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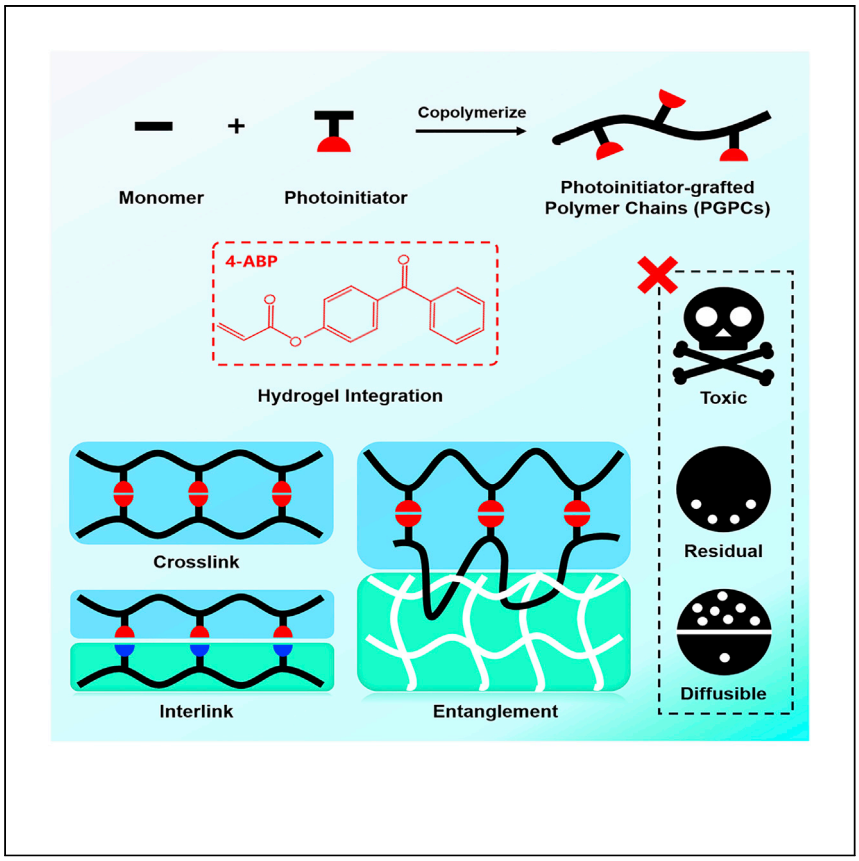

In this work, Yin et al. report a method for hydrogel manufacturing. The proposed photoinitiator-grafted polymer chains (PGPCs) break the concurrency of polymerization, crosslink, and interlink, which enables the integration of hydrogels with both permeable and impermeable materials.

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Highlights

Photoinitiator-grafted polymer chains (PGPCs) are used for hydrogel integration

PGPCs are monomer-free, cure-on-demand, and have a long shelf life

Topological lithography of hydrogel is demonstrated for the first time

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Photoinitiator-grafted polymer chains for integrating hydrogels with various materials

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SUMMARY

Hydrogels are commonly integrated with other materials. In the one-pot synthesis of a hydrogel coating, polymerization, crosslink, and interlink are concurrent. This concurrency, however, is often inapplicable for integrating hydrogels to other materials. For example, a permeable substrate will absorb small molecules in the solution, causing side reactions and even toxicity. Here, we report a method to break the concurrency by using photoinitiator-grafted polymer chains (PGPCs). A type of photoinitiator is copolymerized with various monomers. The PGPCs are uncrosslinked during synthesis, have long shelf lives in dark storage, and can be applied to a substrate by brush, cast, spin, dip, spray, or print. Under ultraviolet light, the polymer chains crosslink into a network and interlink with the substrate. The cured PGPC hydrogels are characterized by mechanical tests. Furthermore, the PGPCs are demonstrated to adhere wet materials, form hydrophilic coatings on hydrophobic substrates, and pattern functional groups on permeable substrates.

INTRODUCTION

Numerous applications require that hydrogels be integrated with other materials. In tissue engineering and drug delivery, hydrogels often attach to living tissues.[1,2] In minimally invasive surgery, hydrogels form hydrophilic coatings on tubes and guidewires.[3,4] In chemical sensing, hydrogels attach to substrates.[5] In ionotronic devices, ionic hydrogels attach to electronic conductors and dielectrics.[6–10] To resist wear and tear, the hydrogels must be tough and adhere to other materials. In a one-pot synthesis of a hydrogel on a substrate, starting with an aqueous solution of monomers, initiators, and crosslinkers, three processes are concurrent: the monomers link into polymers, the polymers crosslink into a network, and the network interlinks to the substrate. This concurrency is inapplicable for integrating a hydrogel and a permeable material, such as a tissue or another hydrogel. The permeable materials would absorb the monomers, initiators, and crosslinkers, causing side reactions and even toxicity.

This concurrency of polymerization, crosslink, and interlink is broken by the notion *hydrogel paint*.[4] A hydrogel paint divides the labor of hydrogel-substrate integration between two players: the maker and the user. The maker synthesizes a paint as polymer chains, which is monomer-free and has a long shelf life. The user applies the paint to a substrate, cures the paint to crosslink the polymer chains into a network, and interlinks the network to the substrate. This division of labor enables the maker to mass produce a paint with sophistication and the user to apply the paint with convenience. The hydrogel paint demonstrated so far is in the form of silane-grafted polymer chains (SGPCs).[4,11–13] During cure, the silanes condense to crosslink and interlink. The condensation, however, lacks a controllable trigger and struggles to satisfy the dual requirements: long shelf

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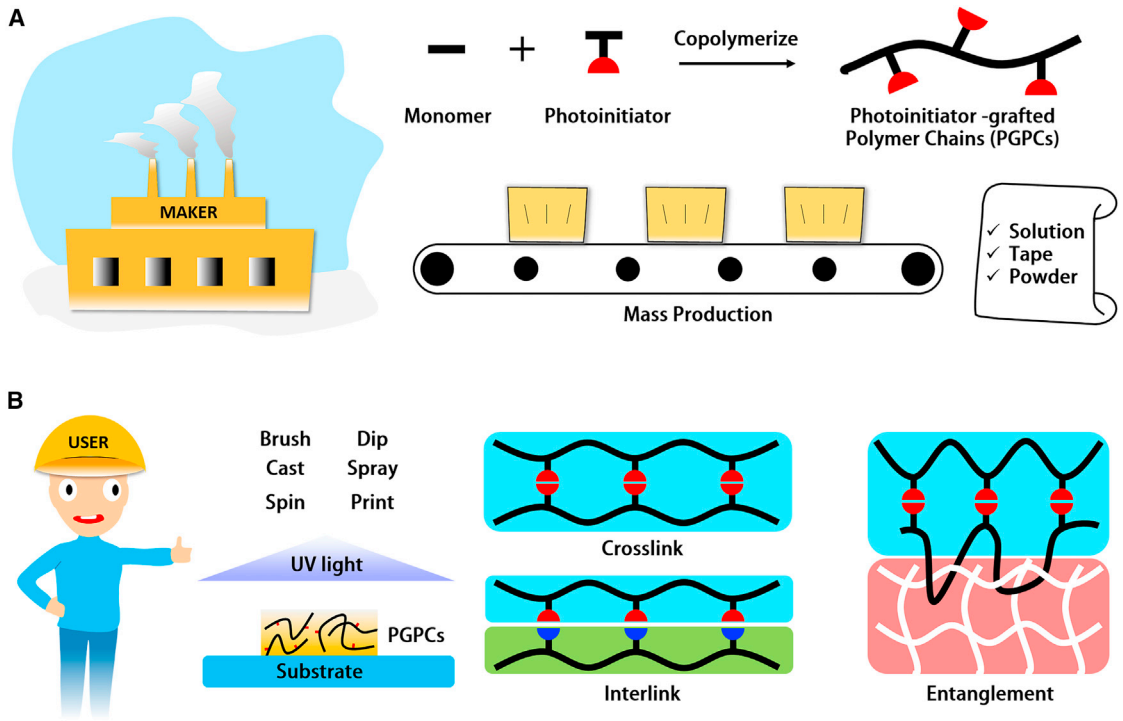

Figure 1. Division of labor between the maker and the user by photoinitiator-grafted polymer chains (PGPCs)

(A) The maker mass produces PGPCs by copolymerizing monomer and photoinitiator, and distributes PGPCs as solutions, tapes, or powders.

