

Inherently UV Photodegradable Poly(methacrylate) Gels

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Organogels (hydrophobic polymer gels) are soft materials based on polymeric networks swollen in organic solvents. They are hydrophobic and possess a high content of solvent and low surface adhesion, rendering them interesting in applications such as encapsulants, drug delivery, actuators, slippery surfaces (self-cleaning, anti-waxing, anti-bacterial), or for oil-water separation. To design functional organogels, strategies to control their shape and surface structure are required. Herein, the inherent UV photodegradability of poly(methacrylate) organogels is reported. No additional photosensitizers are required to efficiently degrade organogels ($d \approx 1$ mm) on the minute scale. A low UV absorbance and a high swelling ability of the solvent infusing the organogel are found to be beneficial for fast photodegradation, which is expected to be transferrable to other gel photochemistry. Organogel arrays, films, and structured organogel surfaces are prepared, and their extraction ability and slippery properties are examined. Films of inherently photodegradable organogels on copper circuit boards serve as the first ever positive gel photoresist. Spatially photodegraded organogel films protect or reveal copper surfaces against an etchant (FeCl_3 aq.).

1. Introduction

Organogels (hydrophobic polymer gels) are 3D networks swollen with organic liquids. These networks can be formed either via self-assembly of low-molecular weight gelators (LMOGs) or via polymerization reactions. Analogue to hydrogels, crosslinking is achieved chemically (covalent bonding,) or physically (cooperative interactions). However, the term organogel is controversial since there is no IUPAC definition, and some prefer to use the term only for non-covalent networks. In the scope of this work, the term organogel includes covalently crosslinked polymers. Applications of organogels include actuators,^[1] anti-biofouling,^[2,3] anti-waxing,^[4] cosmetics,^[5] drug and nutrition carriers,^[6–10] encapsulants,^[11] freeze tolerant elastomers,^[12] oil-water separation,^[13,14] solid edible oils,^[15] and slippery

and self-cleaning surfaces.^[16–19] Control over the structure of organogels is mandatory for their applications or can enhance their functionality. For example, Zhang et al. demonstrated controlled water droplet sliding on a grooved organogel surface.^[20] Moreover, the surface texture of organogels influences their wettability and optical properties.^[21] However, fabrication of structured organogels is not trivial, since established methods for hydrogels cannot be employed readily. For example, the crosslinked polydimethylsiloxane (PDMS) molds utilized in soft-lithography swell in hydrophobic solvents and are thus prone to deformation.^[22–24] If the organogel has thermoreversible properties, micromolding can be used to create a defined structure.^[25] The fabrication of micro- or nano structured organogels can be controlled via supramolecular self-assembly.^[26,27] While this approach does not require templates, it lacks variety and predictability of structures and is restricted to certain starting materials (e.g., LMOGs, block copolymers). The few reports available about photodegradable organogels suffer from long degradation times, require laborious synthesis of photolabile crosslinkers, or are too hydrophilic to serve in the applications mentioned above.^[28–32] There has been no report about organogels that are readily synthesized, contain a large amount of hydrophobic solvent, and degrade fast under UV light. Thus, it is challenging to fabricate structured or patterned organogels. Recently, we reported the inherent photodegradability of poly(meth)acrylate hydrogels and demonstrated their use for biological applications.^[33,34] We hypothesized, that this approach could be extended beyond water infused hydrophilic networks to hydrophobic organogel networks. Since most (meth)acrylate monomers are hydrophobic, the monomer

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pool that can be addressed with our approach is naturally high. Herein, we report for the first time, the inherent photodegradation of poly(methacrylate) organogels under UV light. Organogels were synthesized via free radical polymerization and their chemical composition and swelling properties were investigated. Structured organogels were fabricated via UV light irradiation and the solvent infusing the organogel was identified to be an influential factor for the photodegradation. The inherent photodegradability of poly(methacrylate) organogels reported herein is simple, cheap and was used to create a variety of structured organogels for application as an extractive fluid channel or positive photoresist.

