

Self-Diagnostic Polymers—Inline Detection of Thermal Degradation of Unsaturated Poly(ester imide)s

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Monitoring polymer degradation is an important quest, particularly relevant for industry. Although many indirect methodologies for assessing polymer degradation exist, only few are applicable for an inline-monitoring via optic detection-systems. An inline-monitoring system is introduced for the thermal degradation of crosslinked poly(ester imide)s (PEIs) by embedding trifluoroacetyl functionalized stilbene molecules, serving as chemosensors to track the release of generated alcoholic byproducts. Nucleophilic addition of an alcohol to the sensors trifluoroacetyl functionality triggers hemiacetal formation which is accompanied by significant changes in optical properties, in turn allowing monitoring of sensor activation by direct spectroscopy. Fluorescence spectroscopy offers an easy detection tool for the inline thermal monitoring of PEI-degradation.

1. Introduction

Polymers, indispensable materials in society, are prone to permanent degradation by temperature, mechanical force, or light, resulting in deterioration or loss of the original properties by depolymerization- or cross-linking processes.^[1–3] Since the primordial degradation of polymeric materials may induce serious impact by failure of structural materials or devices, there is increased interest in monitoring the level and nature of degradation, with a focus on its time-dependent profile. Based on the wide structural diversity of different polymers, various

methodologies are used to quantify degradation, either via classical ex situ methods, such as changes in molecular weights, mechanical properties, or changes in their dielectric behavior.^[3,4] However, an examination of the polymer condition during operation, especially for installed parts, proves to be difficult as many common analytical methods to this endeavor, e.g., thermogravimetric methodologies, pyrolytic methods, gel-permeation chromatography (GPC), matrix-assisted laser-desorption time-of-flight mass spectrometry (MALDI-TOF-MS), or ¹H NMR spectroscopy, are often not practical for inline-measurements.^[3,5] Consequently the field of sensor technology offers a promising

approach to overcome the problem of real-time investigations of polymer materials during operation. The continuous detection of polymer degradation requires a trigger, directly associated to the degradation process. Thus sensing systems based on thermochromic,^[6,7] mechanochromic,^[8] electrostatic,^[9,10] and mass-sensitive approaches,^[11] or via molecularly imprinted polymers (MIPs)^[12,13] have been developed to detect and quantify polymer degradation or damage. MIPs frequently have been used to track specific template molecules, enabling analyte detection by, e.g., voltammetry^[14,15] within epoxy- and polycarbonate resins^[14] or the detection of amino containing compounds such as creatinine^[16] or dansylphenylalanine^[17] via optical spectroscopy.^[18] Chemosensors in particular allow the detection of degradation products released during polymer decomposition by activation, constituting a promising sensor class to track polymer degradation.^[19–21] Thus, several optical sensing principles enable a fast and easy visualization by UV-vis and fluorescence spectroscopy, or even by the naked eye.^[10,22,23–25] Conjugated polymers^[6,13,25] such as carbazole-based conjugated polymers display reversible on/off fluorescence in the presence of electron-rich respectively electron-deficient arene vapors,^[26] detecting explosives such as 2,4,6-trinitrotoluene.^[27] Single-stranded DNA mixed with a cationic polythiophene derivative was used to transduce protein binding events into an optical signal.^[28] Other chromophoric sensing principles rely on 1,2-naphthoquinone-4-sulfonic acid sodium salts embedded within a modified PDMS matrix^[24] or on trifluoroacetyl functionalized azobenzenes within polyacrylates and epoxy resins, serving as chromogenic receptor for amines.^[20,29]

We here use stilbene-based sensor-molecules to continuously track the thermal degradation process of a poly(ester imide)-polystyrene (PEI) resin via a fluorescence based