(B) The user applies the PGPCs in various operations, and shines an ultraviolet (UV) light to crosslink the polymer chains into a network, interlink the network to a substrate, or entangle the network with a preexisting network.

life and on-demand cure. For example, during dip coat and extrusion print, silanes start to condense in the aqueous solution before coat and print. It is critical to develop hydrogel paints in the form of polymer chains grafted with linkable groups that respond to a well-controlled trigger.

Here, we develop a family of hydrogel paints in the form of photoinitiator-grafted polymer chains (PGPCs). The photoinitiator readily fulfills the dual requirements of long shelf life and on-demand cure. The maker synthesizes PGPCs by copolymerizing monomers and bifunctional photoinitiators into long chains and distributes them as solutions, tapes, or powders (Figure 1A). The user applies the PGPCs to a substrate by brush, dip, cast, spray, spin, and print (Figure 1B). Under an ultraviolet (UV) lamp, the polymer chains crosslink into a hydrogel network, and the network interlinks to the substrate. The interlink can be achieved by either direct bonds between the PGPCs and substrate or topological entanglement of the PGPC network and the substrate network.

To demonstrate this class of hydrogel paint, we prepare PGPCs using 4-benzoylphenyl acrylate (4-ABP) as photoinitiator, acrylamide (AAM) as monomer, ammonium persulfate (APS) as thermal initiator, *N*,*N*,*N*′,*N*′-tetra-methylethylenediamine (TEMED) as accelerator, and water as solvent. The monomers and photoinitiators copolymerize after 30 min at room temperature. A 4-ABP molecule has two functional groups: a vinyl group for polymerization and a BP group for photoresponse (Figure 2A). The bifunctional molecule 4-ABP gives one functional group to the maker and the other functional group to the user. In the "maker's step," we choose the thermal initiator APS, so that 4-ABP is incorporated into the polymer chains

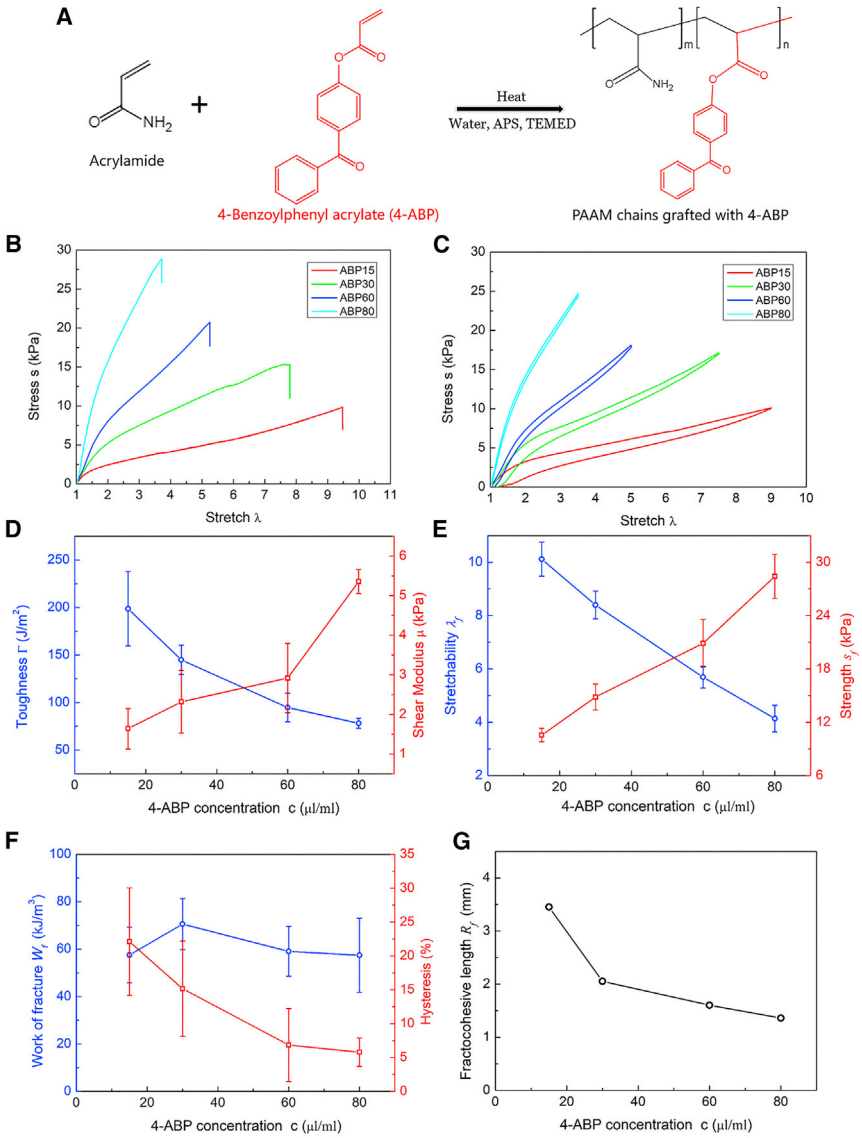

Figure 2. Use mechanical tests to characterize hydrogels fabricated using photoinitiator-grafted polymer chains

(A) Synthesize the PGPCs by copolymerizing monomer acrylamide (AAM) and photoinitiator 4-benzoylphenyl acrylate (4-ABP), in the presence of water, thermal initiator ammonium persulfate (APS), and accelerator *N*,*N*,*N*′,*N*′-tetra-methylethylenediamine (TEMED). PGPCs of 4 concentrations of the photoinitiator are synthesized, concentrations of all of the other ingredients being fixed. Subsequently, the PGPC solutions are cast in molds, and the polymer chains are photocrosslinked into 4 species of polyacrylamide (PAAM) hydrogels.

(B) Stress-stretch curves up to rupture.

(C) Hysteresis curves formed by stretching and releasing the hydrogels.

(D) Toughness and shear modulus.

(E) Stretchability and strength.

(F) Work of fracture and hysteresis.

(G) Fractocohesive length.

Data in (D)–(F) are represented as means ± standard deviations.

through the vinyl group, while the BP group does not participate in polymerization. In the "user's step," the BP groups, triggered by UV light, crosslink the polymer chains into a network and interlink the network to a substrate.

The chemistry of polymer chains grafted with 4-ABP has been studied. For example, 4-ABP has been grafted to methyl acrylate chains by free radical initiation. The reactivity ratio, molar fraction of ABP units, sequence lengths, UV absorption, and so on have been studied using experiments such as ^{1}H nuclear magnetic resonance (NMR) and UV spectrum.[14] 4-ABP has also been grafted to 1-acryloxy-2-ethoxyethane and 4-(*N,N*-dimethylamino) styrene to synthesize macromolecules. The photoinitiation efficiency of these macromolecules has been studied.[15] The bifunctional molecule 4-ABP has been grafted to chains of dissimilar species of polymers, which are then cured together for simultaneous crosslink and interlink.[16–20] Polymer chains grafted with 4-ABP have also been developed as pressure-sensitive adhesives for polyester,[21–25] humidity-sensitive membrane on metals,[26,27] and matrices of composites.[28] In existing applications, the substrates are impermeable.