2. Results and Discussion

Organogels were synthesized via free radical polymerization using a 1:1 vol% mixture of *n*-butyl methacrylate (BMA) and lauryl methacrylate (LMA) as monomers and poly(propylene glycol) dimethacrylate (PPGDMA) as crosslinker in 1-nonanol as solvent (Figure 1A,B). The chemical composition and gel-like properties of the prepared organogels were confirmed with rheometry, infrared spectroscopy (IR), and UV-vis spectroscopy (Figures S1–S3, Supporting Information).

When swollen in 1-butanol or 1-nonanol, the organogels showed inherent photodegradation properties under UV light (Figure 1C). Details about the UV lamp (i.e., power, emis-

sion spectrum) are provided in the Supporting Information (Figure S4, Supporting Information). Increasing the UV irradiation time led to an increase in erosion depth (Figure 2A). Thus, the depth of degradation was controllable by the choice of irradiation time. Structured bulk organogels were prepared by exposing cuboid shaped organogels to UV light for 20 min using a photomask and were analyzed with optical profilometry (Figure 2B).

The depth of erosion of a feature after 20 min UV irradiation was determined to be 1.185 ± 0.039 mm (SD, $n = 3$) based on optical profilometry measurements at different positions of the pattern (Figure S5, Supporting Information). Thin-film organogel patterns were analyzed with microscopy (Figure 2C). Round shapes or patterns with feature sizes as small as 100 μm were readily obtained. Organogels were transparent after all steps, i.e., synthesis, swelling, and degradation, indicating chemical homogeneity. The main difference between hydrogels and organogels is the polarity of the polymer network and thus the selection of solvents that can infuse the network. Hydrogels are inherently suitable for UV photochemistries, as water does not absorb significant amounts of UV light.^[35] However, the choice of the solvent was found to be decisive for the photodegradation of organogels. We hypothesized, that this was due to two main factors: (i) the UV absorbance and (ii) swelling capability of the solvent. For a fast photodegradation process, the UV absorbance of the solvent should be low, and it should swell the organogel network strongly. A high UV absorbance of