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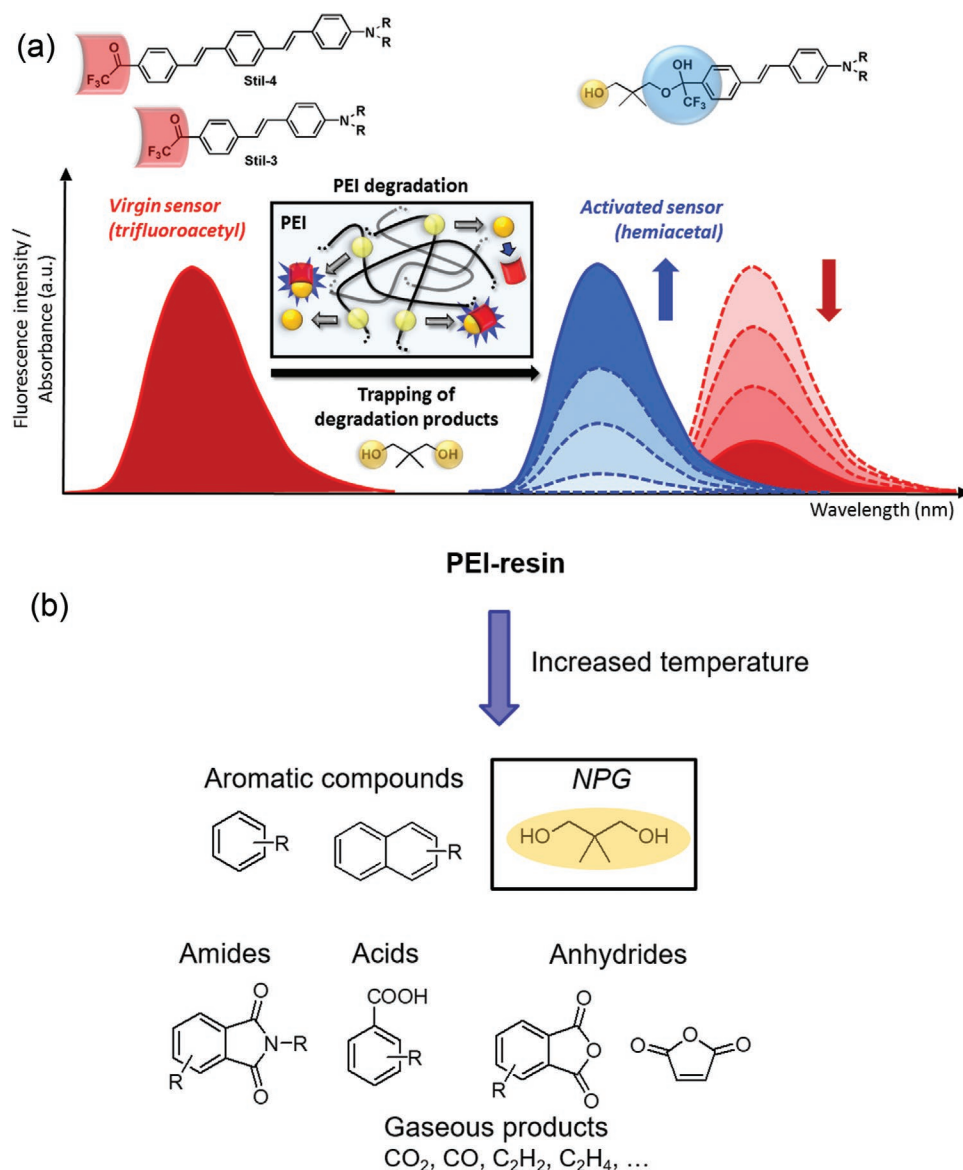


Figure 1. A) Trifluoroacetyl functionalized stilbene dyes **Stil-3** and **Stil-4** are used as sensor molecules, allowing hemiacetal formation by reaction with released neopentyl glycol (NPG) during degradation of a poly(ester imide) PEI triggering detectable optical changes by UV-vis and fluorescence spectroscopy ($R = -\text{C}_6\text{H}_{13}$). B) Chemical identity of the products generated during thermal degradation of the PEI-resins, with NPG being the main detected analyte.

