The Photopolymer Science and Technology Award

The Photopolymer Science and Technology Award No. 202200, the Best Paper Award 2020, was presented to Kevin Wylie, Yuta Nabae, and Teruaki Hayakawa (Department of Materials Science and Technology, Tokyo Institute of Technology) for their outstanding contribution published in Journal of Photopolymer Science and Technology, **32**, (2019) 395-400, entitled “Altering the Self-Assembly of Poly(styrene-*block*-methyl methacrylate) by Introduction of Strongly Dissimilar Molecules at the Block Interface”.

Kevin Wylie

Kevin Wylie is a third-year doctoral student in the Hayakawa group of the Department of Materials Science and Engineering, School of Materials and Chemical Technology at the Tokyo Institute of Technology. He received B.Eng (2014) and M.Eng (2016) degrees in chemical engineering from McGill University in Montreal, Canada under the supervision of Prof. Milan Maric. His research interests include block copolymer self-assembly, polymer simulation, and block copolymer lithography with a focus on studying the effect of post-polymerization functionalization on self-assembly.

Yuta Nabae

Yuta Nabae is an assistant professor in the Department of Materials Science and Engineering, School of Materials and Chemical Technology of the Tokyo Institute of Technology (Tokyo Tech.). He received B.Eng. (2001), M.Eng. (2003) and PhD (2006) degrees from Tokyo Tech., and served as a research fellow at the University of St Andrews in 2006-2008. He joined Tokyo Tech. in 2008 as an assistant professor and started his studies on polymer synthesis. He has a very strong background in physical chemistry including catalysis, electrochemistry and kinetics, and his research interest is being expanded to the synthesis of polymer materials and their application in catalysis and fuel cells. His catalyst prepared from a polyimide precursor is one of the most active platinum-free catalysts in the world. He has received many awards including the Catalysis Society of Japan Award for Young Researchers (2017), Encouragement Award of FCDIC (2018) and Publons Peer Review Awards (2018).

Teruaki Hayakawa

Teruaki Hayakawa is a Professor in the Department of Materials Science and Engineering, School of Materials and Chemical Technology of the Tokyo Institute of Technology. He received B.Sc. (1995), M.S. (1997) and Ph.D. (2000) degrees from Yamagata University with Prof. Mitsuru Ueda for research in the fields of polymer materials science and engineering. During 1997-1998 he was a visiting student with Prof. Christopher K. Ober at Cornell University. In 2000 he joined the National Institute of Advanced Industrial Science and Technology (AIST) as a researcher and moved to the Tokyo Institute of Technology as an assistant professor in 2003, and was promoted to associate professor in 2009 and to full professor in 2017. He has

developed directed self-assembly block copolymer materials, high thermal conducting epoxy materials, and wholly aromatic condensation polymers. He was a chairperson of the research group on Polymers for Microelectronics and Photonics, the Society of Polymer Science, Japan (SPSJ) in 2012-2014. He is currently an executive director of the Society of Polymer Science, Japan. He has received the Award of Encouragement of Research in Polymer Science National Science, the Society of Polymer Science, Japan (SPSJ) 2005, the SPSJ Award for the Outstanding Paper in Polymer Journal 2006 sponsored by ZEON, the SPSJ Hitachi Chemical Award 2010, the SPSJ Wiley Award 2015, the Photopolymer Science and Technology Award, the Best Paper Award 2016, and the Best Poster Award in the 5th DSA Symposium.

As the demand for increasingly smaller pattern sizes used in microchip fabrication continues in accordance with Moore's Law, so-called "bottom-up" approaches are of great interest to overcome the optical limits of the current generation of photolithographic techniques. Block copolymers (BCPs) present a promising way to achieve sub-10 nm patterns using their intrinsic ability to self-assemble into periodic structures with microdomains on the order of 5 nm to 50 nm [1].

