

RESEARCH ACCOMPLISHMENTS

Research efforts in the Genzer research group span a broad range of surface and interfacial phenomena in soft materials pertaining to polymers and other soft matter building blocks. Genzer and his students and collaborators have engaged actively in a variety of projects exploring the assembly of polymers and self-assembled monolayers on surfaces and interfaces, developed novel methods of decorating surfaces with position-dependent soft matter gradients, conceived techniques enabling fabrication of substrates with well-defined hierarchical topographies, and contributed to theoretical understanding of soft material partitioning in confined geometries and surfaces. Several accomplishments are outlined briefly below.

Molecular & macromolecular gradients. The Genzer group has pioneered the development of methodologies leading to the formation of small-molecule and polymer assemblies that possess a gradual variation of at least one of their physico-chemical properties on surfaces. Their techniques – now employed widely by multiple research groups around the world – facilitate the formation of gradients in polymer/monomer grafting density, molecular weight, and chemical composition. Genzer and collaborators demonstrated that such structures facilitate systematic studies of: 1) “surface grafted” polymerization, 2) adsorption and separation of proteins, 3) cell adhesion, 4) distribution of metallic nanoparticles, 5) conformational changes in diblock copolymers associated with selective swelling/collapse of one of the two blocks, 6) formation of organogels and hydrogels with (multi)directional modulus, and others. The group has also developed methodologies leading to creating orthogonal gradients wherein two material properties vary continuously along two mutually perpendicular substrate directions. Working with orthogonal gradient substrates not only saves time and resources but it also minimizes systematic errors associated with carrying out a large set of individual experiments. Moreover, concurrent spatio-temporal variation of the two properties facilitates investigation of their cooperative effect on a given phenomenon. Genzer and co-workers demonstrated the latter in a study, which revealed that complete understanding of protein adsorption on grafted layers can only be gained by monitoring concurrently the amount of adsorbed protein as a function of both the polymer length and grafting density on the substrate.⁵¹



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T. Wu, K. Efimenko, J. Genzer, *Journal of the American Chemical Society* **124**, 9394 (2002).

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R.R. Patil, D. Kiserow, J. Genzer, *RSC Advances* **5**, 86120-86125 (2015).

Structure and stability of polymer brushes. We used computer simulation and experiments to gain insight into the structure of polymer brushes prepared by surface-initiated controlled radical polymerization (SI-CRP). We studied how the rate of polymerization originating from the substrate and the dispersity in polymer length depend on the density of the grafting sites on the substrate, curvature of the substrate, and controlled character of the CRP reaction. We have developed a simple method to determine quantitative the grafting density (*i.e.*, the number of polymer grafts per unit area) by degrafting the chains quantitatively using tetrabutylammonium fluoride (TBAF) from silica-based surfaces, and measuring the complete distribution of molecular weight using size exclusion chromatography. This “on demand degrafting” was further utilized to generate complex polymer brush patterns with spatially varying grafting density and/or chemical composition. We have begun investigating systematically degrafting of covalently-grafted polyelectrolytes.⁵² We have addressed the role of the molecular weight, grafting density, and spatial distribution of charges (as well as their mutual interplay) on the stability of polyelectrolyte brushes.

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⁵² with Harm-Anton Klok (EPFL)

In addition to providing much needed insight into the stability of polymeric grafts on surfaces, our efforts help comprehend the role of “charge regulation” in weak polyelectrolyte brushes (predicted theoretically but not verified experimentally until now) that is responsible for higher stability of weak polyelectrolyte grafts relative to strongly-charged counterparts.

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H.A. Klok, J. Genzer, *ACS Macro Letters* **4**, 636–639 (2015).

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Y. Li, Y. Lin, Y. Ko, D. Kiserow, J. Genzer, *ACS Macro Letters*. **7**, 609-613 (2018).

R. Patil, J. Miles, Y. Ko, P. Datta, B. Rao, D. Kiserow, J. Genzer, *Macromolecules* **51**, 10237-10245 (2018).

Forced (macro)molecular assembly on flexible substrates. Genzer and his students and collaborators have demonstrated that flexible siloxane networks can be employed as multipurpose substrates for assembling grafted molecules.⁵³ This method can be viewed as a derivative of the classical Langmuir-Blodgett methods commonly applied for liquid/air interface. In this solid/air interface situation, molecules are anchored chemically to siloxane networks; mechanical deformation of the network provides convenient means of controlling molecular packing of chemically-anchored moieties. Various variants of the technique are nowadays used to study the effects of molecular packing on creating stable surfaces with tunable physico-chemical characteristics (wettability, weatherability, *etc.*). Genzer and coworkers have demonstrated the multipurpose of this methodology by anchoring both short oligomers (including specialty peptides termed “syntactomers”) as well as polymers and inspired other groups around the world to start adopting this methodology to control chain packing on surfaces.