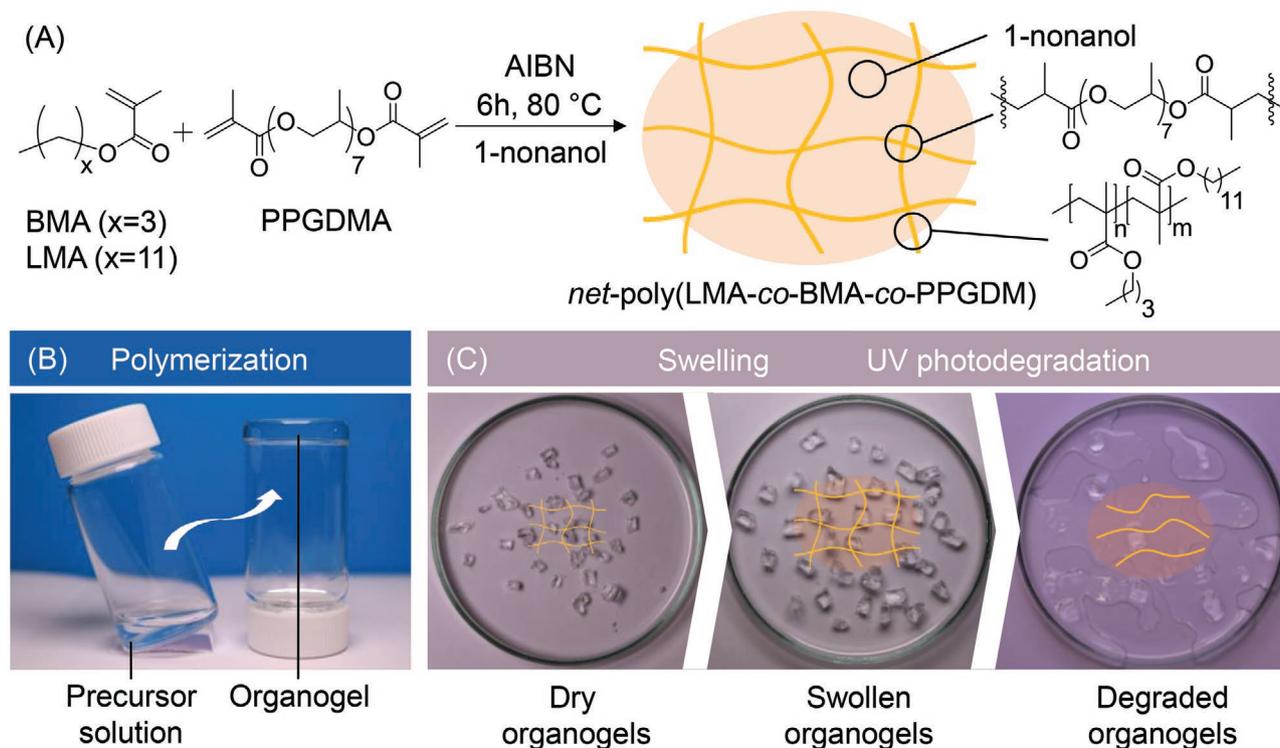


Figure 1. A) Reaction equation for the synthesis of *net*-poly(BMA-co-LMA-co-PPGDMA) organogel from lauryl methacrylate (LMA) and butyl methacrylate (BMA) monomer with poly(propylene glycol) dimethacrylate (PPGDMA) as crosslinker. B) Image of the organogel precursor solution and the as-prepared organogel in a vial. C) Image and schematic molecular structure of organogel pieces without solvent, organogel pieces swollen in 1-nonanol and the swollen organogel pieces after 30 min of UV photodegradation. The diameter of the petri dish is 5 cm.

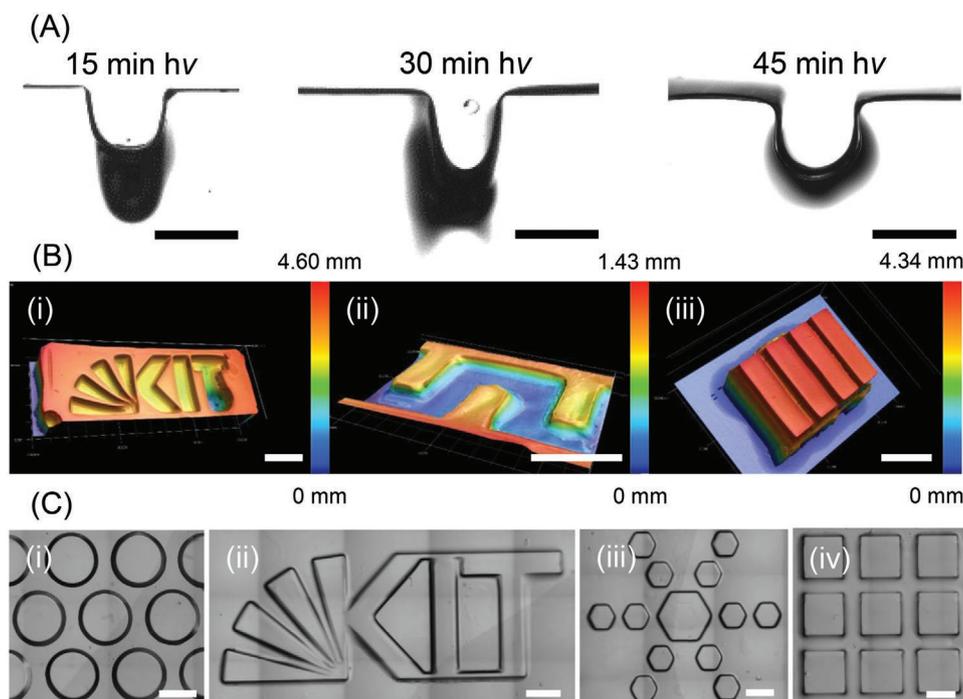


Figure 2. A) Microscopy images of degradation profiles for different UV irradiation times. Scalebars are 1 mm. B) 3D optical profilometry images of patterned bulk organogels such as (i) a geometrical pattern, (ii) a channel and (iii) a stripe pattern. Organogels were sprayed with chalk spray to enable optical profilometry measurements. The height of the organogels is 4 mm, the degradation depth is ≈ 1.2 mm. Scalebars are 10 mm. C) Brightfield microscope images of different patterned organogel films such as (i) an array of circles, (ii) three letters, (iii) an array of hexagons, and (iv) an array of squares. The initial film thickness was 125 μm . Organogel films were exposed to UV light for 10 min using a photomask. Scalebars are 1 mm.

the solvent would reduce the effective light intensity available for the photodegradation, whereas insufficient swelling could cause the gel network to undergo photocrosslinking, due to lower inter-chain distances within the polymer network.^[34] To test our hypothesis, we measured UV-vis spectra of different solvents (Figure S6, Supporting Information) and tested the swelling factor of selected solvents in our organogel networks. The swelling factor was defined as the mass of the swollen organogel (w_s) divided by the dry mass of the polymer network (w_d) (Table 1).