Under the appropriate conditions, BCPs will spontaneously self-assemble into various morphologies including lamellae and cylinders which can be used to generate line-and-space (L/S) patterns and dot patterns respectively. This behavior depends primarily on three different experimental variables, the degree of polymerization (N), the volume fractions of each block (f), and the Flory-Huggins interaction parameter (χ). Furthermore, the periodic length (L_0) scales with both χ and N above a critical lower limit of $\chi N = 10.5$ [2]. Poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) is perhaps the most widely studied BCP due to the ease with which perpendicular orientation can be achieved, but is limited to feature sizes of about 10 nm or greater [3]. As a result, recent efforts have mostly been focused on "high- χ " BCP systems which facilitate the decrease in periodic length by decreasing N . However, these high- χ BCPs often have the significant drawback of very dissimilar surface free energies which complicates the perpendicular alignment of the patterns necessary for pattern transfer [4].

As a result, recent efforts by several researchers have focused on modifying PS-*b*-PMMA with the ultimate goal of enhancing its self-assembly capabilities while simultaneously maintaining the ability to achieve perpendicular orientation in thin films [5,6].

Inspired by these results, Prof. Hayakawa and his group have designed a novel triblock copolymer (triBCP) with enhanced self-assembly behavior by introducing a short, reactive middle block to the traditional PS-*b*-PMMA BCP.

In this paper, a poly(styrene-*block*-glycidyl methacrylate-*block*-methyl methacrylate) (PSGM) triBCP was developed which incorporated a small, reactive glycidyl methacrylate (GMA) middle block which could be further tailored by functionalization with thiols. Using this technique, a variety of self-assembled microstructures could be obtained from a single parent polymer.

Using anionic polymerization which allows for precise molecular control, PSGM was synthesized with a number-average (M_n) molecular weight of 21000 g mol⁻¹ and a dispersity (D) of 1.15. Using ¹H NMR analysis, the middle GMA block was found to have a degree of polymerization of just six relative to over 200 for the whole triBCP. Two different thiols with strongly dissimilar functional groups were subsequently introduced to the GMA units via the thiol-epoxy reaction which proceeded quantitatively as determined by ¹H NMR. Morphological analysis of the bulk state was then carried out using films prepared by slow evaporation from chloroform solutions followed by annealing at 180 °C for 24 h followed by analysis by small-angle x-ray scattering (SAXS) and transmission electron microscopy (TEM).

The SAXS spectra obtained show a clear difference between the modified and unmodified triBCPs suggesting that the introduction of the strongly dissimilar functional groups had the desired effect on self-assembly. In the case where 1-thioglycerol was used to introduce hydroxy groups, the lamellar morphology of the original parent triBCP was conserved but with a 25% increase in L_0 to 24.8 nm, indicating a large increase in χ since N

and f remained largely unchanged. Estimation of the increase in the effective χ parameter (χ_{eff}) using the theoretical scaling law of $L_0 \sim \chi_{\text{eff}}^{1/6} N^{2/3}$, the χ_{eff} of the sample was found to have increased by a factor of 5. On the other hand, when a liquid crystalline perfluorinated alkyl chain was introduced, the self-assembled morphology changed dramatically to a complex phase consisting of a double array of tetragonal cylinders with two periodic lengths of 20.4 nm and 14.6 nm as determined by SAXS. In contrast, diblock copolymers are not typically able to self-assemble into periodic tetragonal arrays, so this result is a promising step towards an industrially relevant morphology. Thus, PSGM, with its tunable morphology and periodic length is a promising candidate for the future of block copolymer lithography.

As described above, the authors have demonstrated comprehensive fundamental research on a methodology for preparing a BCP for self-assembled patterns with tunable morphology and periodic length. These interesting research results were presented at the Annual International Conference of Photopolymer Science and Technology in 2019 (ICPST-36) and published in *Journal of Photopolymer Science and Technology* (2019). This paper contributes to the understanding of the fundamental aspects to form self-assembled nanostructures.

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