In our method, 4-ABP serves as both initiator and crosslinker. During UV irradiation, the BP groups are first excited into singlet states, which are then changed to the lowest triplet states.[29] The BP groups in triplet states can abstract aliphatic hydrogens.[30–32] The hydrogen abstraction process forms BP ketyl radicals and on-chain polymer radicals. Free radicals readily recombine to generate a new carbon-carbon bond,[33–35] resulting in crosslinks in the hydrogel and interlinks at the joining interface.

We characterize cured PGPC hydrogels using mechanical tests. We use the PGPCs to adhere permeable substrates, form hydrophilic coatings on hydrophobic substrates, and pattern functional groups on permeable substrates.

RESULTS AND DISCUSSION

Mechanical properties of PGPC hydrogels

To ascertain the formation of a network, we characterize hydrogels cured from PGPCs by mechanical tests (Figures 2B–2G). The PGPC solutions are poured into acrylic molds and cured under a UV lamp (see also details in the supplemental experimental procedures). When the UV lamp irradiates on a sample for only 2 h, for example, the surface of the hydrogel is still viscous and not fully cured. The conversion ratio of polymerization and the photoinitiation efficiency of the 4-ABP macromolecules have been investigated before.[15] To ensure that the hydrogel can be fully cured, the sample is irradiated by a UV lamp (15 W 365 nm, UVP XX-15L) for at least 4 h. After curing, the surface of the hydrogel is smooth. We prepare hydrogels of 4 concentrations of 4-ABP, and designate them by "ABP-x," where x indicates the number of microliters of 0.25 mol L^{-1} 4-ABP in every milliliter of 2 mol L^{-1} AAM. A higher 4-ABP concentration results in more crosslinks. The shear modulus μ is commonly used as an indicator for crosslink density. Here, crosslinks result from pendant 4-ABP in the PGPCs during cure. As the concentration of 4-ABP increases, the shear modulus μ and tensile strength s_f increase, the work of fracture W_f remains nearly constant, while the stretchability λ_f, toughness Γ, and hysteresis decrease. The fractocohesive length, defined by $R_f = \Gamma/W_f$, is the critical crack length, below which ultimate material properties such as work of fracture, stretchability, and strength are independent of crack length.[36,37] As the work of fracture W_f is nearly constant, the fractocohesive length follows the same trend as the toughness, ranging from 3.5 to 1.4 mm.

We compare the properties of the PGPC hydrogels with the crossliner *N,N*′-methylenebis (acrylamide) (MBAA) (Table S1). With comparable concentrations of 4-ABP and MBAA, a hydrogel prepared by PGPCs is softer and tougher than that prepared

using MBAA, suggesting that not all 4-ABP form crosslinks. Nevertheless, PGPC hydrogels have good mechanical properties.

Wet adhesion

We use PGPCs to adhere wet materials. Wet adhesion has undergone intense development in recent years. Demonstrated methods invoke covalent bonds,[38,39] noncovalent bonds,[40,41] and topological entanglements.[42–47] Existing methods of wet adhesion either require some small molecules or leave crosslink and interlink not well controlled. By contrast, the PGPCs contain no small molecules, and UV light is a well-controlled trigger.

We prepare two polyacrylamide (PAAM) hydrogel adherends using the MBAA crosslinker. When preparing PGPCs, we vary the content of 4-ABP from 15 to 80 μL in a 1-mL precursor solution. We spread the PGPC solution on one PAAM hydrogel, cover it with the other PAAM hydrogel, and cure the laminate under a UV lamp (see also details in the supplemental experimental procedures). The thickness of the PGPC adhesive is on the order of $h \sim 100$ μm. PGPCs can diffuse into the crosslinked networks. After cure, topological entanglement is expected. According to the Rouse model,[48] the diffusivity of a chain in water is $D = kT/(n\eta b)$, where kT is the temperature in the unit of energy, η is the viscosity of water, b is the size of the repeating unit of the chain, and n is the number of the repeating units. Taking representative values for $kT = 10^{-21}$ J, $\eta = 10^{-3}$ Pa s, $b = 10^{-9}$ m, and $n = 10^3$ (estimated from the modulus), we derive that D_{chain} is $\sim 10^{-12}$ m^2 s^{-1}, which is much smaller than that of small monomers ($\sim 10^{-10}$ m^2 s^{-1}).[49] The time needed for the hydrogel chains to diffuse away is $t \sim h^2/D \sim$ hours, which is comparable with its curing time. During cure, the diffusivity of the PGPCs may decrease due to the formation of crosslinks and interlinks. As a result, the diffusion length should be smaller than that estimated from $h \sim \sqrt{D_{chain}t}$. The PGPC adhesive does not require any functional groups on the surfaces of the adherends. Adhesion is achieved by covalent bonds between the networks of the adhesive and adherends, as well as by topological entanglements between the networks of the adhesive and adherends.

We measure the adhesion toughness by 90° peel (Figure 3). The adhesion toughness increases with more 4-ABP. By contrast, the toughness of the PGPC hydrogel decreases with the 4-ABP concentration (Figure 2D). Also, the adhesion toughness can be higher than the toughness of adherends, although the crack propagates along the interface. This can be explained as follows. With higher 4-ABP concentrations, the number of interlinks per unit area increases. During peel, both the adhesive and adherends are highly stretched. Upon rupture, elastic energy stored in the adherends is also dissipated, which is called elastic dissipater.[50] The adhesion toughness here is several hundred J m^{-2}. By comparison, adhesion due to adsorption in silica nanoparticles is on the order of 10 J m^{-2}.[40] In the presence of covalent interlink, adhesion toughness on the order of 10^3 J m^{-2} can be readily achieved by introducing dissipation to the adherends.[38,51]

Hydrophilic coatings

We use PGPCs to form hydrophilic coatings on hydrophobic substrates. A hydrogel coating combines the hydrophilicity of the coating and the strength of a substrate. Applications include drug delivery,[52] implants,[53,54] and anti-fouling.[31,32,55] These users of hydrogels can benefit from monomer-free paints of long shelf lives.

We use a PGPC solution to coat a hydrophobic elastomer in the following steps (Figure 4A, and also see details in the supplemental experimental procedures). (1) Wash

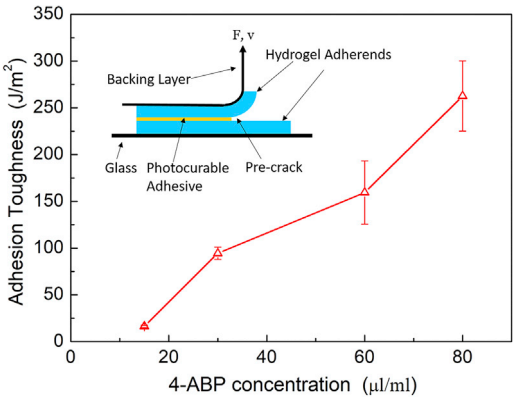

Figure 3. Use a PGPC solution to adhere 2 preexisting hydrogel adherends

The user spreads the PGPC solution on the surfaces of the 2 hydrogel adherends and cures the solution with a UV light. The PGPCs crosslink into a network, in topological entanglement with the preexisting networks of the hydrogel adherends. For each of the 4 species of PGPCs, the adhesion toughness is measured using the 90° peel test.