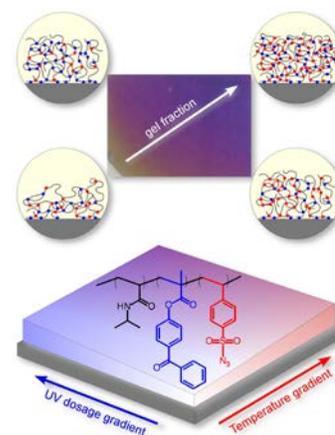
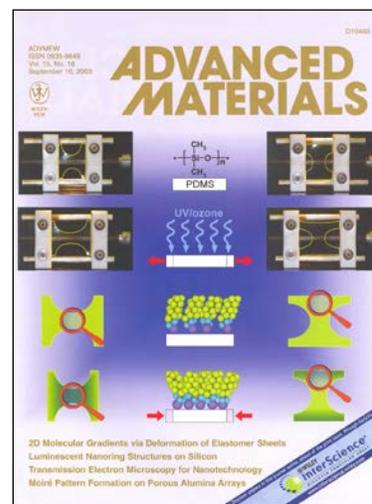
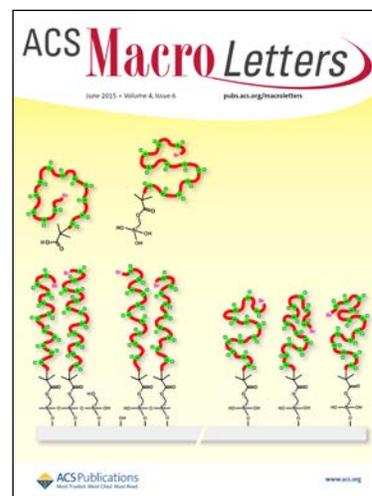
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T. Wu, K. Efimenko, J. Genzer, *Macromolecules* **34**, 684 (2001).

K. Efimenko, J. Genzer, *Advanced Materials* **13**, 1560 (2001).

S. Ahmed, H.-K. Yang, A.E. Ozcam, K. Efimenko, M.C. Weiger, J. Genzer, J.M. Haugh, *Biomacromolecules* **12**, 1265–1271 (2011).

Surface-anchored elastomers and hydrogels. Our interest in gradient materials and functional elastomers/gels has led to the development of new fabrication methods that enable generation of polymer networks with spatially-varying crosslink densities. We have demonstrated that elastomers with spatially-varying crosslink density can be formed by inter-diffusion of chains of various functionalities or/and gradient(s) in crosslinker density. A more general method, adapted to both elastomers and gels, has involved creating gradient polymer networks by spatially varying crosslinking center based on photo- and thermal-activation. We have capitalized on the versatility and orthogonality of the dual crosslinking activation and built hydrogels, in which the crosslinking density varies gradually in vertical and/or



⁵³ with Kirill Efimenko (NC State)

horizontal directions. This is a relatively new research area for our group and we plan to continue extending these concepts to a variety of polymer and crosslink systems.

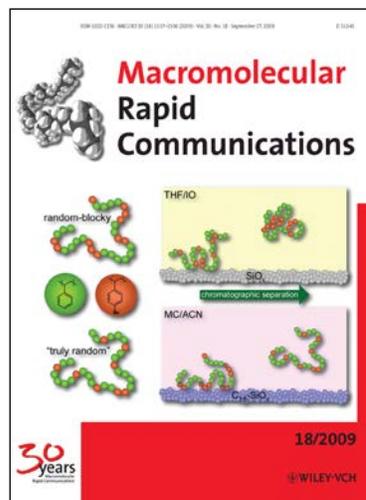
J.A. Crowe-Willoughby, K.L. Weiger, A.E. Özçam, J. Genzer, *Polymer* **51**, 763–773 (2010).

C.K. Panidayarajan, M.R. Rubinstein, J. Genzer, *Macromolecules* **49**, 5076–5083 (2016).

C.K. Panidayarajan, J. Genzer, *Langmuir* **33**, 1974–1983 (2017).

C.K. Panidayarajan, J. Genzer, *Macromolecules* **52**, 700–707 (2018).

