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Editorial: Responsive Polymer Thin Films

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This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as doi: [10.1002/pol.30698](https://doi.org/10.1002/pol.30698)

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Jouha Min is an Assistant Professor of Chemical Engineering at the University of Michigan. Dr. Min has a PhD in Chemical Engineering from MIT, and postdoctoral research experience from Harvard Medical School/Massachusetts General Hospital. Dr. Min's research group focuses on developing advanced biomaterials and biosensors using fundamental chemical engineering principles, with the goal of creating robust engineering solutions to significant health problems such as cancer and life-threatening infectious diseases.



Responsive polymer thin films play an important role as structural components in the emerging fields of soft actuators, wearable electronics, and biomedical devices. These films are capable of changing their physical and/or chemical properties significantly in response to environmental stimuli, such as temperature, light, pH, magnetic fields, and ion strength. The integration of multifunctional designs in the polymer networks enables these films to possess advanced capabilities, including, but not limited to, structure color, self-healing, adhesion, conductivity, antimicrobial properties, and anti-fatigue properties. Polymer and hydrogel films are typically thinner than bulk polymer materials, ranging from nanometers to several hundred micrometers, and are usually made up of thin layers of natural or synthetic polymers. These films can be free-standing or coated on substrates. They offer faster response times, high flexibility, good adaptivity and versatility via integrating with other functional materials. This special issue on responsive polymer and hydrogel films collects a series of review articles that detail the latest progress in this rapidly developing field, as well as original research articles that propose novel approaches to tackle practical challenges.

The review article by Dong et al provides a comprehensive overview of recent progress in the fabrication and application of functional hydrogel films. The authors focus on two main areas: (i) the methods used to fabricate hydrogel films, and (ii) the various applications of hydrogel films in the fields of biomedicine and emerging technologies. Hydrogel films with controllable thickness, fast response times, good compliance, and tunable mechanical properties are ideal for use in artificial muscles, wound dressing, and the construction of soft actuators and flexible electronics. The review article also highlights current challenges, and provides future perspectives on the development of hydrogel films.

Yang et al. reported on the successful fabrication of self-healable, electromagnetic interference (EMI) shielding composite films that exhibit dual responsiveness to temperature and strain. To create these multifunctional films, the team incorporated carbon nanotubes (CNTs) into hydroxyl terminated polybutadiene (HTPB), which was dynamically crosslinked by boric acid (BA). The HTPB-BA substrate showed excellent self-healing ability at room temperature, facilitating the autonomous recovery of electric conductivity and mechanical strength of the composite films. Dual responsiveness to temperature and strain was observed in the composite films, with electric

resistance actively changing in response to variation of temperature and strain. Additionally, the composite films exhibited excellent EMI shielding ability, with an effectiveness beyond 28 dB, making them ideal for commercial applications. The EMI shielding efficiency was also found to be responsive to temperatures. These responsive, EMI shielding, and self-healable composite films have broad potential applications in the fields of flexible electronics and protection of sensitive instruments.

Amphiphilic block copolymer (BCP) thick films with stimuli-responsive pores are emerging as promising candidates for next-generation ultrafiltration (UF) membranes, due to their stimuli-responsive, smart nanochannels which facilitate the removal of fouling, among the biggest challenges in membrane technology. Bouzit et al prepared a well-defined, polystyrene-block-poly(2-vinylpyridine)-block-poly(N-isopropylacrylamide) (PS-b-P2VP-b-PNIPAM) terpolymer using reversible addition-fragmentation chain transfer polymerization. They used a combination of nonsolvent-induced phase separation process and solvent vapor annealing treatment to produce nanostructured pH- and thermo-double sensitive ABC-type, BCP thick films. The NIPS-made PS-b-P2VP-b-PNIPAM thick film, comprising a microporous spinodal-type network substructure topped by a dense thin layer of poorly defined nanopores, was transformed into a monolith composed entirely of a well-ordered, perforated lamellar (PL) phase upon exposure to a chloroform vapor. These PL-structured monoliths, show excellent permeance and temperature cyclability and are highly desirable for the manufacturing of smart, separation-based UF materials that can transition their pore state from hydrophilic to hydrophobic (and vice versa), leading to much more efficient detachment of foulants during the cleaning process.

Dolmat and coworkers developed a method for the dynamic assembly of hydrogen-bonded multilayers of (poly(N-vinylpyrrolidone/poly(methacrylic acid)) [PVPPON/PMAA]) and compared it with static multilayers. They found that dynamic multilayers, in which a planar substrate is shaken during polymer adsorption, leads to a 15-times faster deposition of the planar coatings than with static multilayer films. The thickness and roughness of the dynamic coatings were found to be approximately 30% larger than those of static multilayer films, as measured by spectroscopic ellipsometry and atomic force microscopy. The researchers examined the film growth, mechanical properties, wettability, hydration, and pH stability of the planar static and

dynamic multilayers, and found that these properties were minimally affected by the assembly mode. They discovered that upon release of the multilayer films into a solution to produce free-standing films (either as planar membranes or multilayer capsule shells), the molecular chain rearrangements resulted in decreased roughness for both static and dynamic multilayers and decreased thickness of dynamic multilayers. These findings can aid in developing a rapid synthesis of thicker nanostructured polymer coatings for sensing and controlled delivery applications.

