Supramolecular Polymerization:
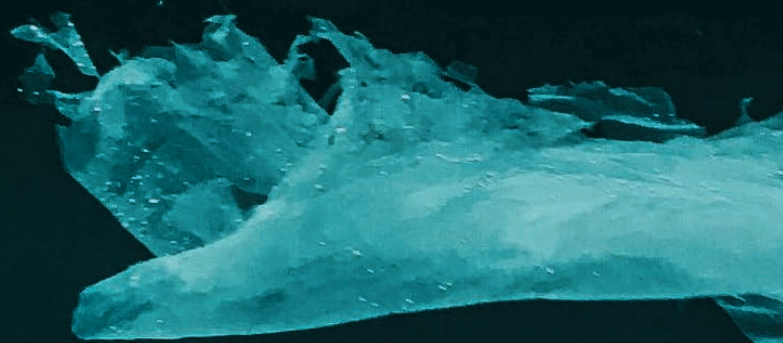# Personal History and Outlook

Takuzo Aida
Takuzo Aida obtained his D.Eng. in Polymer Chemistry from The University of Tokyo in 1984 and began his academic career, working on precision polymer synthesis as an assistant professor at the same university. In 1996, he was promoted to full professor of Chemistry and Biotechnology in the School of Engineering at the University of Tokyo. Since 2013, he has been serving as Deputy Director of the RIKEN Center for Emergent Matter Science. He is recognized as a pioneer in the field of supramolecular polymers and has expanded the basic concept into a diverse range of functional materials such as "bucky gels", "aqua materials", and self-healable polymers. He has been recognized by numerous awards, including the Japan Academy Prize (2018), the Royal Netherlands Academy of Arts and Sciences (2020), and the U. S. National Academy of Engineering (2021).

Kiyoshi Morishita
Kiyoshi Morishita was born and raised in Canada and received his B.A.Sc. in Nanotechnology Engineering from the University of Waterloo, Canada in 2016. Thereafter he moved to Japan to pursue his graduate studies with Professor Takuzo Aida at the University of Tokyo. He obtained his M.Eng. in 2019 and is now a doctoral student, with a Research Fellowship for Young Scientists (DC1) from the Japan Society for the Promotion of Science (JSPS). His research interests include supramolecular, nanoparticle, and polymer chemistry and the functionalization and assembly of proteins. His current project is focused on the supramolecular assembly of the biomolecular machine GroEL into materials with various structures. Outside of the lab he enjoys dragon boat racing, cycling and photography.

2020 was a very special year for polymer science as the 100-year anniversary of its initiation by Staudinger. The past 100 years have been a prosperous time for polymer science, filled with discovery and innovation. Since plastics are lightweight, mechanically robust, and cheap, their use has proliferated, becoming pervasive in all sectors of society and ushering in the so-called heyday of plastics. At the same time however, the plastics and rubbers developed by polymer science have caused catastrophic damage to the environment as long-lasting wastes continue to accumulate in the disposable age. Incinerating these materials generates carbon dioxide, which accelerates global warming, while dumping them into the ocean results in their eventual disintegration into microplastics, small pieces that are consumed and accumulate in the food chain. As of 2015, only 9% of the 6300 million metric tons of plastics produced had been recycled,[1] and unless far-reaching policies are adopted in the next decade to change the social structure that has so far been dependent on disposable polymers, global warming will continue to accelerate and it will certainly be difficult to pass on a livable earth to future generations. Although this crisis is widely acknowledged, society has thus far been unable to give up such convenient and cheap materials. If we fail to shift our economic priorities or invent new materials as alternatives, it will be impossible to escape from this plastic world.

Towards a Sustainable Future

By Takuzo Aida and Kiyoshi Morishita
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WHY ARE TRADITIONAL polymeric materials so pervasive? Because the constituent monomer units that make up polymeric materials are covalently linked, these materials are chemically and mechanically tough, benefiting many applications, but significantly slowing their breakdown. If the constituent monomers were connected by noncovalent bonds, the resulting polymers could be readily depolymerized back to the monomers and recycled. Such polymers are called "supramolecular polymers" and were invented three decades ago. Because of their intrinsically dynamic nature, supramolecular polymers are self-repairable and reconfigurable, meaning that the monomer sequence in a copolymer may in principle be transformable into a different sequence, for example by applying external energy. One can then anticipate that such materials are adaptive, exhibiting intelligent structural transformations in response to changes in the surrounding environment. For supramolecular polymerization, a diverse range of monomers such as biomolecular machines that are not amenable to conventional polymerization can be used (Fig. 2e). Supramolecular polymer materials have long been considered fragile, weak, and unsuitable as structure-forming materials due to the dynamic nature of noncovalent bonds that connect their constituent monomer units.

