Imine-Based Dynamic Polymer Networks as Photoprogrammable Amine Sensing Devices

Michael Kathan @,1 Christoph Jurissek @,1 Petr Kováříček @,2 Stefan Hecht @1,3,4

1Department of Chemistry & IRIS Adlershof, Humboldt-Universität zu Berlin & IRIS Adlershof, Brook-Taylor Str. 2, 12489 Berlin, Germany
2Department of Low-Dimensional Systems, J. Heyrovsky Institute of Physical Chemistry of the ASCR, v. v. i., Dolejškova 2155/3, 18223 Praha 8, Czech Republic
3DWI–Leibniz Institute for Interactive Materials, Forckenbeckstrasse 50, 52056 Aachen, Germany
4Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Woringerweg 2, 52074 Aachen, Germany

Correspondence to: P. Kováříček (E-mail: petr.kovaricek@jh-inst.cas.cz); S. Hecht (E-mail: hecht@dwi.rwth-aachen.de)

Received 25 August 2019; Revised 22 September 2019; accepted 23 September 2019
DOI: 10.1002/pola.29518

Abstract: Here, we describe a “smart” polymeric material, which is able to readily detect and discriminate amine vapors. The dynamic imine-based network can be conveniently prepared by mixing a commercially available, amino-functionalized polysiloxane with small amounts of a diacylethene dialdehyde. The photoswitchable crosslinker allows for reversible imprinting of custom-designed patterns on the polymer surface with (sun)light and thus enables noninvasive information storage in the material, which before, during, and after amine exposure can readily be decoded with commonly used smartphone apps. This feature along with the self-healing nature of the dynamic polymer, an easy recycling and manufacturing procedure, and the overall low cost and toxicity render this material advantageous to develop low-cost and practical amine sensing devices for the broad public. © 2019 The Authors. Journal of Polymer Science Part A: Polymer Chemistry published by Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. 2019

KEYWORDS: adaptive materials; crosslinking; dynamic covalent chemistry; irradiation; molecular photoswitches; polysiloxanes; stimuli-sensitive polymers

Amines are omnipresent in our daily lives, fulfilling numerous roles in biological systems and chemical industry, for example agriculture and food processing. Some derivatives of this family, such as cadaverine or putrescine, exhibit significant toxicity and are being produced during bacterial degradation of proteins, rendering them suitable indicators for food quality and environmental pollution. The latter is also associated with the use of large amounts of amines for post-combustion CO2 capture. Both of these issues demand the development of low-tech sensing devices, giving ideally everybody a practical tool to reliably control the quality of perishable goods and the condition of their environment.

Previous approaches aiming at the detection of (biogenic) amine vapors involved (solid state) sensors based on colorimetric changes as well as “turn-on” and “turn-off” fluorescence. Recently, our group reported on a photoresponsive system, which only in the “on-state” is subject to an amine-induced decomposition, accompanied by either an indicative decoloration or photoluminescence change of the material. Furthermore, due to differently colored switching states (colorless “off-state”), information storage in the device is feasible. Yet, while showing a rather high sensitivity, along with the “photoprogrammable” nature as an incidental cofeature, indicative decoloration of the “on-state” is irreversible, making the material a single use device and preventing possible reprogramming. Consequently, the prerequisites for such amine sensors are high: The employed materials have to be low-cost, the manufacturing/recycling process and handling must be simple and safe, the readout should be viable without the need for sophisticated technology, and the device should ideally work without electricity.

Autonomously adaptive systems have the potential to meet these challenging requirements, since they are able to alter their intrinsic physicochemical properties in direct response to changes of their environment. In recent years, dynamic covalent chemistry has enabled great progress in the field, as it combines the reversibility of supramolecular interactions with covalent bonds and hence provides the

Michael Kathan and Christoph Jurissek contributed equally to this work.

© 2019 The Authors. Journal of Polymer Science Part A: Polymer Chemistry published by Wiley Periodicals, Inc.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.
possibility to incorporate strong yet dynamic linkages into a material. Among the variety of dynamic covalent reactions, reversible imine formation is unique, as it takes place at ambient conditions while relying on highly abundant amine derivatives.

Integrating dynamic covalent bonds in everyday materials can unlock unique properties, as we recently demonstrated by manufacturing an adaptive material by simple mixing of a commodity polysiloxane with a photoswitchable dialdehyde crosslinker. This system autonomously self-repairs, which is based on continuous exchange reactions between imine moieties in the material. However, the property of Schiff bases to efficiently undergo exchange reactions is not only limited to imines of the same structure. Mixing different imine derivatives leads to a dynamic exchange of their respective residues and thus reshuffles the constitution of C=N-based systems.