Random copolymers with tunable co-monomer sequences. Genzer and coworkers have provided experimental and computational evidence that random copolymers with tunable co-monomer sequence distributions can be generated by “chemically coloring” homopolymers; the distribution of the “coloring” species can be adjusted by tuning the solubility of the homopolymer in the solvent, which, in turn, controls the size of the homopolymer coil in the solution and the solubility of the resultant copolymer.^{54,55,56} We have shown that such random copolymers with tune co-monomer sequences can act as efficient compatibilities, thin films stabilizers, and scavengers of molecular cargos, and may also be employed as smart stationary phases in affinity chromatography. While studying the co-monomer distribution of the “random-blocky” copolymers Genzer *et al* have demonstrated that electro-optical Kerr effect apparatus represents a convenient method for investigating chemical composition and monomer sequences in polymeric materials.⁵⁷ Recent collaborative efforts revealed that information about the variation in



chemical composition and co-monomer sequences in random copolymers can be gained by combining experimental efforts with computer modeling. Our interests in these so-called post-polymerization modification methods have led in recent years to numerous system designs that have been utilized in controlling bio-adsorption, molecular capture, controlling surface wettability, and others.

J. Han, B.H. Jeon, C.Y. Ryu, J.J. Semler, Y.K. Jhon, J. Genzer, *Macromolecular Rapid Communications* **30**, 1543–1548 (2009).

A.E. Tonelli, Y.K. Jhon, J. Genzer, *Macromolecules* **43**, 6912–6914 (2010).

W. Powers, C.Y. Ryu, Y.K. Jhon, L.A. Strickland, C.K. Hall, J. Genzer, *ACS Macro Letters* **1**, 1128–1133 (2012).

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R. Malik, J. Genzer, C.K. Hall, *Langmuir* **31**, 3518–3526 (2015).

Propagating waves of self-assembly. By using high resolution X-ray synchrotron measurements in combination with computer simulation studies, Genzer and collaborators⁵⁸ have established that vapor deposition of organosilanes under confinement follows “propagating front” mechanism rather than conventional diffusion. Similar phenomena have recently been established by Genzer and coworkers in related systems involving “frontal polymerizations” under confinement. Genzer and coworkers have shown that these wavefronts do not follow the constant width predicted by mean-field growth models widely assumed to model such “self-propagating” or “autocatalytic” growth processes. Instead, the interface roughens progressively in time and this interfacial broadening is described by a power-law growth, corresponding to the propagating front motion. The results may have implications on many fields of science and technology and can be used to verify dynamics in other (seemingly rather unrelated) phenomena such as the spread of disease, tumor growth, wound healing, the spread of epidemics, and the spread of languages across Europe.

J.F. Douglas, K. Efimenko, D.A. Fischer, F.R. Phelan, J. Genzer, *PNAS* **104**, 10324 (2007)

⁵⁴ with Carol K. Hall (NC State)

⁵⁵ with Chang Y. Ryu (RPI)

⁵⁶ with Alexei Khokhlov & Pavel Khalatur (Moscow State U., Russia)

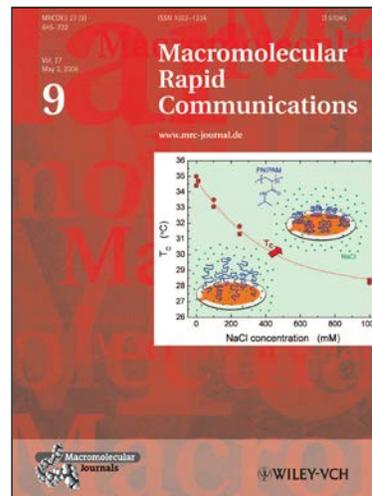
⁵⁷ with Alan Tonelli (NC State)

⁵⁸ with Daniel A. Fischer & Jack F. Douglas (NIST)

P. Datta, K. Efimenko, J. Genzer, *Polymer Chemistry* **3**, 3243–3246 (2012).

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Responsive surfaces. The group's interests in comprehending the responsive nature of polymers at interfaces and in thin film geometries led to multiple studies covering various length scales and time scales. On a molecular-level, the group provided evidence that segmental rearrangement in polymer melts near surfaces is faster than that in bulk. We also studied molecular reorganization of amphiphilic functional groups on the surfaces of polysiloxane networks, and linked the rate of rearrangement of the functional groups to both its amphiphilic nature and altered bulk dynamics due to variation in T_g . The group also performed studies of conformational changes in thermoresponsive and polyelectrolyte macromolecular grafts on surfaces. The latter involved monitoring polymer graft conformations in aqueous solutions (variation of pH and salinity) and in humid environments. On a mesoscale, the group reported on manufacturing of silicone rubbers with tunable color variation in response to the wavelength variation of the external light source.