However, as these concerns are addressed, they may gradually replace traditional plastics to a certain extent in various applications. The reconfigurable and self-repairable nature of supramolecular polymers and their ability to readily be recycled to the monomer state will result in extended product lifespans, reducing energy and raw materials demands in manufacturing, and also reductions in the generation of the pervasive plastic and microplastic wastes that currently harm the environment.

In 1988, 68 years after polymer science was established as a new research field, Aida published, as the first author, a short paper featuring a polymer-like one-dimensional assembly as a prototype of supramolecular polymers, in which the constituent monomer units are connected by a van der Waals interaction (Fig. 1b).[2] Before this work, he had been involved in a project for developing precision covalent polymerization using specially designed metal complexes as polymerization initiators. During the course of this study, he developed "immortal polymerization", a catalytic version of living polymerization, in which polymers with uniform molecular weights are catalytically produced when protonic compounds as chain transfer reagents are present in combination with his special initiator for the living polymerization. In immortal polymerization, polymer chains are formed quantitatively from protonic compounds. Hence, he envisioned the incorporation of a polymer chain of predetermined length into protonic groups in functional compounds and succeeded in the synthesis of an amphiphilic porphyrin with four water-soluble polyether side chains using tetrakis(p-hydroxyphenyl)porphyrin as a protonic compound (Fig. 1a). Due to the water-solubility of the side chains, the amphiphilic compounds with long side chains appeared to be soluble in water. However, those with shorter side chains turned out to stack in a face-to-face manner via the core porphyrin, forming a 1D polymeric assembly. One month after this work was published, Aida noticed that the lid of the flask containing an aqueous solution of this supramolecular polymer had come off. Examining the flask, he was surprised to find the appearance of numerous cracks, which were not actually cracks but rather thin fibers of the supramolecular polymer generated by the evaporation of water from its aqueous solution. Although fascinated by the beauty of the large number of uniform fibers with a metallic luster, he never published this interesting observation or related papers, as he did not have an opportunity to follow up until he became an independent PI. In the meantime, the concept of supramolecular polymers began to take hold. Many early works focused on the assembly of molecules with

complementary H-bonding moieties. One-dimensional H-bonded chains were shown to form in the solid state by the assembly of a dipyridone with non-self-complimentary H-bonding units by Wuest,[3] melamine and cyanuric acid derivatives by Whitesides,[4] and triaminopyrimidine and barbituric acid derivatives by Lehn.[5] Lehn also extended supramolecular polymers to the liquid crystalline state with a triple H-bonded design of monomers that assemble into chiral fiber-like structures.[6] Ghadiri expanded on the scope of monomers by introducing the H-bond directed stacking of cyclic peptides.[7] Percec reported on the columnar supramolecular polymerization of branched oligomers as monomers.[8] Finally, Meijer reported his seminal 1997 paper on a supramolecular polymer consisting of a quadruple hydrogen-bonding interaction[9] and pushed the research field to the forefront of chemistry by disclosing for the first time the viscoelastic properties of supramolecular polymers in solution and under dry conditions.

Aida reinitiated the project on supramolecular polymerization nearly 10 years after his pioneering paper in 1988 and reported the first self-sorting phenomenon in the stereochemical copolymerization of two enantiomers of a chiral monomer in 2002.[10] In 2004, he reported one of his seminal works featuring the nanotubular supramolecular polymerization of an amphiphilic molecular graphene to obtain electronically conductive nanotubes with a very high structural integrity (Fig. 2b).[11] Despite the prevalence of supramolecular polymers with H-bonding interactions, analogous to his original work published in 1988, he employed only a van der Waals interaction to connect the monomer units, and further obtained radial

and linear supramolecular block copolymers in 2006[12] and 2011,[13] respectively.