In this work, we make use of this exchange reaction to sense and even discriminate between amines. The general idea is to use a dynamic, imine-crosslinked polymeric material, which can be penetrated by small monoamine molecules, to enable a competing reaction between the permeating nucleophiles and the ones inherently present in the material. As a consequence, this leads to a reduced degree of crosslinking in the polymer network, which softens and eventually liquefies the material (Fig. 1).

In order to manifest this idea, we took an aminopropyl functionalized polysiloxane (AS), which is commercially available as a viscous liquid [80–120 cSt, ~3 wt % (3-aminopropyl)methyilsiloxane in dimethylsiloxane] and crosslinked it with bifunctional aldehydes, providing a viscoelastic dynamic polymer network (Fig. 2).

For the crosslinking dialdehydes, we have chosen nontoxic terephthaldehyde (TA) and a bis-formylated diarylethene (DAE). The latter is a photochromic molecule, able to switch between a thermally stable open (DAEo) and closed (DAEc) isomer. By applying UV light (λirr ≈ 313 nm) electrocyclic ring-closure of DAEo is induced to yield a photostationary state composed of >95% of DAEc, whereas green light (λirr ≈ 550 nm) is used to induce ring-opening and quantitatively recover DAEo. Due to the different absorption behavior in the UV-vis spectrum, the photoisomers have different colors, that is, DAEo is yellow whereas DAEc is purple, enabling patterns to be reversibly imprinted in the polymer and thus adding an attractive feature to the material.

The procedure for preparing the polymeric material is truly simple and can be readily performed on a multigram scale. To do so, the crosslinker (TA or DAE) is dissolved in toluene and the solution is added to the liquid polysiloxane AS. This mixture can be

**Figure 1** Schematic representation of a liquefying process in a dynamic covalent polymer network (yellow block) upon exposure to amines. Amine functionalities in the polymer compete with the analyte (blue spheres), which leads to decrosslinking of the polymer chains and softening/liquefaction (yellow pancake). [Color figure can be viewed at wileyonlinelibrary.com]

**Figure 2** Crosslinking of amino functionalized polysiloxane AS with dialdehyde crosslinkers and their molecular structures: terephthaldehyde, open diarylethene (DAEo), and closed diarylethene (DAEc).
processed by established methods such as drop-casting, spin-coating, or molding and is ready for use after solvent evaporation.29

According to the design, a volatile amine permeating into the crosslinked network competes with the amino-functionalized side chains, which leads to a decrease of crosslink density and thus to a reduction of the material’s glass transition temperature. To check if our hypothesis for amine sensing is valid, we drop-casted a toluene solution of the polymer, crosslinked with TA or with DAE to yield TA@AS and DAE@AS, respectively, on small glass slides (1.8 cm × 1.8 cm, thickness ~0.6 to 0.7 mm). For TA@AS, prepared by mixing commercially available AS and TA, the material costs add up to ~€0.10 per device (see Supporting Information for materials and preparation). Once in hand, we exposed the dried, rubberlike films to vapors of highly volatile propylamine in a closed vessel (~1 mL amine in 100 cm³, see Supporting Information for the detailed setup). Much to our delight, both polymer films liquefied completely within 10 min. When the polymer films were removed from the amine-containing atmosphere, the dynamic nature of the imine network allowed the competing amine to evaporate, leading to reformation and thus regeneration of the initial polymer films. Encouraged by these first results, we tested the reactivity of the polymer films towards several other amines. Cadaverine, one of the most prominent products in protein decomposition processes,4–7 also causes the crosslinked system to collapse, although the process is slower (~4 h) due to a lower volatility of the diamine.

In a next step, we imprinted patterns onto the polymer films to visualize the breakdown of the polymer network in a more straight-forward fashion, storing information on the polymer films, and thus making our approach appealing for an application as an amine sensing device. In the case of TA@AS, we simply drew lines with a commonly used permanent marker on the polymer surface. Sensing experiments with the two different amines clearly showed that the polymer film liquefies (see Supporting Information Fig. S6). A complete liquefying process in case of volatile propylamine took place within 10 min, whereas cadaverine needed 4 h to decrosslink the polymer network, in line with our initial experiments. However, the permanent dye and thus color from the marker remains irreversibly inside the polymer network. On the one hand, this limits the reusability of the material, but on the other hand, it enables a read-out by naked eye and prevents counterfeiting of positive indication results.

