiator. We developed several strategies for catalyst supporting to facilitate catalyst recovery and re-use. Using the supported catalysts, we found that it is a small amount of leached catalyst in solution (at a ppm level) that is mainly responsible for mediating the ATRP system. This finding led to a reduction of three orders of magnitude in the catalyst use. We also developed a continuous supported-catalyst packed-column reactor system that easily produces block copolymers by simply adjusting monomer flow rates (*AIChE J* 2002, 28, 2609-2619).
- Development of reactor technology for gradient copolymers (In collaboration with ZJU): Gradient copolymers are a novel class of polymers that have composition varying from end to end along chain backbone. In conventional methods, it takes only seconds for individual chains to fully grow. Within a time scale of seconds, it is impossible for engineers to exercise control over the composition of individual chains. In contrast, the chain growth in ATRP and other living methods such as RAFT and SFRP takes hours. The composition control becomes practical. However, copolymers prepared by batch reactors have as-synthesized gradient profiles determined by comonomer reactivity ratios. We developed a model-based semi-batch reactor technology that allows precise designing and control of any desired composition variations at will (*AIChE J* 2007, 53, 174-186; 2008, 54, 1073-1087).

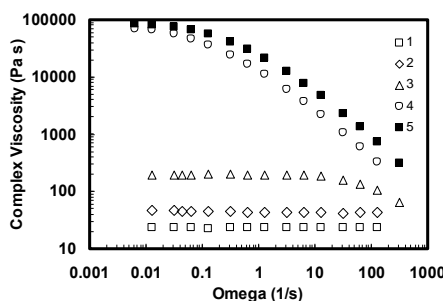


2/ Metallocene polymerization and branched polyethylenes: Metallocene/methylaluminoxane catalyst was discovered by Dr. Kaminsky of Hamburg in the early 1980's and used for production of polyolefins. Due to its single site type nature, the catalyst yields polymer products having narrower molecular weight distribution and more homogeneous chain microstructural properties than Ziegler-Natta catalyst. The development of metallocene and other single site type catalysts have had the strongest impact on polyolefin industries since Ziegler-Natta, with various high-quality commercial products. We made significant contributions to the research and development of branched polyolefins.

- Establishment of chain microstructure and material processability relationship: A unique high-temperature high-pressure continuous stirred tank reactor (CSTR) system was set up in our lab and metallocene polyethylene (mPE) products having various branch densities were prepared. The mPE's shear-thinning property was correlated to its branch density. The work quantitatively demonstrated that branched PE has higher melt strength and better shear thinning than linear PE, the best combination of property and processability (*Macromolecules* 1998, 31, 8677-8683; *Polymer* 1999, 40, 1737-1744).



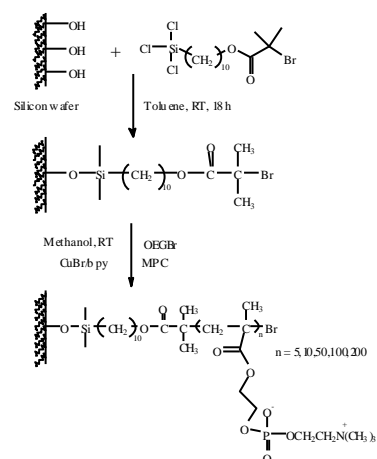
- Development of high-molecular-weight low-viscosity Newtonian polyethylene materials: Using Pd-diimine catalyst and varying reactor conditions, we prepared PE products that have various branch densities, from linear to hyperbranched (>100 br/1000C), but have similar molecular weights at a 10⁵ g/mol level. It was demonstrated that hyperbranched PE have viscosities four orders of magnitude lower than linear one and have a Newtonian flow behavior. This type of materials is tested in industries as high-performance lubricant viscosity-index improver of high shear stability (*Macromolecules* 2003, 36, 2194-2197; *Ind Eng Chem Res* 2007, 46, 1174-1178).



3/ Preparation of non-biofouling surfaces by polymer grafting:

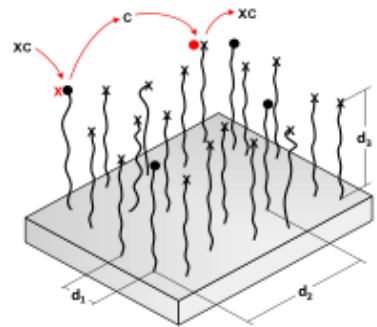
Biocompatibility is a critical issue for medical devices and body implants. Protein adsorption from blood leads to thrombus formation, foreign body reaction, bacterial infection and other undesirable responses. Surface modification is often required to improve biocompatibility. We developed a method based on surface-initiated atom transfer radical polymerization (SI-ATRP), which has demonstrated to be very useful.