In 2020, Aida had the opportunity to jointly write a review article with Bert Meijer on supramolecular polymers for a special issue of the Israel Journal of Chemistry in celebration of the 100-year anniversary of polymer science.[14f] The joint review article daringly included the special subtitle, "We've Come Full Circle", as a reference to the historical background of polymer science. Before polymer science was launched as a new field of research in 1920, there had been a long-term debate between two groups, pushing the "macromolecular theory" by Staudinger and the "colloidal theory" by van't Hoff, Fischer, Wieland, et al. After Staudinger experimentally substantiated the existence of long and gigantic molecules in 1920,[15] the "colloid theory" declined. However, it is meaningful to consider the idea of supramolecular polymerization, which started in 1988, to be a modernized version of the "colloid theory" with a flavor of physical organic chemistry.

Over the past 30 years, supramolecular polymerization has grown into a very hot research field,[14] in which our group has enjoyed contributing to its progress and conceptual expansion. Our major achievements include nanotubular supramolecular polymerization (Fig. 2b),[11-13,16,17] living chain-growth supramolecular polymerization (Fig. 2f),[18] supramolecular block copolymerization,[13,19] stereoselective supramolecular polymerization,[16a] and thermally bisignate supramolecular polymerization.[20] These concepts are integral to conventional polymer science and our contributions filled in the critical gap between supramolecular and conventional

polymerizations. Furthermore, we extended the basic concept of supramolecular polymerization to the development of a variety of innovative soft materials such as bucky gels (Fig. 2a),[21] carbon nanotubes noncovalently crosslinked by ionic liquids, and their use in the first metal-free stretchable electronics[22] and battery-driven dry actuators,[23] aquamaterials (Fig. 2c),[24] robust and dynamic materials consisting mostly of water, with small amounts of additives, ATP-responsive nanotubular DDS carriers using the biological machine GroEL as the monomer (Fig. 2e),[25] and stimuli-responsive columnar liquid crystalline materials (Figs. 2d and 2g).[26]

In 2018, our group also reported a major advancement towards mechanically robust materials with self-repairable features.[27a] We showed that low molecular weight ether thiourea oligomers (Fig. 3a), which can quickly and easily self-heal under ambient temperatures by swapping H-bonded thiourea pairs at fractured edges, display high mechanical robustness due to a dense nonlinear array of H-bonds (Fig. 3b). This work swept away the preconceptions that mechanically robust polymers necessarily have ultra-high molecular weights and are unable to self-heal due to the sluggish diffusion of such long polymer chains. We recently reported an updated version of this material in which copolymerization with dicyclohexylmethane thiourea units imparts humidity resistance to the material, expanding the potential range of usage conditions (Figs. 3c and 3d).[27b] Considering the short polymer chains employed in these reports, the next target is to further reduce their molecular weights into a range of ordinary monomers, which may unlock the full potential of supramolecular polymer materials in terms of complete reconfigurability and recyclability.