H.K. Yang, A.E. Özçam, K. Efimenko, J. Genzer, *Soft Matter* **7**, 3766–3774 (2011).

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Reconfigurable/shape-memory materials. Dickey & Genzer and collaborators⁵⁹ have developed methods for hands-free folding of 2D polymer sheets with printed patterns into 3D objects using remote external light (IR, LED, and halogen) sources. We have also extended the strategy to perform hands-free folding using microwaves or heat gun. We have demonstrated that sequential folding of multiple hinges on the same sample can be programmed by changing the wavelength of the light source and the ink color of the hinge. We have also explored two strategies to convert thermoplastic shape memory polymer sheets into 3D shapes with controllable curvature by dictating where the polymer shrinks. This shrinking is controlled spatially by patterning 2D sheets with black ink, which, upon exposure to infrared (IR) light, converts the absorbed IR light into heat. A key element in this work is the ability to place IR-absorbing ink in predetermined regions of the polymer sheet.



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A.M. Hubbard, R.W. Mailen, M.A. Zikry, M.D. Dickey, J. Genzer, *Soft Matter* **13**, 2299–2308 (2017).

Control of biofouling on surfaces. Our interest in modification of surfaces using chemical and/or physical means led designing coatings with antifouling characteristics. We studied protein adsorption in the

⁵⁹ with Michael D. Dickey (NC State)

context of a variety of surface designs. Those involved substrates featuring polymer brushes 1) with systematically varying polymer brush density and/or molecular weight, 2) amphiphilic copolymer brushes, 3) surface anchored polymer networks. In our work we designed and employed novel chemistries based on silicones and amphiphilic polymeric coatings. Our work on biofouling, particularly that related to marine fouling, has utilized surfaces with topographical corrugations that are based either on buckling instabilities or have been created by photolithography. We have utilized computer simulation to model settlement of adhesive spherical particles (monodisperse as well as polydisperse in size) onto sinusoidally-corrugated substrates. Recent efforts (unpublished) involved optimization of the surface topography by means of genetic algorithm.

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P.K. Schoch, J. Genzer, *Langmuir* **30**, 9407-9417 (2014).

Stability of thin polymer films. One topic we explored in detail involved organization of block copolymers and microgel nanoparticles at polymer surfaces and at interfaces between two immiscible homopolymer laminates.⁶⁰ We were the first to report that in-plane organization of the interfacial modifiers led to rich phase behavior that altered the film destabilization from nucleation & growth (NG) to spinodal-like dewetting and back to NG as the concentration of the interfacial modifier increased. We also explored the stabilization of immiscible polymer/polymer interfaces by using mixtures of two block copolymers featuring complementary chemical composition of the two blocks. Our studies revealed a very rich phase behavior, stabilization/destabilization, which was governed by the interplay between the lengths of the blocks of the two copolymers and the concentration of the two copolymers in the copolymer mixture.⁶¹ We demonstrated that microgel particles embedded inside polymer melts can segregate to the interface by entropically-driven autophobicity and either roughened the interface (in case of polymer/polymer interfaces) or remained segregated just below the flat sub-surface structure of the film (in case of polymer/air surface). We documented that the magnitude of the surface/interfacial tension dictated which of the two phenomena took place. We capitalized on this finding to demonstrate that surfaces of thermoplastic polymers can be patterned reversibly at nanoscale on the basis of tunability of surface/interfacial tension.

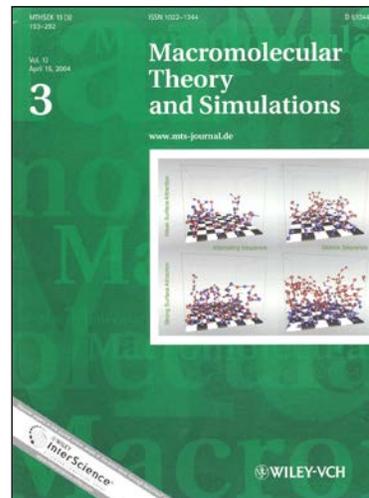
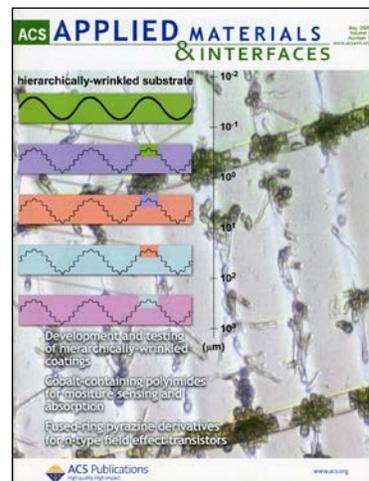
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A.O. Gozen, J. Genzer, R.J. Spontak, *Applied Physics Letters* **101**, 101602 (2012).