response (Figure 1). PEIs, widely used in the electrical industry as electrical insulating materials for copper wires and coils in electric motors,^[30,31] are known to degrade thermally by releasing alcohols and amines by cleavage of imide- and ester bonds via a main-chain scission mechanism.^[2,32] Although PEIs feature high temperature and mechanical resistance,^[30,33] they are thermally degraded over a period of several years making a continuous monitoring of their degradation an attractive feature by detecting the release of alcoholic degradation products. Conceptually (see Figure 1A) we have used substituted stilbenes as sensors, as their molecular design can be linked to the optical properties of choice for a specific sensor-application,^[19,20,34] reversibly altering their emission from non-fluorescent to fluorescent.^[23,35] The designed trifluoroacetyl-functionalized stilbene dyes **Stil-3** and **Stil-4**, when embedded into a PEI matrix, can react with the target molecule

neopentyl glycol (NPG) released during their thermal aging via a nucleophilic addition, in turn triggering hemiacetal formation (Figure 1A,B). This sensor activation can easily be followed by a shift of $\lambda_{\text{abs,max}}$ and $\lambda_{\text{em,max}}$ to smaller wavelengths via UV-vis and fluorescence spectroscopy as depicted in Figure 1A. Monitoring the signals of both, the virgin and the activated sensor molecule, enables to calculate the thermal degradation process of the poly(ester imide)-polystyrene resins.

2. Results and Discussion

2.1. Sensor Activation in Solution

We aimed to develop a sensor system for the detection of thermal polymer degradation within a solid poly(ester imide)