Lastly, we highlight our new achievement, "solvent-free autocatalytic supramolecular polymerization (SF-ASP)" (Fig. 4),[19] its significance in the field and relevance to the emergent environmental issues caused by plastic waste introduced above. Historically, supramolecular polymerization has been extensively studied in solution, with its mechanical interpretations being greatly elaborated in the last decade. Nevertheless, much work remains when considering the practical applications of supramolecular polymers. One common concern is that the structure of a supramolecular polymer in solution is not guaranteed to be the same as that in the dry state. This concern would be avoided if supramolecular polymers were synthesized under solvent-free conditions. Note also that solvent-free chemical manufacturing is an awaited green technology for the realization of a sustainable society, because of its reductions in raw materials usage, pollution and CO_2 emission. However, there exists a preconception that supramolecular polymerization under solvent-free conditions may proceed heterogeneously,
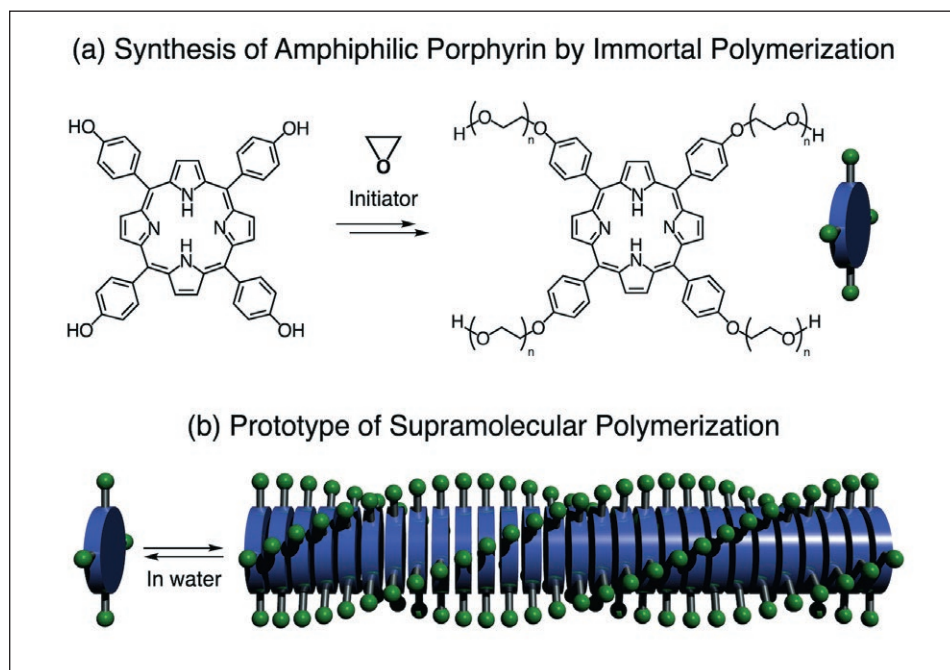
Figure 1. (a) Synthetic scheme for the synthesis of an amphiphilic porphyrin with PEG side chains of well-defined chain lengths. **(b)** 1D polymeric assembly of an amphiphilic porphyrin in water as a prototype of supramolecular polymerization.[2]

resulting in polymeric assemblies of poor structural integrity. Our new finding of SF-ASP casts aside this preconception and features two unexpected advantages, that under solvent-free conditions, the monomer is produced in an autocatalytic manner from its precursor and that polymerization occurs in a living manner without any inhibition to afford block copolymers.