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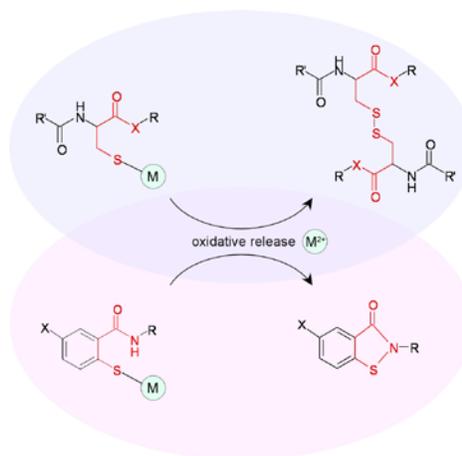


⁶⁰ with Richard J. Spontak (NC State)

⁶¹ with An-Chang Shi (McMaster U., Canada)

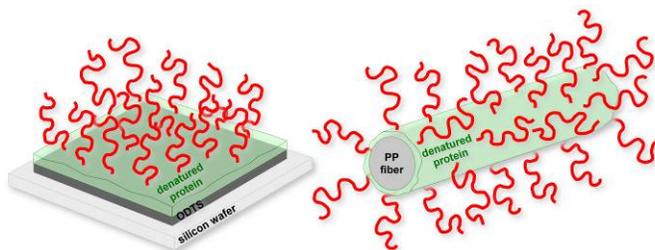
Polymer physics & chemistry at work: Purification of contaminated waters.

In recent years, the Genzer group has devoted substantial efforts to applying its expertise in polymer physics and chemistry and interfacial science to helping solve pressing environmental issues, in particular developing methods leading to environmentally-friendly approaches towards minimizing non-specific bioadsorption and removal of metals/toxins and volatile organic compounds (VOCs) from contaminated waters. Specifically, they have utilized experimental methods and computer simulations to address the combined effects of the surface topography and chemistry on minimizing non-specific biological adsorption. In addition, the group has been engaged actively in developing novel means of removing VOCs from waters by designing effective “sponges” made of polysiloxanes. In collaboration with organic chemists,⁶² Genzer and coworkers have developed new effective methods utilizing organic mimics of metallothioneins, high cysteine containing peptides, for removing heavy metals and toxins from contaminated waters.



I. Park, K. Efimenko, J. Sjöblom, J. Genzer, *Journal of Dispersion Science & Technology* **30**, 318-327 (2009).
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Functionalization of synthetic fibers. One of the outstanding issues facing today’s textile engineering involves tailoring the surfaces of synthetic fibers. Because of their great mechanical strength and low cost, polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), and nylons are materials of choice for most synthetic fibers on the market. Due to high chemical resistance, rendering PE and PP fibers hydrophilic is not an easy task. Over the past few decades, methodologies have been developed that offer routes for modifying the surfaces of such fibers, which involve either surface segregation of functionalized additives from the fiber bulk or physical treatment, *e.g.*, corona or plasma modification. While the latter techniques are widely used in industry, these methods are not very reproducible, difficult to control, and fibers exposed to such “harsh” physical treatments often lose some mechanical strength during the modification process. In collaboration with others,^{63,64} we have developed novel methods of modifying the surfaces of PET fibers and have devised novel means of creating functional fibers from PE and PP by controlled adsorption of functional species, including denatured proteins and amphiphilic copolymers. We have further demonstrated the formation of antifouling coatings that resist non-specific bioadsorption. Work is currently underway that aims at forming low-friction fiber surfaces as well as fiber mats, which feature coatings that are capable of capturing targeted biological moieties (*e.g.*, toxins, viruses).



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A.E. Özçam, K. Efimenko, R.J. Spontak, D.A. Fischer, J. Genzer, *ACS Applied Materials & Interfaces* **8**, 5694-5705 (2016).

⁶² with Jiri Srogl (NC State)

⁶³ with Orlando J. Rojas (NC State/Aalto University, Finland)

⁶⁴ with Behnam Pourdeyhimi (NC State)