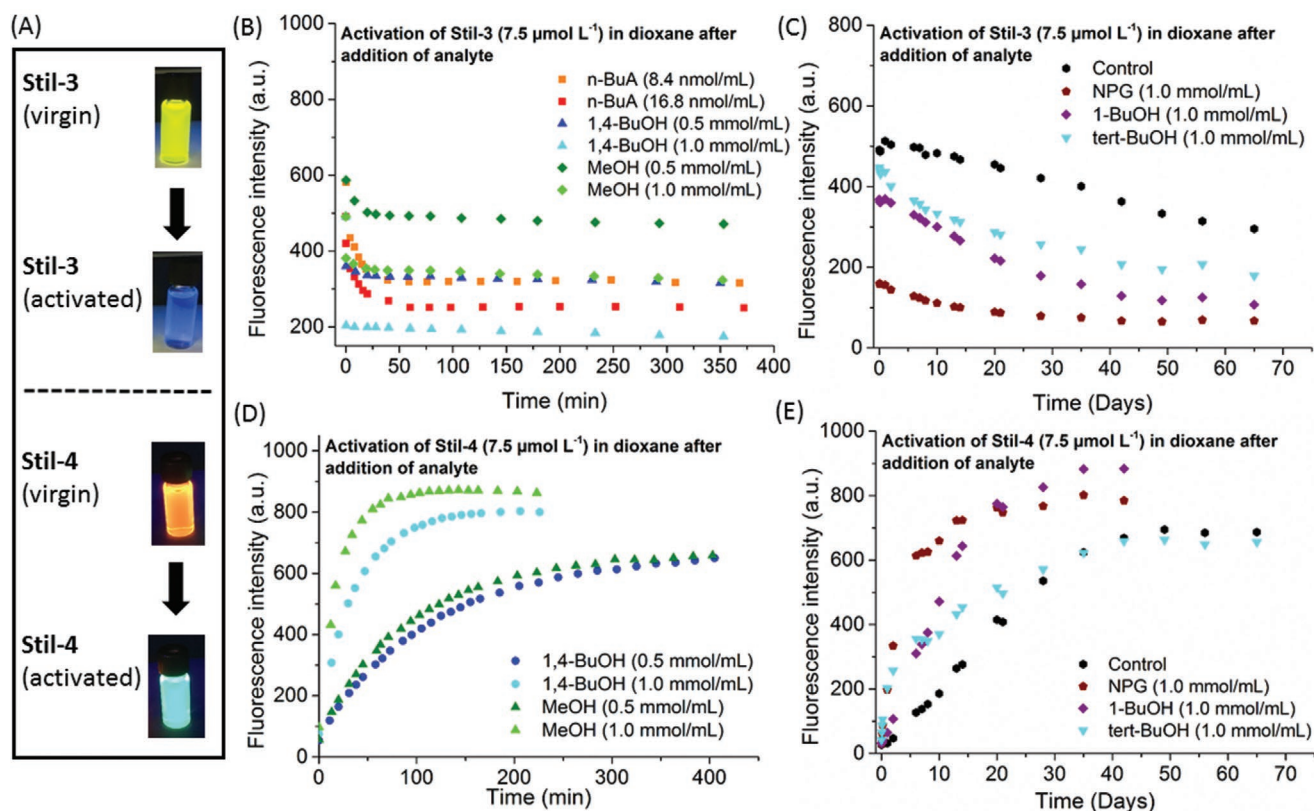


Figure 2. A) **Stil-3** and **Stil-4** in dioxane under UV light ($\lambda = 366$ nm) before and after activation with methanol. B,C) Sensor activation of **Stil-3** ($7.5 \mu\text{mol L}^{-1}$, $\lambda_{\text{ex}} = 442$ nm, $\lambda_{\text{em}} = 557$ nm) after addition of different analytes monitored by fluorescence decay of the trifluoroacetyl emission maxima. D,E) Sensor activation of **Stil-4** ($7.5 \mu\text{mol L}^{-1}$, $\lambda_{\text{ex}} = 406$ nm, $\lambda_{\text{em}} = 496$ nm) after addition of different analytes monitored by fluorescence increase of the hemiacetal emission maxima.

PEI resin crosslinked with styrene. Prior to investigations of solid samples by fluorescence spectroscopy, preliminary experiments in solution using dioxane were performed to evaluate the suitability of both sensor molecules, **Stil-3** ($\epsilon_{\lambda=440\text{nm}} = 26\,500 \text{ L mol}^{-1} \text{ cm}^{-1}$) and **Stil-4** ($\epsilon_{\lambda=438\text{nm}} = 42\,700 \text{ L mol}^{-1} \text{ cm}^{-1}$), especially with regard to response and specificity. Linear absorption and fluorescence behavior were observed for concentrations up to $9 \times 10^{-3} \mu\text{mol mL}^{-1}$ (Figures S1 and S2 in the Supporting Information), as response of **Stil-3** and **Stil-4** toward various analytes, especially amines and alcohols via nucleophilic addition to the trifluoroacetyl group and the subsequent change in their fluorescence spectra. Results are summarized in Figure 2 and Figures S3 and S4 (Supporting Information) exemplarily show the shift of emission spectra associated with the sensor response. For kinetic measurements a dye concentration of $7.5 \times 10^{-3} \mu\text{mol mL}^{-1}$ and analyte concentrations between 0.5 and 1.0 mmol mL^{-1} were used, except for *n*-butylamine ($c = 8.4$ and 16.8 nmol mL^{-1}) due to its fast response time.

Both sensor molecules, **Stil-3** and **Stil-4**, can be well activated by addition of *n*-butylamine as well as by alcohols in reasonable response-times of seconds. Whereas **Stil-3** shows a decrease of the fluorescence intensity after activation **Stil-4** shows an increase in fluorescence of its generated hemi-form (compare Figures S3 and S4 in the Supporting Information). A focus was placed on neopentyl glycol, later serving as the main analyte during thermal PEI degradation. Sensor response is accelerated