To first test the influence of the swelling on the photodegradation rate, as-prepared organogels were freed from 1-nonanol or swollen in excess 1-nonanol for different times (0, 6, and 48 h) to obtain organogels with a different content of 1-nonanol (0, 60.7, 67.5, and 76.3 wt%, respectively). The organogels were then exposed to UV light for different times and the mass fraction (m_t/m_0), defined as the mass of the organogels after irradiation (m_t) relative to their initial mass (m_0), was determined

Table 1. Properties of solvents investigated for their influence on the photodegradation properties of organogels. Data are given as mean \pm SD ($n = 3$).

Solvent	1-Nonanol	1-Butanol	Toluene	PDMS
Swelling Factor ^{a)}	3.78 ± 0.17	3.48 ± 0.07	15.88 ± 0.37	1.02 ± 0.01
UV Transmission ^{b)} (%)	19	94	< 1	92
Boiling Point (°C)	214	118	111	–

^{a)}Defined as w_s/w_d ; ^{b)}Determined at 250 nm.

(Figure 3A). To ensure comparable results, the exposed surface area of the organogels was kept the same. The rate of photodegradation was found to increase with increasing 1-nonanol content. For example, after 30 min of irradiation 87 wt% of organogels swollen for 0 h (60.7 wt% 1-nonanol) remained, whereas organogels swollen for 48 h (76.3 wt% of 1-nonanol) were fully degraded into a polymer solution, i.e., a liquefied organogel. For dry organogels (0 wt% of 1-nonanol), no loss of mass was detected. GPC measurements of organogels irradiated for different times revealed monomodal molecular weight distributions. The molecular weight averages (M_N , M_W) and the dispersity (D) decreased with increasing irradiation time (Figure S7, Supporting Information). The photodegradation products were separated from 1-nonanol by precipitation in cold methanol and their chemical composition was analyzed with IR, UV-vis, and NMR spectroscopy (Figures S8–S10, Supporting Information). ^1H and ^{13}C NMR spectra of degraded polymers did not differ significantly for different irradiation times and closely resembled those of pure poly(butyl methacrylate) or poly(lauryl methacrylate), whereas UV-vis spectroscopy and IR spectroscopy showed indications of photo-oxidation. To clarify the influence of the UV absorbance and swelling factor of the solvent on the speed of photodegradation, organogels immersed into an excess of toluene, 1-butanol, or PDMS (10 cSt) for 48 h, respectively, were irradiated with UV light for 10 min (Figure 3B). Toluene and PDMS were chosen as model solvents to represent a low transmission but high swelling solvent (toluene) and a high transmission but low swelling solvent (PDMS).