We serendipitously found the basic principle of SF-ASP while investigating the ferroelectric nature of H-bonding phthalonitrile derivatives (PN_{C4}). Upon heating a powdery sample of PN_{C4} sandwiched between glass plates, we noticed that, approximately 4 h after heating at 160°C, numerous thin, green-colored fibers composed of the corresponding phthalocyanine (PC_{C4}) (Fig. 4b) began to appear and rapidly elongate (Fig. 4c). After 24 h, the reaction mixture no longer included the precursor PN_{C4} and we obtained analytically pure PC_{C4}
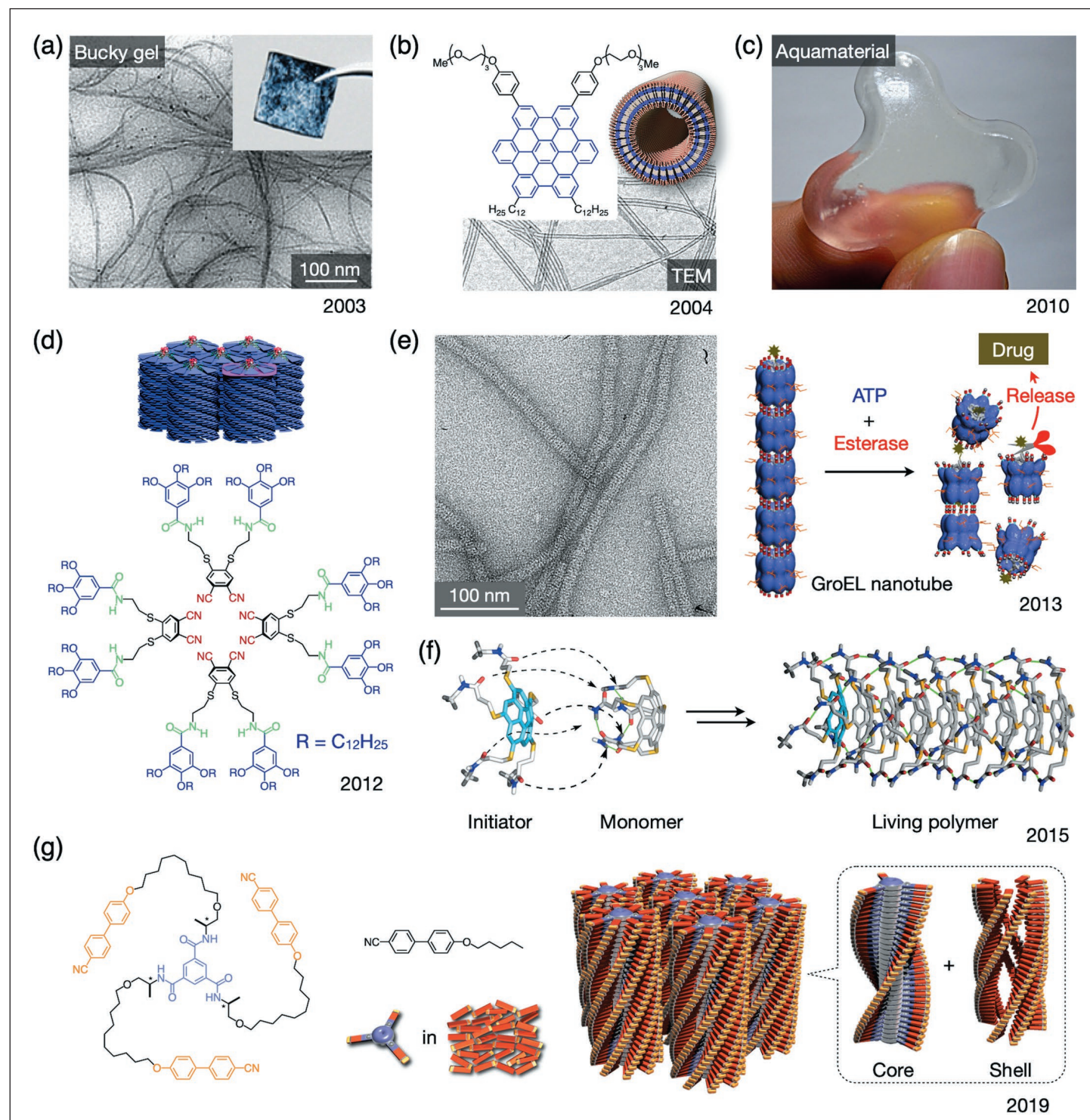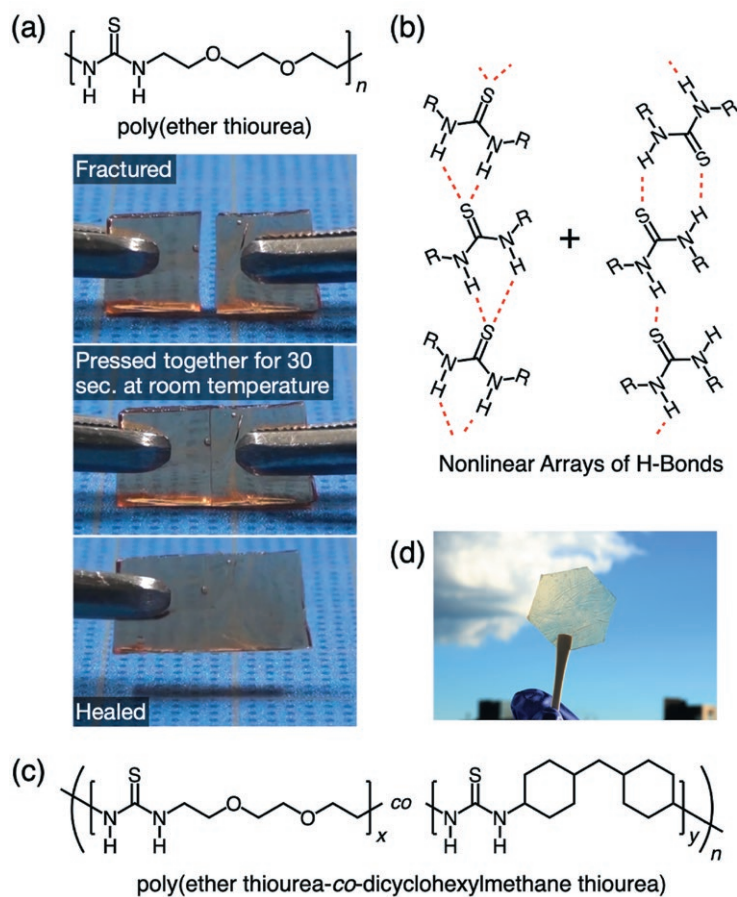