Data are represented as means ± standard deviations.

an elastomer with isopropyl alcohol (IPA) and water to prepare a clean surface, which is hydrophobic. (2) Plasma treat the elastomer to introduce hydroxyl groups, which turns the surface temporarily hydrophilic. (3) Dip the elastomer into the PGPC solution. (4) Draw the elastomer out at a constant velocity, resulting in an uncured PGPC coating of uniform thickness. (5) Seal the PGPC-coated elastomer in oil to prevent dehydration. (6) Cure the PGPCs under a UV lamp. We coat several types of elastomers, including natural rubber, styrene-butadiene rubber (SBR), silicone, ethylene propylene diene monomer rubber (EPDM), and urethane rubber (Figure S1). When preparing PGPCs, the content of 4-ABP in a 1-mL precursor solution is 30 μL. Upon UV irradiation, the benzoylphenyl groups generate free radicals on the polymer chains and possibly on the substrate surface. When two free radicals meet, a crosslink forms between two PGPCs, or an interlink forms between a PGPCs and the substrate. After cure, contact angles are measured using a homemade setup.[12] The contact angle of water is higher than 55° on a bare substrate, and decreases to <20° on a coated substrate (Figure 4B). A hydrogel coating, thickness ~50 μm, on a SBR substrate is observed under a microscope (Figure 4C). We cast and cure PGPC hydrogels on various substrates, and measure the adhesion toughness by the 90° peel test (Figure 4D). For every elastomer used here, peel takes place on the hydrogel-elastomer interface. The adhesion toughness is lower than the toughness of PGPC hydrogels (Figure S2). The energy of the van der Waals interaction is on the order of $U \sim 10^3$ J mol^{-1}.[56,57] The diameter of a molecule is on the order of $d \sim 10^{-10}$ m. Consequently, the adhesion toughness due to the van der Waals interaction can be estimated as $\sim U/d^2/N_A \sim 1$ J/m^2, where N_A is Avogadro's number. This value is on the order of the measured adhesion toughness between the hydrogel and the urethane, indicating that weak adhesion is due to physical interaction. By contrast, adhesion on other elastomers is tougher, indicating possible covalent bonds, but still much weaker than the adhesion between hydrogels (Figure 3). Several reasons are possible. First, the PGPC chains cannot diffuse into an elastomer substrate, so that topological adhesion is impossible. Second, an elastomer is much stiffer than a hydrogel, and contributes negligibly to energy dissipation. Third, as we mentioned above, the process of forming crosslinks and interlinks consists of two steps: abstraction of hydrogen atoms and formation of covalent bonds. The 4-ABP may not be able to abstract hydrogen atoms from some species of polymer chains.

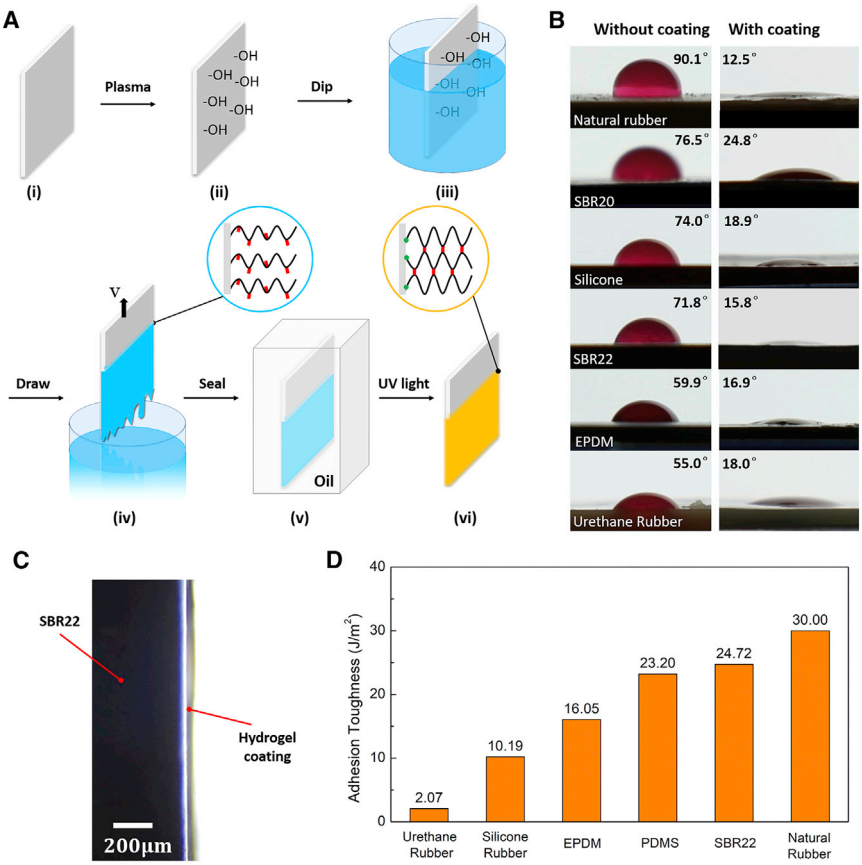

Figure 4. Use a PGPC solution to form hydrophilic coatings on various hydrophobic elastomers

(A) Plasma treat a hydrophobic elastomer to introduce hydroxyl groups on its surface. Dip the substrate into a PGPC solution and then draw it out. Seal the sample in oil to prevent dehydration. Shine a UV light to crosslink the PGPCs into a hydrogel network and interlink the network to the elastomer.

(B) Contact angles of drops of water on bare elastomers and on hydrogel-coated elastomers.

(C) A photograph of a hydrogel-coated elastomer.

(D) Adhesion toughness of hydrogels cast and cured on various plasma-treated elastomers.

See also Figure S1 for the molecular structures of various substrates and Figure S2 for the toughness of the hydrogel.

Hence, covalent bonds cannot form in these cases. Fourth, the adhesion may partially originate from other non-covalent interactions such as hydrogen bonds and hydrophobic bonds. We did not study the details here. Incidentally, an elastomer can always be functionalized, for example, by using silanes to anchor vinyl groups. The functionalized elastomer will covalently bond with PGPCs upon UV irradiation.

Topological lithography

We use PGPCs to pattern a functional group X on a hydrogel substrate (Figure 5). Patterns of functional groups often exist on surfaces in nature. For example, cells recognize each other through position-dependent functional groups.[58] Functional groups have also been patterned on impermeable substrates to guide cells.[59] PGPCs enable patterning functional groups on permeable substrates. We copolymerize monomer, photoinitiator, and functional group X, and designate the resulting polymer chains by PGPC-X (Figure 5A). We then pattern an aqueous solution