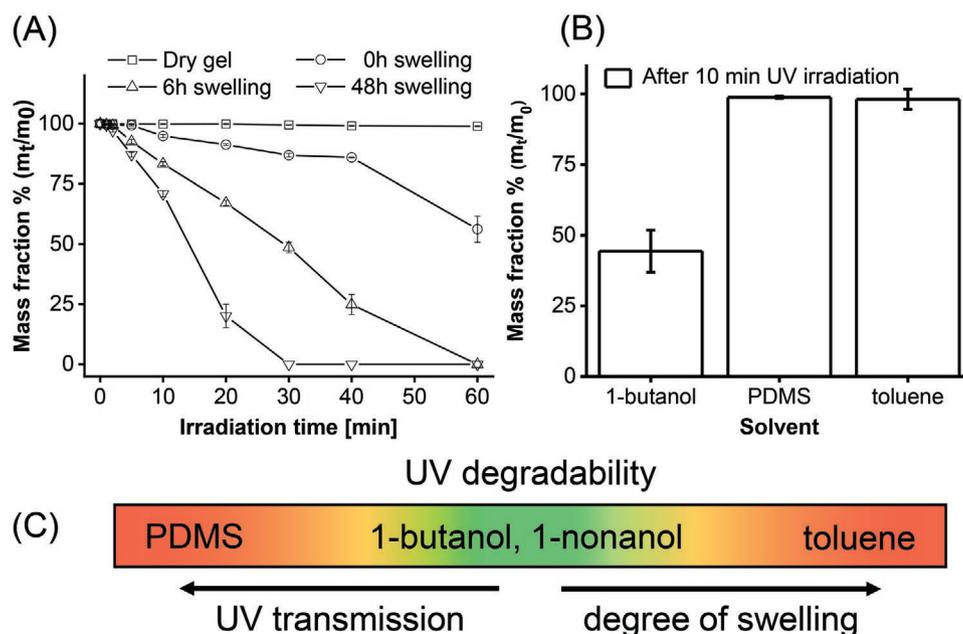


Figure 3. A) Photodegradation speed of dry and as-prepared organogels swollen in 1-nonanol for 0, 6, and 48 h. The resulting 1-nonanol content of the organogels was 0, 60.7, 67.5, and 76.3 wt%, respectively. Data are given as mean \pm SD ($n = 4$). B) Photodegradation of organogels swollen in 1-butanol, PDMS, and toluene after 10 min of UV light irradiation. C) Scheme summarizing how the solvent properties affected the photodegradation of organogel. Solvents with low UV light transmission or swelling capability inhibited the photodegradation of organogels (red), whereas highly swelling, UV-transmitting solvents such as 1-butanol or 1-nonanol enabled the photodegradation of organogels (green).

Toluene had the highest swelling factor (15.88 ± 0.37) but does not transmit UV light below 280 nm, whereas PDMS possesses a negligible UV absorbance but a very low swelling factor (1.02 ± 0.01). Interestingly, neither the toluene infused organogel nor the PDMS infused organogel showed significant photodegradation after 10 min irradiation time. In contrast, organogels infused with 1-butanol showed an even faster photodegradation than those infused with 1-nonanol, which we attributed to the lower UV absorbance of 1-butanol compared to 1-nonanol. In conclusion, an ideal solvent for the photodegradation of organogels can swell the organogel network strongly whilst being transparent for UV light. If only one of these conditions was fulfilled, it could not compensate the other requirement, as shown by the incapability of organogels swollen in toluene or PDMS to degrade under UV light (Figure 3C). It is expected that all *n*-alcohols between 1-butanol and 1-nonanol (C_5 - C_8) are suitable as solvents for the photodegradation of organogels due to their hydrophobicity, low UV absorbance, and high boiling point. For this study, 1-nonanol was preferable over 1-butanol due to its higher boiling point, lower hazard potential, and more pleasant smell (Figure S11, Supporting Information).

To investigate the application of inherently photodegradable organogels as slippery lubricant infused porous (SLIP) materials, we investigated whether the wettability properties of bulk organogels infused with 1-nonanol could be altered via UV light irradiation (Table 2).

For 30 and 60 s of irradiation we could not detect an effect on the water contact angle hysteresis ($\Delta\theta$) before and after degradation outside the frame of errors. For 120 s of UV irradiation, $\Delta\theta$ decreased by 2.1° between the pristine and irradiated state, which could be attributed to a surface erosion induced release of 1-nonanol. For all irradiation times, a decrease in the advancing (θ_a) and receding (θ_r) water contact angles was observed. In conclusion, the organogels' slippery properties were slightly more pronounced after photodegradation, which we attributed to the formation of an excess layer of 1-nonanol serving as lubricant. The low contact angle hysteresis of water droplets suggested that the critical sliding angle of 1-nonanol infused organogels should be low, which is a relevant property for substrates in microfluidics applications. Indeed, when tilted, water could easily slide off the surface of a 1-nonanol infused organogel or pass through an organogel channel without leaving traces (Figure 4A). To provide an understanding

Table 2. Wettability of organogels before and after UV irradiation. Data is given as mean \pm SD ($n = 5$).