Figure 2. Major achievements in supramolecular polymerization and related materials. (a) Bucky gels, materials made from the dispersion of carbon nanotubes in ionic liquid – adapted from Science.[21a] (b) Nanotubular supramolecular polymerization – adapted from Science.[11] (c) Aquamaterials, mechanically robust materials made from water with a small amounts of additives.[24] (d) Ferroelectric columnar liquid crystal – adapted from Science.[26a] (e) Nanotube made by the chaperonin protein GroEL and its use as an ATP-responsive drug delivery system – adapted from Nature Chemistry.[25] (f) Living chain growth (ring opening) supramolecular polymerization – adapted from Science.[18] (g) Supramolecular polymerization in mesogenic media affording a stimuli responsive core-shell columnar liquid crystal – adapted from Science.[26b]

Figure 3 (left): Seal-healable and mechanically robust polymers. (a) Chemical structure and demonstration of the quick self-healing of poly(ether thiourea) at ambient temperatures.[27a] (b) Nonlinear H-bonding arrays ensure the mechanical robustness of the polymer. (c) Chemical structure of the humidity resistant, self-healable, and mechanically robust poly(ether thiourea-co-dicyclohexylmethane thiourea).[27b] (d) Image of the material shown in (c).

in an exceptionally high yield of 83% by simply washing the reaction mixture with methanol. This value far exceeds the 20 to 25% yield reported for the typical solution-phase synthesis of phthalocyanine derivatives. As illustrated in Fig. 4a, the crystalline fibers preorganize the monomer precursor PN$_{C4}$ on