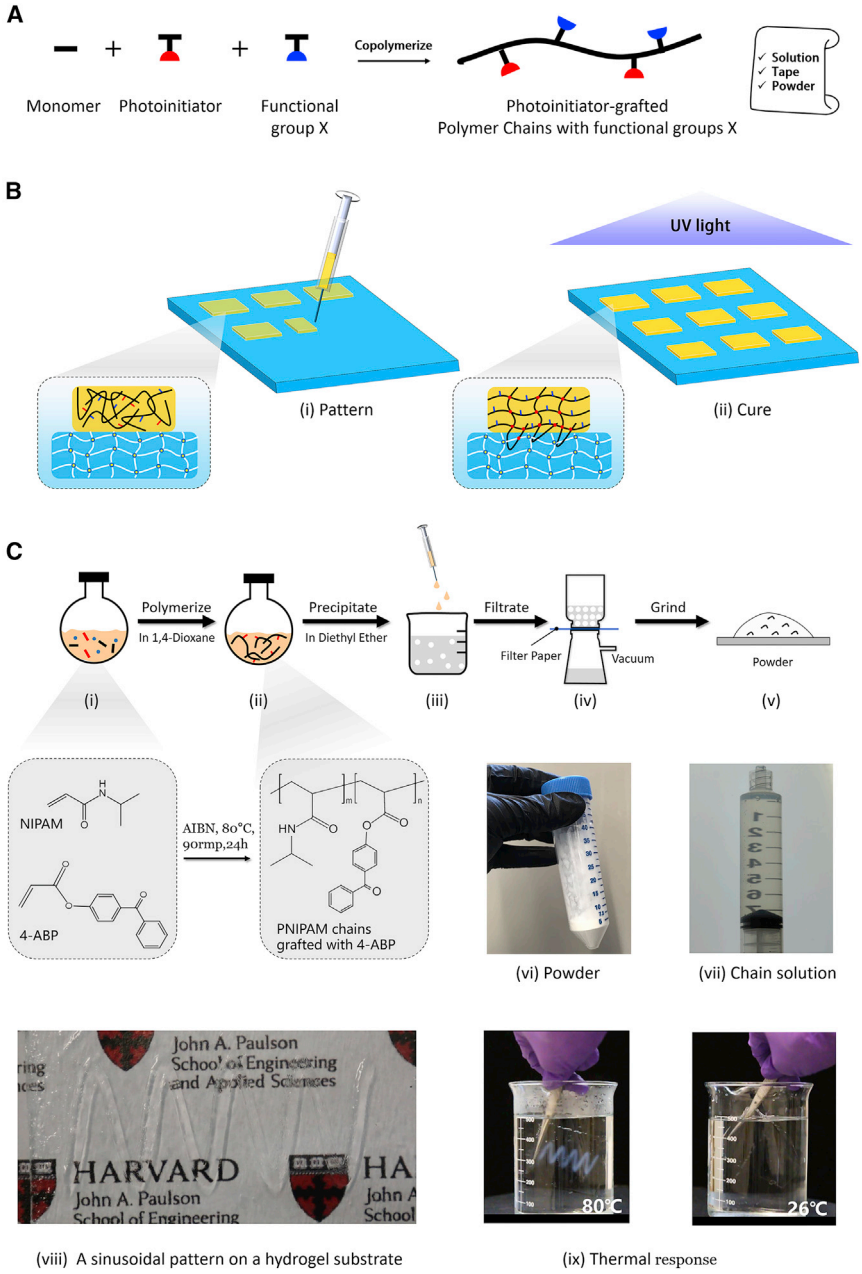

Figure 5. Use a PGPC solution to pattern functional group X on a preexisting hydrogel substrate by topological lithography

(A) The maker mass produces photoinitiator-grafted polymer chains, copolymerized with the functional group X. The product, labeled PGPC-X, is distributed as solutions, tapes, or powders.

(B) The user (i) uses a PGPC-X ink to form a pattern on the surface of preexisting hydrogel and (ii) cures the pattern by shining a UV light to crosslink the polymer chains into a network, in topological entanglement with the network of the preexisting hydrogel.

(C) Steps (i–v) to synthesize PGPC-NIPAM, where NIPAM serves as both the monomer and the functional group, and 4-ABP serves as the photoinitiator. Photographs of (vi) PGPC-NIPAM powder, (vii) PGPC-NIPAM solution, and (viii) a sinusoidal pattern of poly-NIPAM hydrogel cured on the surface of a preexisting polyacrylamide hydrogel. (ix) The pattern is visible in hot water and invisible in cold water.

See also Figures S3 and S4.

of PGPC-X on a hydrogel surface, and shine UV light to crosslink the polymer chains into a network, in topological entanglement with the network of the preexisting hydrogel (Figure 5B). We call this method *topological lithography*.

We demonstrate the method by patterning poly (*N*-isopropylacrylamide) (PNIPAM) on the surface of PAAM hydrogel. Here, NIPAM serves as both the monomer and the functional group, and is copolymerized with 4-ABP (Figure 5C, see also details in supplemental experimental procedures). We prepare PGPC-NIPAM as follows. NIPAM monomers, 4-ABP, initiators, and accelerators are dissolved in 1,4-dioxane followed by heating to form PGPC-NIPAM chains (Figure 5C, i and ii). The weight ratio between 4-ABP and NIPAM powder is 0.02253:1. The solution is then precipitated from diethyl ether (Figure 5C, iii). Powders of PGPC-NIPAM chains can be obtained by vacuum filtration (Figure 5C, iv and v). The powder is re-dissolved in water to obtain a transparent aqueous solution of PGPC-NIPAM (Figure 5C, vi and vii). We prepare a PAAM hydrogel substrate using MBAA crosslinker and place a patterned acrylic spacer on the surface of the substrate. We use a syringe to inject the PGPC solution into the patterned pacer, cover the spacer using a glass, and then cure the solution under UV light. During patterning, rapid diffusion is avoided because the PGPC-NIPAM does not contain any small molecules. During cure, long polymer chains diffuse slowly into the substrate and form a topological entanglement with the substrate. We fix a sinusoidal pattern on the PAAM surface and the resulting hydrogel is transparent (Figure 5C, viii). The pattern appears when the sample is immersed in hot water and disappears when immersed in cold water (Figure 5C, ix). The pattern has good interlinks with the hydrogel substrate and no debonding occurs when the sample is stretched (Figure S3). The resolution of the pattern depends on the rheology of PGPC-X solutions and patterning methods. We have achieved ~100 μm resolution by using a knife edge to form a pattern (Figure S4). In this example, the maker provides powders and the user redissolves the powders into the PGPC solution for topological lithography. The proposed method is applicable to radical-polymerizable monomers, and no other functional groups are required for both substrates and PGPC solutions.

We have demonstrated PGPCs using two model systems, PAAM and PNIPAM hydrogels. However, 4-ABP has also been used in many other polymer systems. For example, 4-ABP has been copolymerized with acrylamide and acrylonitrile for preparing hydrogel films.[18] 4-ABP has also been copolymerized with NIPAM and acrylic acid to prepare hydrogels.[20]

The PGPCs are tunable for various purposes. The viscosity of a PGPC solution can be tuned using additives or solvents. For example, the viscosity of PGPC solutions is tunable over orders of magnitude by changing the water content (Figure S5). The PGPC solutions are shear-thin, making them good candidates for 3-dimensional (3D) printing. The PGPCs have a long shelf life in UV-free storage. Besides powders and solutions, the maker can also distribute PGPC tapes partially crosslinked by thermal crosslinkers, with dangling photoinitiators on the chains. Upon UV irradiation, the photoinitiators form additional crosslinks between the chains, as well as interlinks between the chains and substrates. During cure, the presence of oxygen interferes with hydrogen abstraction by mechanisms such as the quenching of triplet benzophenone and the formation of chain-terminating peroxide molecules.[60] Benzoylphenyl groups act as oxygen scavengers,[61] so that PGPCs of high concentrations of 4-ABP are oxygen tolerant.

In summary, we have described PGPCs for integrating hydrogels with other materials. The bifunctional molecule 4-ABP enables a division of labor between the maker and the user. The maker mass produces PGPCs of long shelf lives, and the user

applies the PGPCs to substrates, monomer-free, rheology-tunable, and cure-on-demand. Besides the applications described above, other applications include fabricating surfaces of hydrogels with patterns of functional groups for cell culture.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Prof. Zhigang Suo (suo@seas.harvard.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All of the data associated with this study are included in the article and supplemental information. Additional information is available from the lead contact upon reasonable request.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.xcrp.2021.100463.