	Before UV irradiation			UV exposure [s]	After UV irradiation		
	θ_a [°]	θ_r [°]	$\Delta\theta$ [°]		θ_a [°]	θ_r [°]	$\Delta\theta$ [°]
	49.1 ± 2.2	45.4 ± 0.8	3.9 ± 0.8	30	45.7 ± 0.8	43.9 ± 1.1	3.1 ± 1.2
	49.7 ± 1.1	44.6 ± 0.7	6.5 ± 1.0	60	46.6 ± 0.9	40.0 ± 0.7	7.7 ± 0.7
	50.6 ± 1.4	44.6 ± 0.7	7.7 ± 0.5	120	47.2 ± 1.8	41.6 ± 0.7	5.6 ± 0.8

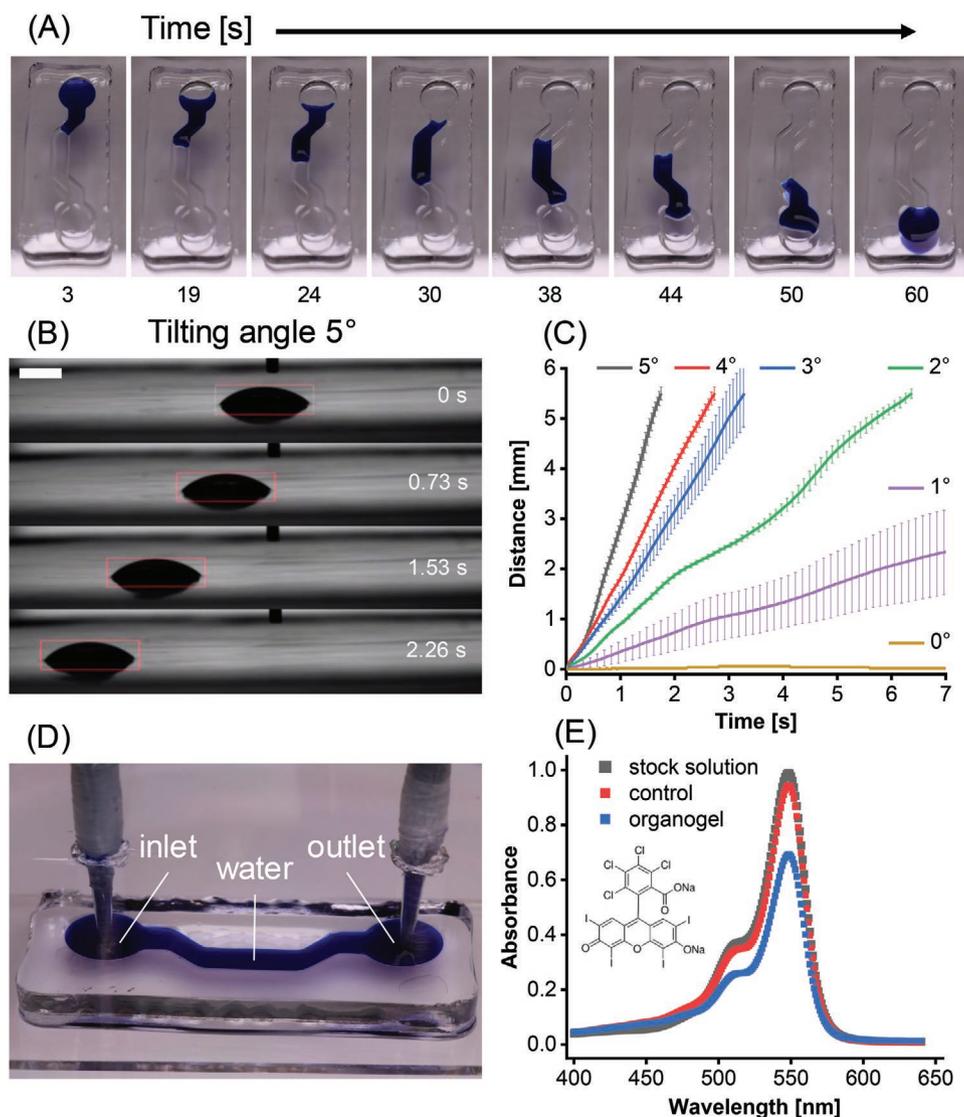


Figure 4. A) Images of water (dyed blue) sliding through a tilted organogel channel without leaving traces. The tilting angle was 10° and the dimensions of the organogel are $4 \times 55 \times 20$ mm ($h \times l \times w$). B) Tracing a water droplet sliding on a tilted organogel disc using a template matching algorithm (red box). Scalebar is 1 mm. C) Water droplet movement on organogels for different tilting angles (0° – 5°). Each line resembles an average of five experiments. Error bars are the standard deviation (SD) of the average ($N = 5$). D) Image of water (dyed blue) cycling through an organogel channel using a syringe pump. The dimensions of the organogel are $4 \times 55 \times 20$ mm ($h \times l \times w$). E) UV–vis spectra of a stock solution of Rose Bengal (17.5 mg mL^{-1} in water) before and after being cycled through the organogel channel for 30 min at a rate of $10 \mu\text{L s}^{-1}$. The concentration of Rose Bengal decreased by 30% due to absorption by the organogel.

of the sliding of the water droplets from the organogels surface, the movement of water droplets was recorded, and the droplet position was detected with a template matching algorithm (Figure 4B). A schematic understanding of the template matching algorithm is provided in the Supporting Information (Figure S12, Supporting Information). Analysis of the droplets' coordinates over time yielded the velocity of the droplet (Figure 4C). For all tilting angles, the velocity of water droplets was found to be approximately constant throughout the observable distance, as apparent by the constant slope of the distance versus time plots. No acceleration of the water droplet was observed, as would generally be expected for water droplets sliding down a hydrophobic plane.^[36] For a tilting angle of 1° ,

water droplets started to slide off, but eventually stopped after ≈ 15 s, thus the critical sliding angle (CSA) was determined to be 2° . A tilting angle of 0° was tested as a control, which showed no movement of the water droplet.