Poly (vinylidene fluoride) (PVDF) has garnered significant attention in recent decades due to its properties, particularly pyro- and piezo-electricity, which are linked to its electro-active β -phase in PVDF. The production of β -PVDF through mechanical stretching of non-polar α -PVDF have been reported, but the impact of strain and temperature on phase changes in spin-coated PVDF thin films has been unclear. In a recent study by Pilla et al, the mechanical properties of spin-coated PVDF freestanding thin films were investigated with a focus on the effects of thermal annealing and in-plane anisotropy. Full-field deformation was measured under in-situ tensile loading, in conjunction with digital image correlation to observe correlations between the stress-strain behavior of spin-coated β -PVDF/ α -PVDF and the mechanical stretch-induced phase transformation in α -PVDF. The study found that spin-coated and annealed α -PVDF exhibited significantly higher mechanical strength and failure strain (~ 35 MPa and ~ 5.5) than spin-coated β -PVDF (~ 10 MPa and ~ 0.45). Fourier transform infrared and Raman spectroscopy were used to confirm that mechanical stretching at room temperature caused α -PVDF to transition to β -PVDF beyond a stretch ratio of ~ 1.2 . Furthermore, the study suggested that the in-plane anisotropy observed in β -PVDF is due to the spin-coating process.

The unique properties of Janus two-dimensional (2D) polymeric materials, with asymmetric dual surfaces, make them ideal for applications such as biosensors, catalysts and drug delivery systems. In their recent paper, Zhao and colleagues successfully constructed micro/macro-scale Janus polypeptoid-based 2D structures at the air-water interface using evaporation-induced interfacial self-assembly of amphiphilic block copolymer poly(ethylene glycol)-b-poly(N-(2-phenylethyl) glycine) (PEG-b-PNPE). Initially, the PEG-b-PNPE was assembled into a monolayer with a uniform thickness of $\sim 2.5 \pm 0.1$ nm, which was then mechanically compressed

into a bilayer structure by Langmuir–Blodgett (LB) technology by increasing surface pressure beyond the critical collapse pressure. The resulting monolayer and bilayer nanostructure spanned hundreds of microns in both dimensions, and exhibited asymmetric wettability on the air and water sides, as determined by dynamic/static optical contact angle/interface tensiometer. The evolution from a monolayer to a bilayer was further tracked using atomic force microscope. The team was also able to prepare macroscopic Janus films with a diameter of ~ 3.5 mm using the same methods. These micro/macro-scale 2D materials have potential applications in nanoscience and biomedicine, and the results of this study provide a valuable contribution to the field of Janus 2D materials.

In another example, Kashem et al. developed a high-performance and multifunctional film using poly (diallyldimethylammonium chloride) (PDDA) and poly(acrylic acid) (PAA) via a spin-spray-assisted layer-by-layer (SSA-LbL) assembly. The SSA-LbL method was found to be highly efficient and timesaving, resulting in a homogeneous thick film in the tens of micrometer range compared to the conventional immersive assembly method, which typically produces thin films in the nanometer range. When scratches occurred, the film displayed a quick and durable self-healing capability, thanks to the dynamic movement of the flexible polyelectrolyte complex chains at the scratch edges. Additionally, the film effectively blocked UV rays by incorporating graphene oxide (GO) and titanium dioxide (TiO_2) nanoparticles as UV-blocking additives. Because of the hydrophilic feature of the PDDA/PAA molecules, the film also showed anti-fog characteristics in different environmental conditions. The researchers investigated the effect of GO and TiO_2 nanoparticle concentration on self-healing and UV-protection properties, and identified the optimum concentration range of GO and TiO_2 nanoparticles in polyelectrolyte solutions for producing the film with self-healing, UV-blocking, and anti-fogging features.

Silk is renowned as the “queen of fibers” due to its lightness, smoothness, and luster. A study by Zhu and colleagues reported an easy care solution for silk fabrics by crosslinking a thermo-responsive copolymer film onto the surface. The thermo-responsive copolymer — poly (N-isopropylacrylamide-co-oligo[ethylene glycol] methyl ether methacrylate-coethylene glycol methacrylate) (abbreviated as P(NM-co-OA300-co-EA360)) -- was synthesized using sequential atom transfer radical polymerization. By using 1,2,3,4-butanetetracarboxylic acid as crosslinker,

the thermos-responsive P(NM-co-OA300-co-EA360) film can be placed onto silk fabric with a transition temperature of around 46°C. The reversible transition behavior effectively reduces the attachment between lipophilic stains and the film, leading to efficient stain removal. A 30-second rinse with deionized water at 25°C (below its transition temperature) can remove 60% of stains. Moreover, during outdoor activities or drying, the crosslinked P(NM-co-OA300-co-EA360) film becomes hydrophobic, allowing water molecules to quickly evaporate from the silk fabrics; the drying process was found to be 25% faster than without the crosslinked film. These excellent properties make silk fabric crosslinked with the thermo-responsive copolymer film suitable for designing silk-based clothing.

In recent years, researchers have made significant advancements in the development of soft actuators that can morph into complex shapes, taking inspiration from nature. One noteworthy example of this is the work of Peeketi et al, who have reported a new type of thin-film based bioinspired actuator. Drawing inspiration from the calla lily, they demonstrated a splay-nematic liquid crystal polymer network tapered actuator that can morph from a flat film to a cone, mimicking the blooming of a calla lily flower. Using both finite element simulations and experiments, Peeketi et al. have successfully produced conical tubes. The researchers analyzed the influence of tapering and alignment orientations with respect to the edge of the film on the cones through simulations, and found that the design with tapering and splayed alignments oriented at 45°C to the edge is the optimal choice for forming conical tubes.

This collection offers a glimpse into the many recent works published in the *Journal of Polymer Science* on responsive polymer thin films. Our aim is to provide a summary of these selected publications, which will, we hope, inspire readers to develop new approaches to solve fundamental problems and explore novel functional devices for practical applications. We thank all the authors, reviewers, and editorial staff for their significant contributions to this special issue.



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