Figure 4 (below): (a) Schematic representation of solvent-free autocatalytic supramolecular polymerization (SF-ASP).[19] (b) Chemical structures of the phthalonitrile precursor, PN$_{C4}$, and the phthalocyanine monomer, PC$_{C4}$, formed at the cross-sectional ends of the polymer chain. (c) Optical images of PN$_{C4}$, sandwiched between glass plates at 160°C, at different reaction times – adapted from Nature Materials.
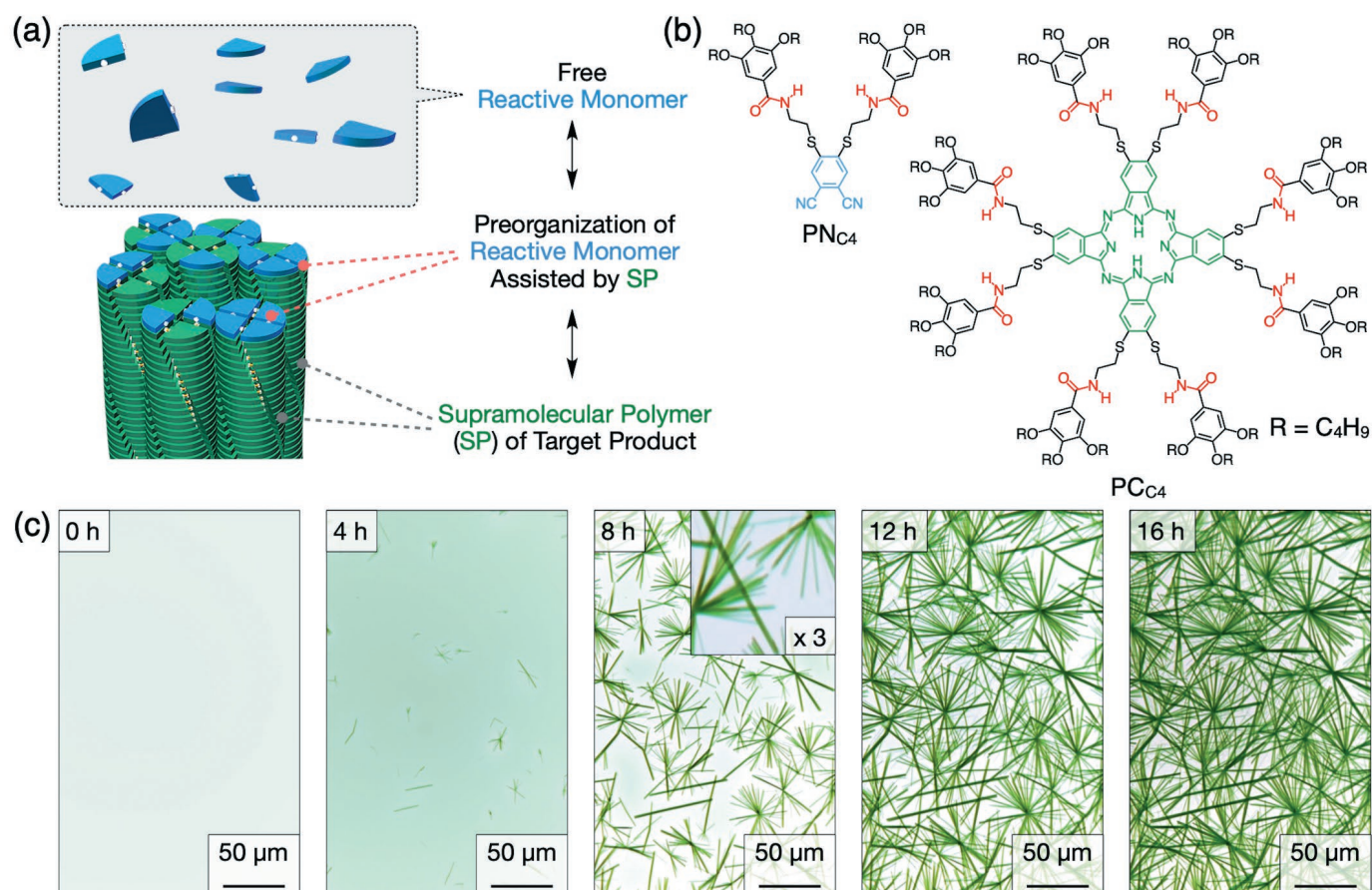
their cross-sectional ends via H-bonding and dipole–dipole interactions, thereby enabling reductive cyclotetramerization of PN_{C4} into PC_{C4}, the monomer for supramolecular polymerization, in an autocatalytic manner. The newly formed PC_{C4} monomer remains at the cross-sectional ends and likewise autocatalyzes the next cycle of reductive cyclotetramerization of PN_{C4} into PC_{C4}. The repetition of these elementary steps results in elongation of the crystalline fibers of supramolecularly polymerized PC_{C4}. Terminal coupling of the crystalline fibers, which would lead to a decrease in the total cross-sectional area for autocatalysis, barely took place in SF-ASP, likely due to their very sluggish diffusion in the hot melt of PN_{C4} under solvent-free conditions. When metal oleates are present, SF-ASP produces metallophthalocyanines as crystalline fibers again in exceptionally high yields, which grow in both directions without terminal coupling until the phthalonitrile precursors are completely consumed. Taking advantage of the living nature of this supramolecular polymerization, multistep SF-ASP without/with metal oleates results in the precision synthesis of ABA and ABCBA types of multi-block supramolecular copolymers. The finding of all of these qualities of SF-ASP that occur only under environmentally friendly solvent-free conditions was beyond our expectations. This demonstrates the significant potential of supramolecular polymerization to bring about change in chemical manufacturing processes and in the utilization of polymeric materials for the realization of a sustainable society. We hope that this report will encourage polymer chemists to focus much needed attention on the solid-state properties of supramolecular polymers.

Certainly, to have a chance at finding widespread practical use and replacing traditional polymers, supramolecular polymer materials showing mechanical robustness under a range of usage conditions must be realized. Although dynamicity and mechanical robustness of polymeric materials have been considered mutually exclusive, by an advanced molecular design, one might sweep away this preconception, and make mechanically robust polymers that are recyclable or structurally reorganizable at the monomer level under particular conditions. We envision a world in which society overcomes its chronic dependency on traditional plastics, through the gradual adoption of supramolecular polymers and other green materials. The intrinsically reversible nature of noncovalent bonds affords supramolecular polymers the potential for self-healing, reconfigurability and complete recycling, enabling materials whose lifespan can be extended and whose properties can be enhanced in subsequent life cycles. ◆

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