in the presence of amines due to their higher nucleophilicity compared to alcohols. Furthermore a strong dependence on the nature of the alcohol was observed, which essentially results from the steric demands of the analyte. Fastest sensor response was found for methanol and 1,4-butanediol, the slowest conversion was observed for *tert*-butanol, displaying the highest steric demand of all investigated analytes. It is important to note that neopentyl glycol shows a good reaction with both sensors molecules, **Stil-3** and **Stil-4**, despite its two methyl groups, constituting a significant steric hindrance. The faster response of **Stil-4** into the optical detectable hemi-form, resulting from the weaker electron-donor properties of the distyryl substitution compared to **Stil-3**, is highlighted together with the higher quantum yield of its hemiacetal form, potentially advantageous for the subsequent solid-state reactions, where diffusion is restricted and detection thus reduced due to additional matrix interference.^[34] As the response of **Stil-4** toward *n*-butylamine was fast, it prevented a reliable monitoring of the kinetics even though low concentrations (8.4 and 16.8 nmol L^{-1}) were used. Both sensors show an only low conversion triggered by moisture through nucleophilic addition of water molecules, unavoidable for long-term measurements over 70 d but less prominent in the later application due to restricted diffusion processes in the solid-state. Overall, both **Stil-3** and **Stil-4** showed excellent and promising response in solution with an only low response to water.

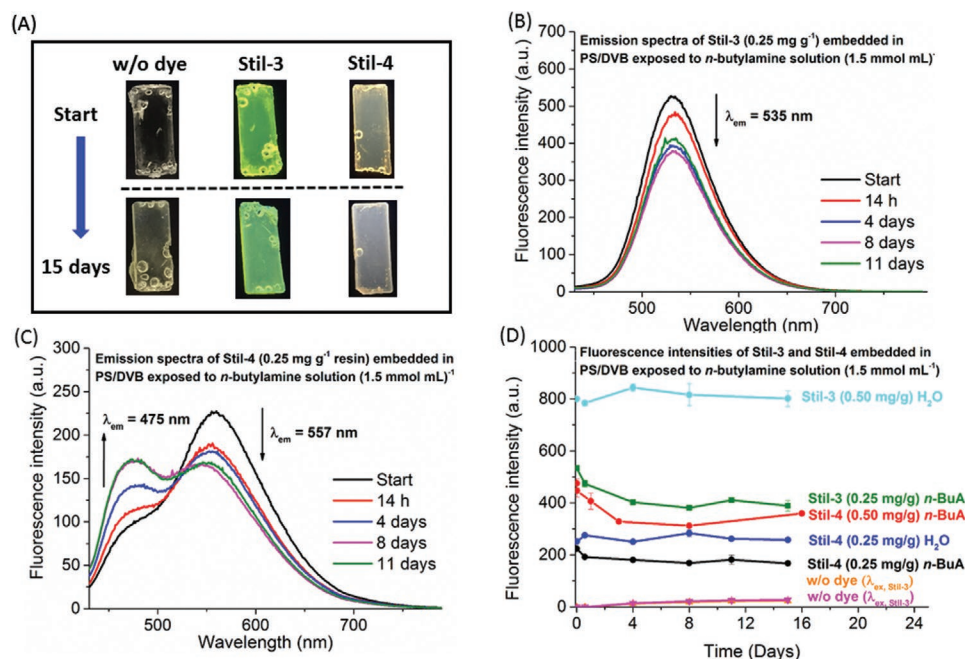


Figure 3. A–C) Specimen of PS/DVB: A) with embedded Stil-3 and Stil-4 dye under UV light ($\lambda = 366$ nm) before and after 15 d storage in *n*-butylamine solution, B) with Stil-3 (0.25 mg g⁻¹ resin, $\lambda_{ex} = 414$ nm) and C) with Stil-4 (0.25 mg g⁻¹ resin, $\lambda_{ex} = 409$ nm) embedded in PS/DVB after storage in *n*-butylamine solution (1.5 mmol mL⁻¹) monitored by fluorescence spectroscopy. D) Summarized results showing fluorescence intensities plotted versus time together with corresponding control experiments.