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AUTHOR CONTRIBUTIONS

T.Y. and Z.S. conceived the project. T.Y. and S.R.L. conducted the experiments. T.Y. collected the data, analyzed the results, and drafted the manuscript. T.Y., S.Q., and Z.S. revised the manuscript, and all of the authors commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental information

Photoinitiator-grafted polymer chains for integrating hydrogels with various materials

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Supplemental items

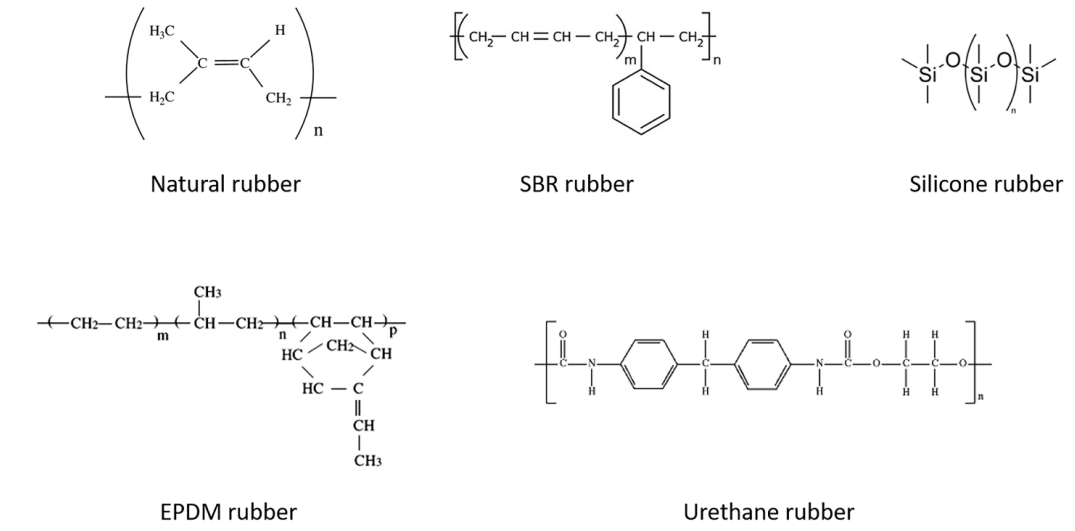

Figure S1. Molecular structures of various substrates used for hydrophilic coating. Related to Figure 4.

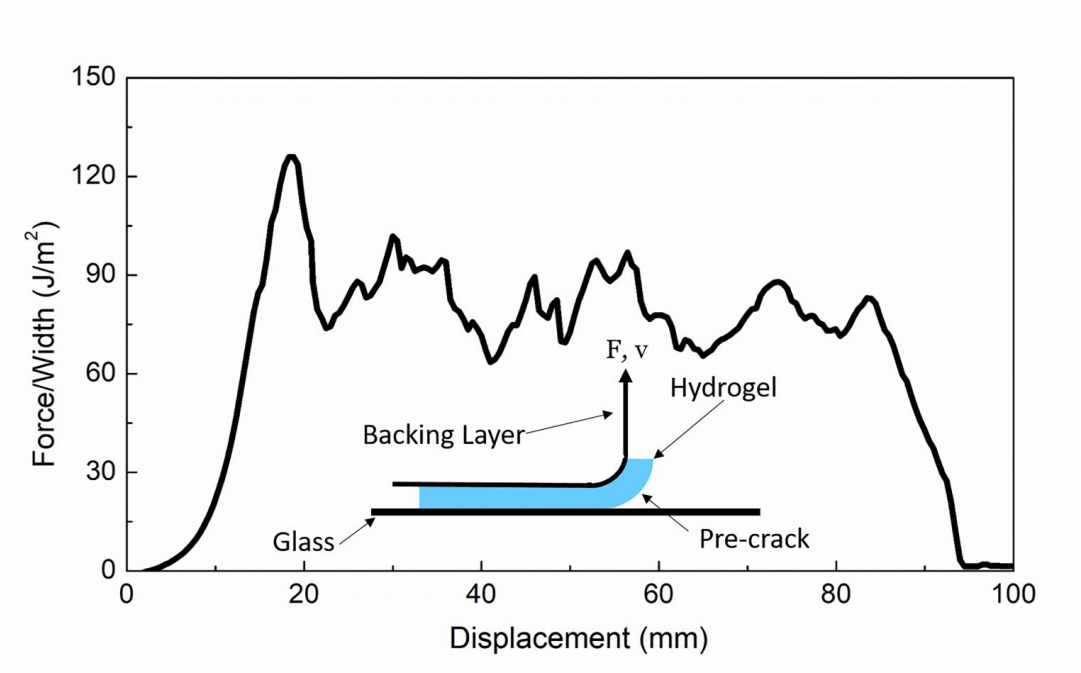

Figure S2. Toughness of hydrogel prepared using the recipe in the hydrophilic coating section. The PAAm solution is poured into an acrylic spacer (2 cm*8 cm*0.3 cm), which is fixed onto the glass substrate and then covered with glass. After curing under UV light, 90° peel tests are performed. Related to Figure 4.

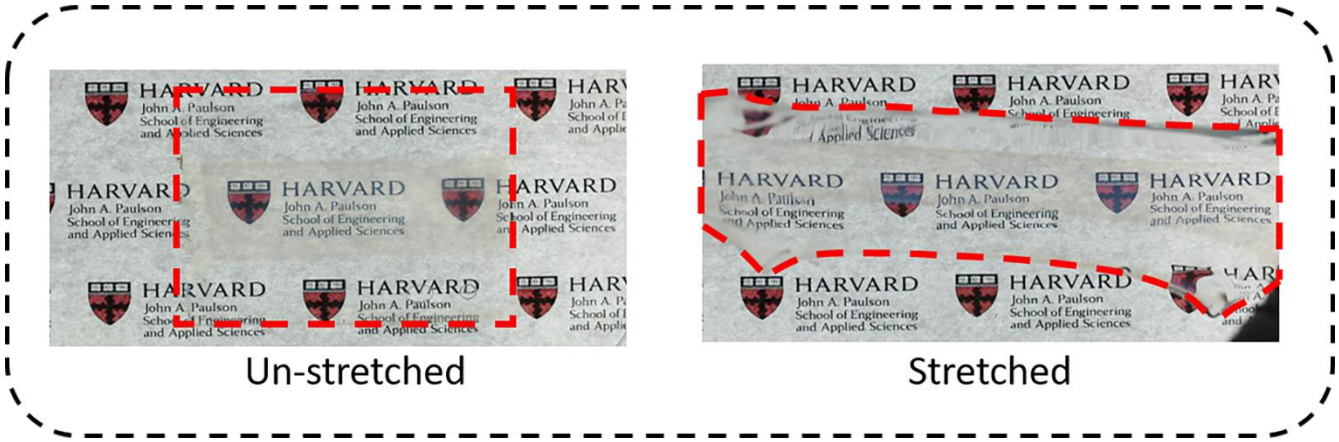

Figure S3. Stretchable pattern. When the patterned substrate is stretched, no debonding occurs. Related to Figure 5.