- Biomimetic phosphorylcholine (PC)-containing polymer was grafted by the method from various substrates with designed graft densities and molecular weights. The quantitative relationship

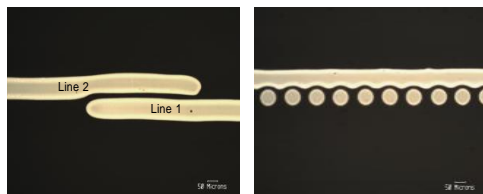


between grafted polymer properties and surface's protein repelling performance was established. Reductions in protein adsorption over 98% were achieved with <1 chain/nm² graft density and tens of PC units chain length (*J Polym Sci Chem* 2004, 42, 2931-2942; *Langmuir* 2005, 21, 5980-5987).

- Termination of surface radicals: How the polymer radicals constrained to a surface are terminated remains to be a fundamental question. Some think they can be terminated easily because of high concentration at surface. Others believe they cannot be terminated because of lack of chain migration. Through modeling and experiment verification, we discovered a new mechanism: While chains cannot migrate, radicals move around rapidly through activation-deactivation cycles facilitated by catalyst molecules in solution (*Macromolecules* 45, 1197-1208, 2012). This discovery was appraised to be “very exciting and important” by reviewers, in understanding the mechanisms of surface-initiated controlled radical polymerization.



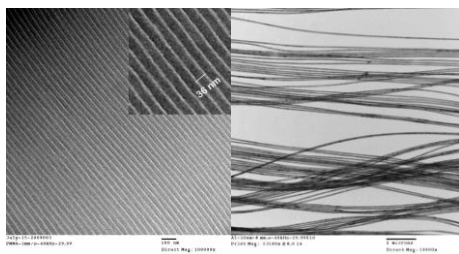
4/ Ink-jet printing of plastic microelectronics (in collaboration with XRCC):



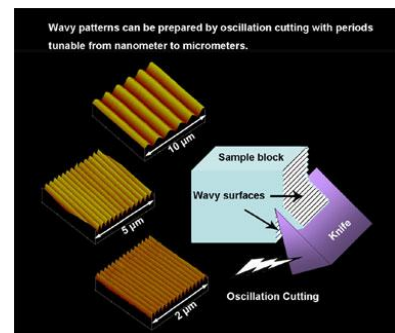
In recent years, there have been tremendous interests in printed thin film transistors (TFTs) which promise applications such as low-cost RFID tags and liquid crystal displays (LCD). Printing conductive materials to achieve reproducible small channel length (<50 μm) is mandatory yet very challenge. We developed a new

method to achieve reproducible small channel length for thin film transistors. It is based on simultaneously modification of the substrate by first printed line or drops, followed by self-assembly of the second printed line or drops to automatically form small channels. Experiments showed the very reproducible small gap (25-30 micron) could be achieved via this invented method (*US Patent* 8,361,891 2013). Due to the self alignment nature, small printing errors could be automatically self-corrected, allowing for large defect-free source drain arrays to be printed with a very narrow distribution of channel length (*ACS Appl Mat Interf*, 2, 2189-2192, 2010).

5/ “Cutting-edge” nanotechnology for large-area and long-range nanowaves and nanowires:



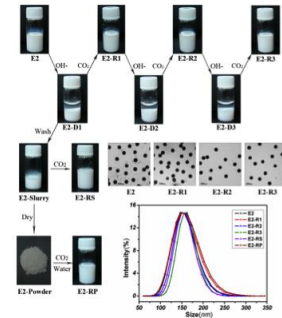
in cutting process could be precisely controlled for fabrication of highly ordered surface structures. This is a surprising discovery; we thus developed a one-step “cutting-edge” technology that allows us to produce wavy- or strip-patterns at lowest costs over large-area and long-range scales. It involves no chemical reactions or byproducts, having clear advantage over conventional lithographic technologies. Patterns having feature sizes from 30 nm to 1 μm can be achieved using same facility by changing cutting speed and frequency of



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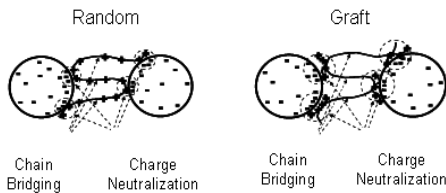
oscillation applied to cutting knife. Thus patterned surfaces have potential applications in gratings/waveguides, biological patterning/sorting and, as templates to fabricate other nanostructures (*Nanotechnology* 21, 355302, 2010, <http://nanotechweb.org/cws/article/lab/43724>). Further work on this “cutting-edge” technology allows us to produce nanowires for a wide range of polymeric and metallic materials (*Nanotechnology* 22, 265305, 2011).