2.2. Sensor Activation in a PS/DVB Resin by Amines

As a model resin to probe application in crosslinked resin systems a poly(styrene divinylbenzene) resin PS/DVB was synthesized by free radical crosslinking of styrene with 4 mol% of divinylbenzene, 1 mol% of azobisisobutyronitrile (AIBN) containing 2.5×10^{-4} to 5.0×10^{-4} w% of Stil-3 or Stil-4. Activation was triggered by exposing the specimen to aqueous *n*-butylamine solution, providing a fast response. Subsequently we focused on solid-state fluorescence as it proves more suitable compared to solid-state UV-vis spectroscopy. The corresponding fluorescence spectra after sensor activation are depicted in Figure 3b,c. As PS/DVB itself is non-fluorescent (compare Figure S5 in the Supporting Information) it provides a simple model system, proving the embedding of the sensor molecules in a solid polymer and its successful activation and detection in their virgin and activated forms. To exclude cross reaction or solvent/matrix interference proper control experiments were conducted by exposing specimen of PS/DVB with or without Stil-3 or Stil-4 to either water or an aqueous *n*-butylamine solution. Results are presented in Figure 3d. Sensor-containing specimen stored in *n*-butylamine solution show a distinct decrease of the original emission maximum at 535 and at 557 nm, corresponding to the virgin trifluoroacetyl form, indicating the formation of the activated hemiaminal. As the fluorescence quantum yield of the virgin trifluoroacetyl moiety is higher for Stil-3 compared to Stil-4,^[34] fluorescence intensity is significantly higher for Stil-4 albeit at the same concentration. Fluorescence intensity decreases with a maximum value of 24% for Stil-4 at a concentration of $c = 0.5$ mg g⁻¹ down to 27% for Stil-3 at $c = 0.25$ mg g⁻¹. Formation of the hemiaminal form of Stil-4 can be observed by

a second emission maximum at 475 nm, which is not the case for the hemiaminal form of Stil-3 due to its low quantum yield. Overall, the findings from solid-state measurements correlate to results from solution experiments. Reference specimen of PS/DVB containing Stil-3 and Stil-4 stored in water lack the initial drop of fluorescence intensity, and the overall change is in the order of $\sim 1\%$ and 2% , hence being significantly smaller. Additionally, a sample of PS/DVB without dye stored in *n*-butylamine solution, shows only negligible changes of its fluorescence intensity. Therefore matrix/solvent interference can be excluded and measurable changes are attributed to sensor activation by the *n*-butylamine analyte with an excellent stability against water.

2.3. Sensor Activation in PEI Resin by Amines

The PEI matrix, a network of an unsaturated poly(ester imide) crosslinked with styrene, shows thermal degradation into amines and alcohols with neopentyl glycol being one of the main volatile analytes, according to a main chain scission reaction in the first pyrolysis step.^[32] To assess the thermal stability of the used PEI, a sample was measured by TGA and it was found that PEI smoothly decomposes between 350 and 450 °C (compare Figure S6 in the Supporting Information). PEI degradation experiments were conducted at 200 and 220 °C, below its decomposition temperature and more representative for application, by inserting a resin sample into a glass-tube, placed in a sand-bath for continuously heating. This chosen temperature is also inducing an accelerated kinetics, representative for a long-term aging of the resin at the usually lower temperatures of such electrical devices of ~ 100 °C. Gaseous degradation

products were flushed into an equipped adsorber column by applying a constant flow of oxygen (4 mL min^{-1}) and all condensable degradation products were collected after 500, 1000, 3000, and 5000 h by thoroughly washing the adsorption material with acetone. The mass loss of the specimen was recorded by weighing the PEI specimen after each degradation step and is depicted in Figure S7 in the Supporting Information. Within the first 500 h the mass loss of PEI at degradation temperatures of 200 and 220 °C is attributed to evaporation of monomeric residues, additives and residual moisture from the resin dominating the actual polymer degradation. After 500 h a significantly slower degradation is observed for PEI at 200 °C compared to 220 °C, explained by the progressive crosslinking- and cyclization processes in PEI, leading to a slower mass loss for the sample at 220 °C after 3000 h.^[3,36] Presence of neopentyl glycol during degradation was proven by analysis of the desorbed degradation products using ^1H NMR spectroscopy and HPLC/ESI-TOF MS and calculated values are presented in Table S1 (see Supporting Information, recorded spectra are exemplarily shown in Figures S8 and S9). PEI was fabricated as a two component systems by mixing two formulations in a ratio of 50:50 w%, containing the poly(ester imide), styrene and radical initiator. To the mixture either Stil-3 or Stil-4 (1 w%) were added and the specimen were cured at 80 °C for 50 min, followed by 5 min at 140 °C.