Two relevant applications of organogels are oil cleanup and water repellent surfaces, due to their capability of hosting a large amount of hydrophobic liquid relative to their own weight and their inherent slipperiness and hydrophobicity when infused with a hydrophobic liquid. The ability to structure organogels with UV light allowed us to merge those two applications in a fluid channel. An organogel with a channel was prepared via photodegradation (Figure 4D). Then, a solution of Rose Bengal in water as a model impurity was cycled through the channel

on the organogels surface for 30 min using a syringe pump. After 30 min, the concentration of Rose Bengal was reduced from 175 to 12.25 $\mu\text{mol L}^{-1}$ as quantified with UV vis spectroscopy (Figure 4E). This corresponds to a total amount of 16 μg Rose Bengal taken up by the organogel. As a control, an identical solution was cycled only through the silicone tubing of the pump and no significant decrease in the concentration of Rose Bengal was observed. Thus, the removal of Rose Bengal can be solely attributed to the organogel channel, which demonstrated how UV patterned organogels could be useful in wastewater treatment or microfluidics applications.

The transfer of light-induced structures onto substrates that are not photodegradable themselves is the key principle of photoresist technology. To date, no positive gel-based photoresists have been demonstrated, even though gels offer advantages over established procedures using linear polymers such as PMMA.^[37] First, no designated step is required to remove irradiated polymer fragments from the copper surface using a solvent (“developer”), since the degraded organogel dissolves into the solvent released upon gel degradation. Second, the inherently photodegradable organogels can be removed with affordable UV lamps, whereas PMMA typically requires X-ray or electron beams to degrade efficiently.^[37] To test the suitability of inherently photodegradable organogels as a photoresist, we coated a copper circuit board with a thin film of organogel (200 μm). The organogel film was then spatially degraded with UV light for 10 min using a photomask and immersed into 0.5 M aq. FeCl_3 solution for 2 h. Unprotected copper was etched by the FeCl_3 , whereas copper covered by the organogel remained (Figure 5A).

To test whether thin conducting features can be obtained, we used a photomask with a slit length of 50 mm and a slit width of

100 μm together with the organogel photoresist. The respective copper pattern conducted the electric current (Figure 5B). This method could offer a cheap and simple alternative to fabricate circuit boards for labs and businesses without access to expensive x-ray and electron beam setups. Photopatterned organogels could further be used as stamps for contact printing. The resolution of the stamped patterns, however, was rather low due to the soft nature of the organogels (Figure S13, Supporting Information).