To tackle this problem and to add an additional level of sustainability and function to the material, photoswitchable DAEo was applied as the crosslinker. Among others, this enables reversible control over the material’s color by UV and visible light irradiation, turning it purple or light yellow, respectively, with high spatial and temporal precision. This can be utilized to imprint delicate patterns in a sparing and noninvasive manner onto the surface of DAEo@AS films, as we demonstrated by generation of a barcode (Code 93, information: “1”) on a drop-cast DAEo@AS film (Fig. 3) by using a photomask and a simple UV lamp (366 nm). The thus imprinted information can be read out by smartphones with common apps for barcode decoding. Similar to TA@AS films, the information stored on the DAE@AS film cannot be decoded by customary smartphones after 4 h of exposure to cadaverine vapors [Fig. 3(a)]. In case of more volatile propylamine, sensing again occurs rapidly and the barcode is illegible already after 10 min [Fig. 3(b)]. A series of other primary amines were tested and led to similar results, whereby response and sensing time were found to depend on volatility and lipophilicity of the respective analyte (see Supporting Information Fig. S7).

Again, after storing the polymer films overnight under ambient conditions, the volatile amines evaporate and the DAE@AS material can be reused. By applying visible light, the barcodes can be erased without leaving a trace of purple color on the polymer surface and the film is ready to be imprinted with
new information using a suitable mask and UV light (see Supporting Information Fig. S8).

Importantly, vapors of less nucleophilic secondary and tertiary amines, such as diisopropylamine and trimethylamine, do not cause the polymer stripes to liquefy. However, due to the high gelling capability of the silylone polymer,29 the imprinted barcodes are illegible after 1 day of exposure, even though the material is still solid [see Supporting Information Fig. S9(a,b)]. This effect is even more pronounced for highly volatile, but amine-free solvents, such as dichloromethane, proving that no decrosslinking is involved in the process [see Supporting Information Fig. S9(c)]. Under ambient conditions (~50% humidity) or in presence of ammonia vapors, however, the barcodes are readable for days (see Supporting Information Fig. S10).

Due to good fatigue resistance of the photoswitchable molecule and a high extinction coefficient of the ring-closed crosslinker DAEc, we could generate composite polymer networks, containing mostly (95%) of the low-cost and nontoxic TA crosslinker and only 5% of the photoswitchable DAE. Using this method, the nonirradiated composite polymer containing DAEo appears completely colorless (see Supporting Information Fig. S4) and large amounts of photoswitch can be saved, without losing switching or sensing performance [see Supporting Information Fig. S6(c)], which greatly decreases the overall cost of our system. In addition to that, reversible switching of the DAE can be even performed with sunlight,29 which greatly advances the practicality of our material, making it a reliable, cheap, and easy-to-handle tool for amine sensing.

In order to promote real-life application of the device, sensitivity tests towards propylamine and cadaverine were conducted. We found that 25 μL of an amine analyte in a closed vessel of ~250 mL (100 ppmv) are sufficient to observe full liquefaction of the polymer network (see Supporting Information Fig. S11). To evaluate if the material could be applied as a sensor for food quality, we performed a sensing experiment with fish. For this purpose, we exposed a barcode imprinted composite device to a piece of 3 days old cod in a closed vessel. After 2 days, the imprinted barcode was completely illegible (see Supporting Information Fig. S12), thus showing a positive response toward a perished consumable. This result indicates that the adaptive material is capable of determining quality of foods. Please note, however, that biological samples show considerable variability thus rendering quantitative conclusions very difficult.

In a simplistic and applicable approach, we developed a di-aldehyde containing dynamic polymer network as a solid, autonomously working device able to sense and discriminate between amine vapors, giving reliable and fast response in presence of primary aliphatic amines without any cross-sensitivity for ammonia. The photoswitchable component allows for reversible information storage in the material, due to highly precise light-induced imprinting of defined patterns. The information can be read out either by naked eye or common smartphone apps. As the photochromic molecule stays intact throughout the whole procedure, and the polymer network is restored each time the analyte is evaporated, information can repeatedly be imprinted and the material continuously be reused. The easy handling and recycling paired with its low cost make this adaptive material a highly sustainable and user-friendly amine sensing device, which represents an interesting alternative for applications in environmental protection, chemical, and food industries.

ACKNOWLEDGMENTS

M. Kathan and C. Jurissek are indebted to the Studienstiftung des deutschen Volkes and the Einstein Foundation Berlin (ESB) - Einstein Center for Catalysis (EC2), respectively, for providing doctoral fellowships. Generous support by the European Research Council (via ERC-2012-STG 308117 “Light4Function”) is gratefully acknowledged.