Similar to PS/DVB resin, sensor activation was first probed under accelerated conditions by storing the specimen in aqueous *n*-butylamine solution and monitoring emission decay by fluorescence spectroscopy as depicted in Figure 4b,c. Results are summarized in Figure 4d. Specimen containing sensor molecules again show a significant drop in emission intensities of 56%, with the response of Stil-4 being faster compared with Stil-3, coinciding with the observation from solution experiments. The

total fluorescence decrease is significantly higher than for PS/DVB, explained by a better diffusion of the aqueous solutions within PEI, facilitating sensor activation in bulk material.^[37] Therefore a fluorescence decrease of 21% for Stil-3 and 23% for Stil-4 was observed for reference specimen stored in water, which was not observable for PS/DVB specimen. Additional control experiments demonstrate that water has no influence on the intrinsic fluorescence of the PEI matrix (compare Figure S10 in the Supporting Information) and storage in *n*-butylamine solution only slightly increases fluorescence intensity. The major drawback of the PEI resin is the lack of a second emission maximum of Stil-4 which corresponds to the activated sensor.

2.4. Sensor Activation in PEI Resin by Neopentyl Glycol

Both, Stil-3 and Stil-4 were embedded in cross-linked PEI and specimen were exposed to neopentyl glycol to access sensor activation. Since thermal stress leads to aging of PEI and thus to the release of neopentyl glycol, two approaches were pursued. First, PEI samples (a) containing sensor molecules were stored in neopentyl glycol at room temperature in vacuum to exclude PEI aging. Second, PEI samples (b) with embedded sensor molecules were placed in a lid of a petri dish where the lower part was covered with neopentyl glycol. Subsequently, the petri dish was placed in a sand bath at 180 °C, thus being exposed to the gaseous neopentyl glycol atmosphere, at the same time reducing direct thermal load on PEI due to the distance from the sand bath. Additionally PEI samples (c) without sensor molecule were equally treated as samples (b), serving as control experiment. Results for Stil-3 are shown in Figure 5d, results for Stil-4 are shown in Figure S11 in the Supporting Information. As expected, for sample (a) containing Stil-3, a