3. Conclusion

Organogels with customized 3D or surface structure can improve the performance of organogels in applications such as oil-water separation, drug delivery, or as slippery-, anti-waxing, anti-bacterial or self-healing surfaces. Herein, inherently photodegradable poly(methacrylate) organogels offer a simple and versatile way to fabricate structured organogels without the need for additional photolabile crosslinks. The UV transmission and swelling ability of the infusing organic solvent were identified as the key factors influencing the photodegradability of organogels, which will presumably hold true for other photo-responsive or photoreactive organogels in the future. Moreover, the first ever use of a gel as a positive photoresist has been demonstrated, which is interesting for photolithographic fabrication processes in the electronics industry. Since the solvent (developer) for the polymer is already incorporated in the organogel network, the degraded polymer does not need to undergo a dissolution step but can be rinsed off immediately. Since organogels are hydrophobic soft-materials, inherently photodegradable organogels could serve as an alternative to the frequently used soft-lithography.

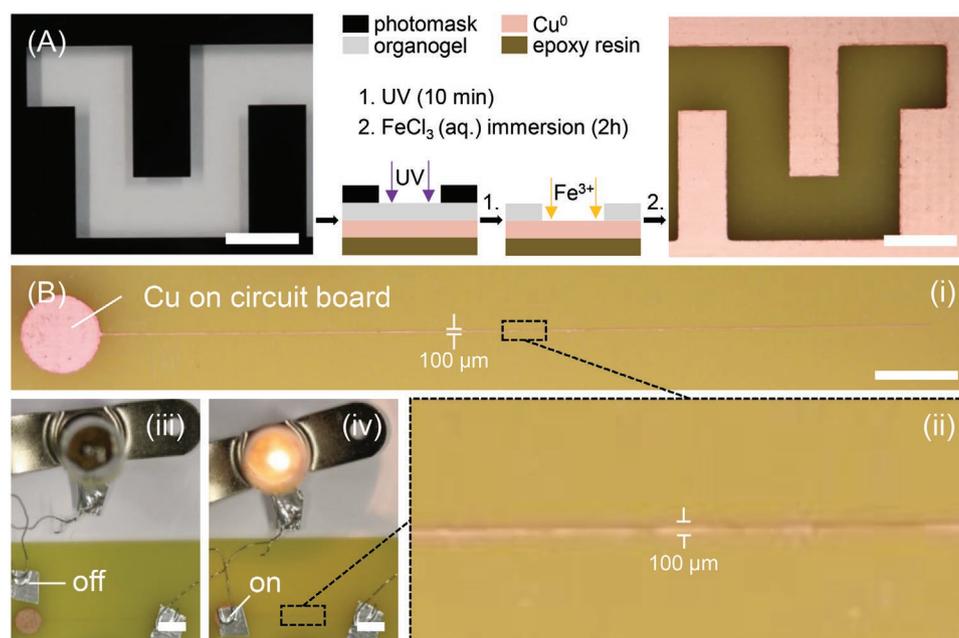


Figure 5. A) Preparation of a copper pattern on an epoxy resin circuit board. B) Image (i) and magnification (ii) of a thin (100 μm) and long (50 mm) Cu^0 stripe on a circuit board. The stripe conducted the electric current, as apparent by a light bulb turning on upon connecting a battery and a bulb along the copper stripe (iii, iv). Scalebars are 5 mm.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

J.M.S. and S.L. contributed equally to this work. J.S. proposed the original idea, performed and evaluated experiments, and wrote the paper. S.L. performed and evaluated experiments. The authors would like to thank Stefan Heissler for help with ATR FTIR, Lukas Arens for help with rheometry, and Julius Höpfner for help with NMR. J.S. would like to thank the DBU (Deutsche Bundesstiftung Umwelt) for financial support. S.L. would like to thank the CSC (China Scholarship Council) for the Ph.D. scholarship. This project was supported by the DFG no. LE 2936/9-1 (Heisenberg-Professur).

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Conflict of Interest

Findings of this study related to photoresists are part of a patent application filed by the first authors and the corresponding author.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

lubricant-infused surfaces, organogels, photodegradation, positive photoresist, UV light

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