REFERENCES AND NOTES

1 R. Benigni, L. Passerini, Mutat. Res. 2002, 511, 191.
2 S. Amb, H. G. Neumann, Toxicol. Appl. Pharmacol. 1996, 139, 186.
3 H. Greim, D. Bury, H.-J. Klimisch, M. Oeben-Negele, K. Ziegler-Skalakakis, Chemosphere 1998, 36, 271.
4 D. R. Morris, R. H. Fillingame, Annu. Rev. Biochem. 1974, 43, 303.
5 S. Bover Cid, M. J. Miguel-Arribazado, B. Becker, W. H. Holzapel, M. C. Vidal-Carou, Food Microbiol. 2008, 25, 269.
6 J. L. Pablos, S. Vallejos, A. Muñoz, M. J. Rojo, F. Serna, F. C. García, J. M. García, Chem. A Eur. J. 2015, 21, 8733.
7 J. E. Stumpel, C. Wouters, N. Herzer, J. Ziegler, D. J. Broer, C. W. M. Bastiaansen, A. P. H. J. Schenning, Adv. Opt. Mater. 2014, 2, 459.
8 A. E. Poste, M. Grung, R. F. Wright, Sci. Total Environ. 2014, 481, 274.
9 J. Kumpf, J. Freudenberg, K. Fletcher, A. Dreuw, U. H. F. Bunz, J. Org. Chem. 2014, 79, 6634.
10 J. Kumpf, J. Freudenberg, S. T. Schwaebel, U. H. F. Bunz, Macromolecules 2014, 47, 2569.
11 S. Rochat, T. M. Swager, Angew. Chem. Int. Ed. 2014, 53, 9792.
12 V. Valderrey, A. Bonasera, S. Fredrich, S. Hecht, Angew. Chem. Int. Ed. 2017, 56, 1914.
13 S. Fredrich, A. Bonasera, V. Valderrey, S. Hecht, J. Am. Chem. Soc. 2018, 140, 6432.
14 G. J. Mohr, D. Citterio, C. Demuth, M. Fehlmann, L. Jenny, C. Lohse, A. Moradian, T. Nezel, M. Rothmaier, U. E. Spichiger, J. Mater. Chem. 1999, 9, 2259.
15 X. Chang, J. Fan, M. Wang, Z. Wang, H. Peng, G. He, Y. Fang, Sci. Rep. 2016, 6, 31187.
16 Y. Zhou, Y. Ren, L. Zhang, L. You, Y. Yuan, E. V. Anslyn, Tetrahedron 2015, 71, 3515.
17 X. Wu, X.-X. Chen, M. Zhang, Z. Li, P. A. Gale, Y.-B. Jiang, Chem. Commun. 2016, 52, 6981.
18 S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, Angew. Chem. Int. Ed. 2002, 41, 898.
19 J.-M. Lehn, Angew. Chem. Int. Ed. 2015, 54, 3276.
20 P. T. Corbett, J. Leclaire, L. Vial, K. R. West, J.-L. Wietor, J. K. M. Sanders, S. Otto, Chem. Rev. 2006, 106, 3652.
21 M. E. Belowich, J. F. Stoddart, Chem. Soc. Rev. 2012, 41, 2003.
22 R. J. Sarma, S. Otto, J. R. Nitschke, Chem. A Eur. J. 2007, 13, 9542.
23 S. P. Black, J. K. M. Sanders, A. R. Stefankiewicz, Chem. Soc. Rev. 2014, 43, 1861.
24 N. Roy, B. Bruchmann, J.-M. Lehn, Chem. Soc. Rev. 2015, 44, 3786.
25 G. Vantomme, S. Jiang, J.-M. Lehn, J. Am. Chem. Soc. 2014, 136, 9509.
26 H. Wang, S. C. Heilshorn, Adv. Mater. 2015, 27, 3717.
27 Q. Ji, R. C. Lirag, O. Š. Miljanić, Chem. Soc. Rev. 2014, 43, 1873.
28 G. Leonetti, S. Otto, J. Am. Chem. Soc. 2015, 137, 2067.
29 M. Kathan, P. Kovafiček, C. Jurisšek, A. Senf, A. Dallmann, A. F. Thünemann, S. Hecht, Angew. Chem. Int. Ed. 2016, 55, 13882.
30 M. Ciaccia, S. Di Stefano, Org. Biomol. Chem. 2014, 13, 646.
31 J. Biscarat, B. Galea, J. Sanchez, C. Pochat-Bohatier, Int. J. Biol. Macromol. 2015, 74, 5.
32 L. N. Lucas, J. J. D. de Jong, J. H. van Esch, R. M. Kellogg, B. L. Feringa, Eur. J. Org. Chem. 2003, 1, 155.
33 M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, Chem. Rev. 2014, 114, 12174.