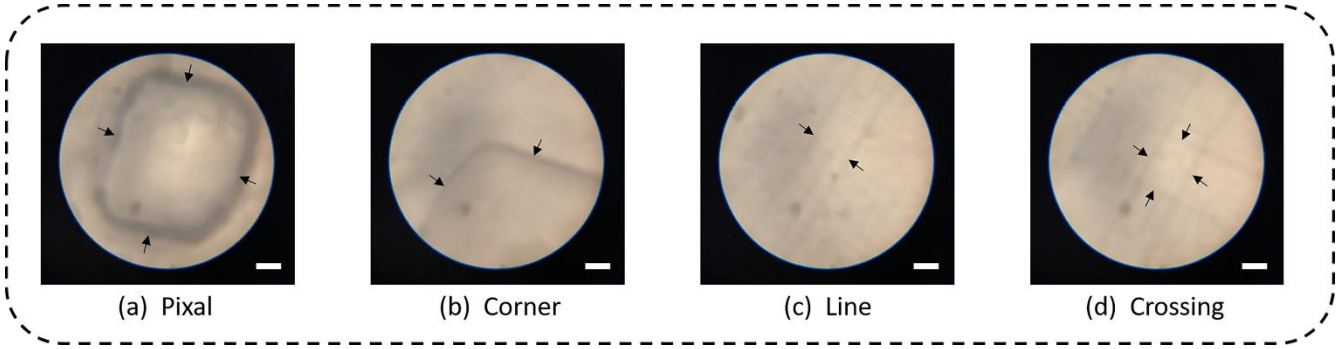

Figure S4. Patterns on a hydrogel. We can pattern a pixel (a), a line (c), and a crossing (d) on a hydrogel substrate. (b) A corner of a rectangular pixel. Scale bars in (a), (c), and (d) are 100μm, and the scale bar in (b) is 200μm. Related to Figure 5.

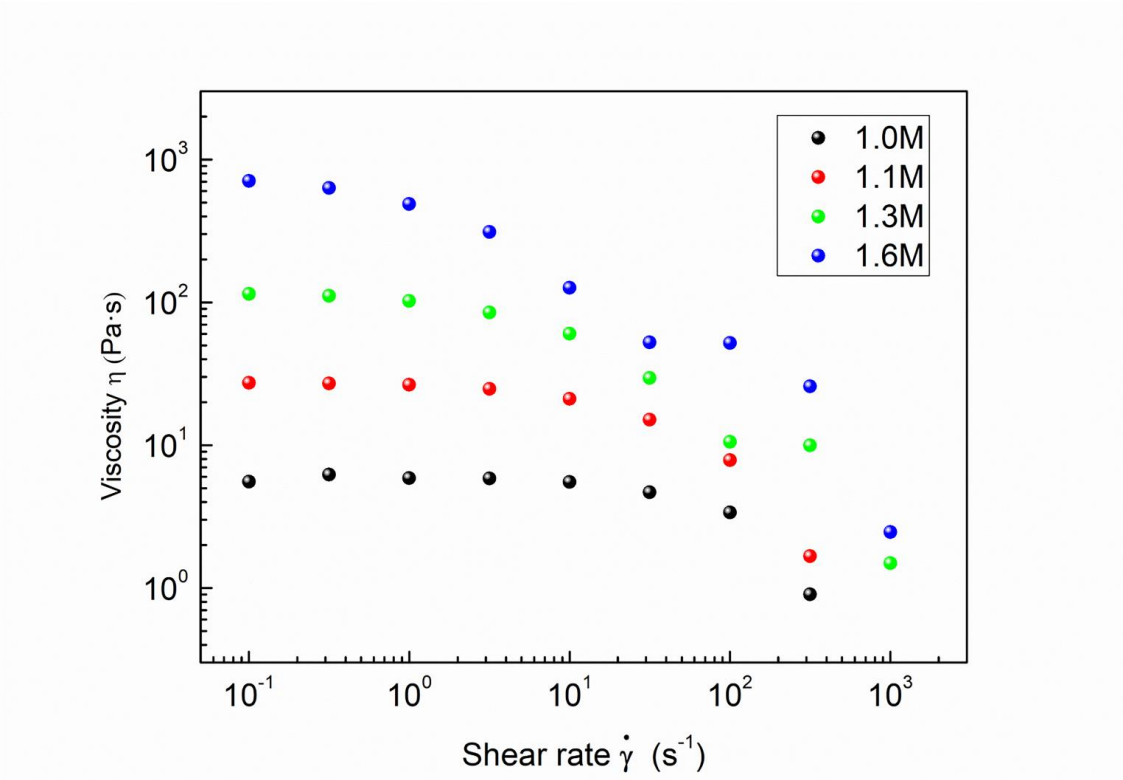

Figure S5. The viscosities of photoinitiator-grafted PAAm solutions of various monomer concentrations. For 1 mL AAm solution, we add 15 µL of 4-ABP (0.25 mol L-1), 40 µL of APS (0.15 mol L-1), and 5 µL of TEMED (diluted 10 times in water). The obtained mixture in a centrifuge tube is vigorously vibrated for 15 s to obtain a uniformly dispersed precursor. After 30 minutes, the precursor is polymerized into a PAAm chain solution. The applied shear rate spans four orders of magnitude and viscosity can be tuned over three orders of magnitude.

Table S1. Mechanical properties of MBAA- and 4-ABP- crosslinked PAAm hydrogels.

Crosslinker	n[a)]	λ_f	s_f (kPa)	µ (kPa)	W_f (kJm^{-3})	Toughness (J m^{-2})	Fractocohesive length (mm)
MBAA	3627	11.1	30.5	4.6	150	163.5	~1
	500	5.4	29.2	5.67	79	60	~0.76
4-ABP	533	10.1	10.5	1.6	57	198.7	~3.45
	100	4.1	20.4	5.4	57	78.2	~1.36

[a)] n is the theoretical value of the number of monomers per chain. To prepare the MBAA-crosslinked PAAm hydrogels, AAm powder is dissolved into DI water to obtain 2 mol L^{-1} AAm solution and MBAA powder is dissolved into DI water to obtain 0.1 mol L^{-1} MBAA solution. For 1 mL of AAm solution, 1.5 µL of Irgacure 2959 (initiator, 0.1 mol L^{-1} in ethanol), and corresponding amount of MBAA (0.1 mol L^{-1}) are added. The obtained mixture is vigorously vibrated for 15 s to obtain a uniformly dispersed precursor. Then the precursor is poured into an acrylic mould and

cures by a UV light for 75 minutes.

Supplemental experimental procedures

Materials: All chemicals listed below are used as purchased without further purification. acrylamide (AAm, Sigma-Aldrich, A8887), N-isopropylacrylamide (NIPAM, Sigma-Aldrich, 415324), 4-Benzoylphenyl acrylate (4-ABP, Ambeed Inc., A398305), N,N′-Methylenebis(acrylamide), (MBAA, Sigma-Aldrich, 146072), Ammonium persulfate (APS, Sigma-Aldrich, 248614), 2,2′-Azobis(2-methylpropionitrile) (AIBN, Sigma-Aldrich, 441090), 2-Hydroxy-4-(2-hydroxyethoxy)−2-methylpropiophenone (Irgacure 2959, 410896), N,N,N′,N′-Tetramethylethylenediamine (TEMED, Sigma-Aldrich, T22500), ethanol (Sigma-Aldrich, 459844), DI water (Poland Spring), 1,4-Dioxane (Sigma-Aldrich, 296309), Diethyl ether (Sigma-Aldrich, 100926), Isopropyl alcohol (IPA, VWR International LLC, BDH11744LP), 3-(trimethoxysilyl) propyl methacrylate (TMSPMA, Sigma-Aldrich, 440159), Acetic acid (Sigma-Aldrich, A6283), PDMS (Dow Corning, Sylgard 182), Urethane rubber (Smooth-On, VytaFlex™30), SBR style 20 (WARCO BILTRITE, 607220901311), natural rubber (WARCO BILTRITE, 0044227137), EPDM (WARCO BILTRITE, 0044222852), silicone (WARCO BILTRITE, 0044225432), abrasion-resistant SBR style 22 (McMaster-Carr, 8634K41) sheets, Silica glass (VWR International LLC, 48382-179).