6/ Reversibly coagulatable and re-dispersable styrenic latexes (in collaboration with ZJU): Millions of tons of polymer latexes are produced annually by emulsion polymerization. The unique properties of latex products offer a variety of applications in rubber, plastic, coating, paper, textile, leather, and construction industries, as well as biomedicine and pharmaceuticals. Most emulsion products contain about 45 to 60 vol% water. In solid form, latexes are coagulated by large amount of salts or acids, washed and dried. Wasteful water and intensive energy are big problems. In liquid form, half of the costs spent in storage and transportation are for water.



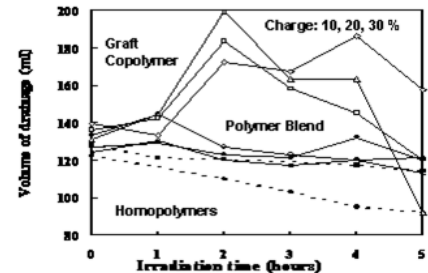
We developed polymer latexes that can be coagulated by N₂ and re-dispersed by CO₂ bubbling. Our approach is by incorporating a small amount amine- or amidine-containing derivative as comonomer or reactive surfactant in emulsion polymerization. The coagulation/re-dispersion processes can be repeated many times, even with washed and dried latexes (*Macromolecules* 44, 6539-6545, 2011; 46, 1262-1267, 2013).

7/ Development of water-soluble polymer flocculants: Polymeric flocculants are widely used in paper making, mineral processing, oil recovery, and waste water treatment industries. They are mostly



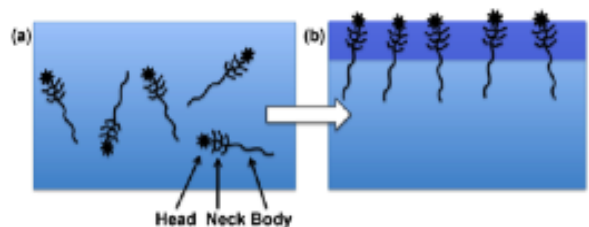
acrylamide-based polyelectrolytes. Charges are randomly distributed along PAM chains. We hypothesized that graft copolymers with charge units concentrated to certain sections of PAM

chains are more effective flocculants than the random copolymers. We grafted low molecular weight high charge density cationic diallyldimethylammonium chloride onto high-molecular-weight PAM by gamma radiation. The resulted copolymers gave indeed much better performance in dewatering paper mill sludge (*Colloid Polym Sci* 1999, 277, 115-122; 123-129).



8/ Surfadditive approach for surface modification:

“Surfadditive” is an abbreviation for “surface-active-additive”. Unlike conventional coatings, the surfadditive approach is to in-situ modify plastic surface properties while parts are molded, thus saving costs incurred from pre- or



post-treatments. We designed a type of surfadditive copolymers that have “head-neck-body” chain microstructure. The “head” provides required surface functionalities, the “neck” enables migration of the additive molecules to surface, and the “body” offers interactions with the part matrix. As an example, we synthesized tri-block methacrylate containing triethoxysilylpropyl, perfluorodecyl and methyl side chains using atom-transfer radical polymerization. A small amount of the block polymer was added to polymethyl methacrylate syrup in casting acrylic sheets and improved surface adhesion. A clear advantage of this approach is its versatility for parts of large area or complex geometry such as inner surface (*Macromol Mat Eng* 297, 261-271, 2012).

9/ Polymerization modeling and kinetic theory of gelation: Modeling has become a powerful tool in both academic research and industrial development. We made pioneering contributions in modeling controlled radical polymerization processes such as ATRP (*Macromol. Theory Simul* 1999, 8, 29-37), RAFT (*J Polym Sci Chem* 2003, 41, 1553-1566) and SFRP (*J Polym Sci. Phys* 1999, 37, 2692-2704); in modeling semi-batch reactor processes for design and control of tailor-made copolymer chain microstructure (*Macromol Theory Simul* 2006, 15, 356-368; *AIChE J* 2007, 53, 174-186); in modeling gelation behaviors of divinyl systems (*Macromolecules* 2009, 42, 85-94; 1996, 29, 456-461; 1993, 26, 3131-3136). The modeling work provided great insight into the molecular processes involved in the polymerization systems. Among many others, the famous Flory theory of gelation was extended to describe the formation of heterogeneous networks (*Macromolecules* 1992, 25, 5457-5464).