Preparing polyacrylamide hydrogels crosslinked by 4-ABP. AAm powder is dissolved in DI water to obtain AAm solution of concentration 2 mol L^{-1}. 4-ABP powder is dissolved in pure ethanol to obtain 4-ABP solution of concentration 0.25 mol L^{-1}. APS powder is dissolved in DI water to obtain APS solution of 0.15 mol L^{-1}. Pure TEMED is diluted 10 times with DI water. For 1 mL AAm solution, we add x = 15, 30, 60 or 80 µL of the 4-ABP solution, 40 µL of the APS solution, and 5 µL of the TEMED solution. The obtained mixture is vigorously vibrated for 15 s to obtain a uniformly dispersed precursor. The precursor is poured into an acrylic mould for 30 minutes to obtain polyacrylamide chains grafted with 4-ABP. The sample is irradiated by a UV lamp (15 W 365 nm, UVP XX-15L) for at least 4 h to crosslink the polyacrylamide chains into a network. The obtained hydrogel is denoted by 'abp-x', with x indicating the amount of 4-ABP.

Preparing hydrogels crosslinked by MBAA. MBAA powder is dissolved in DI water to obtain an MBAA solution of concentration 0.1 mol L^{-1}. For 1mL the AAm solution (2 mol L^{-1}), we add 5.5 µL of the MBAA solution (0.1 mol L^{-1}), 20 µL of the APS solution (0.15 mol L^{-1}), and 5 µL of the TEMED solution. The obtained mixture is vigorously vibrated for 15 s to obtain a uniformly dispersed precursor. The precursor is poured into acrylic moulds and waits for 30 minutes to obtain an MBAA-crosslinked hydrogel.

Preparing photocurable adhesive. The polyacrylamide chains grafted with 4-ABP, are prepared by the method described above. We spread 1 mL of the PGPC solution (adhesive) onto a piece of MBAA-crosslinked hydrogel (adherend) and then cover it with another piece of MBAA-crosslinked hydrogel (adherend). The size of each adherend is 2.5 cm*6 cm*0.3 cm. The thickness of adhesive is estimated to be 66 µm. Irradiated under the UV lamp, the PGPC chains crosslink into a network, and interlink with the adherends by direct bonds or topological entanglement. The adhesion toughness is measured by 90° peel.

Preparing hydrogel coating. Various hydrophobic elastomer substrates are first washed by IPA and DI water. The samples are then treated with plasma for 20 s with power 30 W (Gala Instrumente, PlasmaPrep2) to introduce hydroxyl groups on the surfaces to make them temporarily hydrophilic. We dissolve AAm powder in DI water to prepare an AAm solution of concentration 1.33 mol L^{-1}. For 1 mL AAm solution, we add 30 µL of 4-ABP, 40 µL of APS, and 5 µL of TEMED. The obtained mixture in a centrifuge tube is vigorously vibrated for 15 s to obtain a uniformly dispersed precursor. The mixture is then kept at room temperature for 30 minutes to form a PGPC solution. An elastomer substrate is dipped into the PGPC solution and then drawn out vertically by a tensile machine (Instron 5966) at a fixed velocity v=15 mm min^{-1}. The obtained sample is sealed in an oil tube to prevent dehydration, and is then irradiated by UV light. Contact angles are measured by a home-made set-up at ambient temperature. 10 µL of dye-colored DI water is dripped onto the substrate. A digital camera (Canon, EOS 70D) is used to take a side-view photo. Contact angles are obtained from the photos. To measure adhesion toughness between a hydrogel and an elastomer, a PGPC solution is poured into an acrylic spacer (2 cm*8 cm*0.3 cm), which is fixed on the elastomer and then covered with glass. After irradiation under UV light, the adhesion toughness is measured by 90° peel.

Topological lithography. We fabricate a PNIPAM pattern on a PAAm substrate. Since 4-ABP has low solubility in water and PNIPAM chains become hydrophobic once temperature is high during polymerization, we prepare the PGPC-NIPAM solution as follows. 1 g of NIPAM powder, 0.02253 g of 4-ABP, and 0.7265 g of AIBN are dissolved in 6 mL of 1,4-dioxane. The solution is stirred magnetically at 80°C for 24 h for polymerization. We use

a syringe to inject the PGPC-NIPAM solution as droplets into a beaker of diethyl ether, which is vigorously stirred on a professional magnetic stirrer (VWR International LLC). The PGPC-NIPAM precipitate to form particles of ~1 mm diameter. The suspension is then filtered using vacuum for 24 h for thorough evaporation of the solvent. The dry sediment is hand-grinded into fine white powder using a porcelain herb grinder. We dissolve 1 g of the powder in 5.89 mL of DI water to obtain an aqueous solution of PGPC-NIPAM. We place a patterned acrylic spacer on the surface of a MBAA-crosslinked PAAm hydrogel. We then use a syringe to inject the aqueous solution of PGPC-NIPAM into the acrylic spacer and cover the spacer with a glass. The sample is placed in a plastic bag, and UV-irradiated for 4 h. A PNIPAM hydrogel pattern forms on the surface of the PAAM hydrogel substrate.

Tensile test. We prepare samples of hydrogels, each being 1.5 mm thick, 6 cm long, and 4 cm high, and glue an acrylic gripper on each long edge of the hydrogel using a cyanoacrylate glue (Krazy Glue). After glue, the deformable part of the hydrogel is 1 cm high. The two acrylic grips are pulled at a constant velocity of 10 mm s^{-1} using a tensile machine (Instron 5966). To measure a stress-stretch curve, a sample is loaded monotonically to rupture. The work of fracture W_f is the area under the stress-stretch curve up to fracture. Shear modulus equals one fourth of the initial slope of stress-stretch curve. To measure a hysteresis curve, a sample is loaded near the breaking point and is then unloaded.

90° peel. We measure the toughness of 4-ABP-crosslinked hydrogels as follows. We prepare an aqueous solution of silane by adding 10 µl of acetic acid and 2 mL of TMSPMA in 100 mL of DI water. The solution is vigorously vibrated for 60 s using a Vortex Mixers (VWR International LLC). A glass plate is immersed in the silane solution for 2 h. Silanes hydrolyze into silanol groups, and condensate into siloxane bonds with the hydroxyl groups on the glass surface. Then, the glass is washed with IPA, followed by air drying. Next, we place an acrylic spacer with dimensions 2 cm*8 cm*0.3 cm on the silane-treated glass. We pour hydrogel precursor, which contains AAm monomers, 4-ABP crosslinkers, APS initiators and TEMED accelerators, into the spacer and cover it with an untreated clean glass. The precursor is left at room temperature for 30 minutes to polymerize. During this period, hydrogel chains are covalently bonded onto the bottom glass. The sample is cured under UV light and demoulded. A flexible but inextensible thin polyester backing layer is glued using the Krazy Glue on the top surface of the hydrogel and a precut is introduced into one end of the hydrogel using a razor blade. Finally, the sample is loaded by a tensile machine (Instron 5966). As the machine pulls the backing layer vertically, a motor moves the substrate horizontally at the same velocity, so that the peel angle is kept at 90°. The peel velocity v is fixed at $h/v = 0.6$ s, where h is the sample thickness.

To measure the adhesion toughness of hydrogel/hydrogel or hydrogel/elastomer, we introduce a precut at one end of the bonding interface and glue the sample onto a glass substrate using Krazy Glue. Backing layer is glued on the top surface and the sample is loaded. The force-displacement curve is recorded. Bulk and adhesion toughnesses are calculated using the plateau force divided by the sample width.

Rheology test. Rheology of PGPCs prepared by various water concentrations are tested using a rheometer (DHR-3, TA Instruments) with a plate indenter of diameter 20 mm at room temperature. For each test, the PGPC solution is extruded onto the rheometer platform. During testing, the gap between the indenter and testing plate is set to be 20 µm. The exceeded primer is carefully removed. Viscosities are measured against angular velocity.