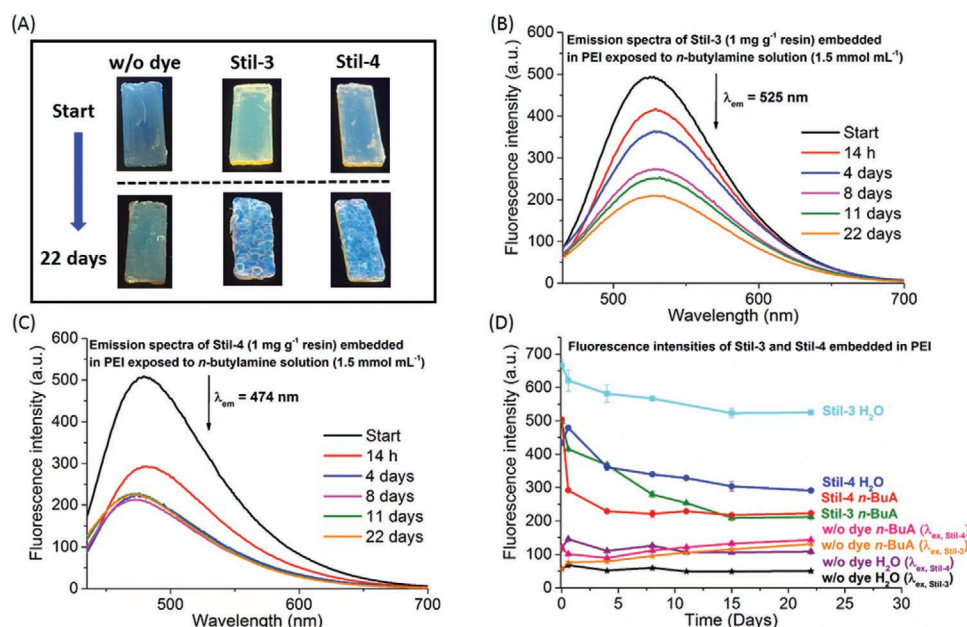


Figure 4. A) Specimen of PEI with embedded Stil-3 and Stil-4 dye under UV light ($\lambda = 366 \text{ nm}$) before and after 22 d storage in *n*-butylamine solution. B,C) Sensor activation of Stil-3 (1 mg g⁻¹ resin, $\lambda_{ex} = 447 \text{ nm}$) (B) and Stil-4 (1 mg g⁻¹ resin, $\lambda_{ex} = 410 \text{ nm}$) (C) embedded in PEI after storage in *n*-butylamine solution (1.5 mmol mL^{-1}) monitored by fluorescence spectroscopy. D) Summarized results showing fluorescence intensities plotted versus time together with corresponding control experiments.

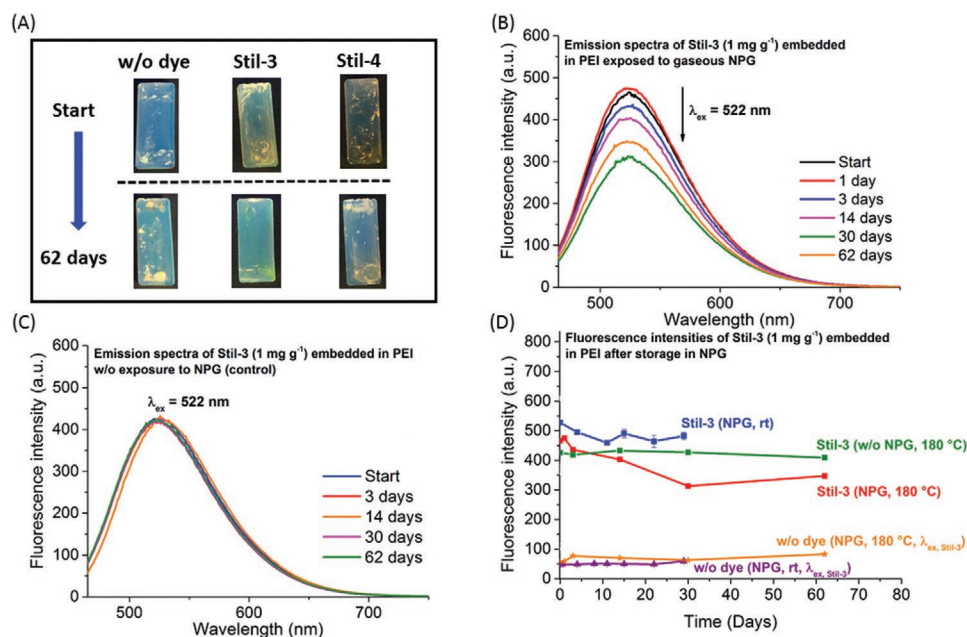


Figure 5. A) Specimen of PEI under UV light ($\lambda = 366$ nm) before and after 62 d storage in neopentyl glycol atmosphere at 180 °C. B) Sensor activation of Stil-3 (1 mg g⁻¹ resin, $\lambda_{ex} = 447$ nm) embedded in PEI after storage in neopentyl glycol atmosphere at 180 °C monitored by fluorescence spectroscopy. C, D) Control experiment under the same conditions as listed for (B) without neopentyl glycol summarized results showing fluorescence intensities plotted versus time together with corresponding control experiments.

total decrease of the fluorescence intensity of 8% was observed, indicating its successful activation by neopentyl glycol.

Sample (b) with embedded Stil-3, indicates a decrease of fluorescence by 26%, proving a faster sensor activation in gaseous neopentyl glycol atmosphere (Figure 5b). For sample (c) containing the sensor molecule Stil-3 devoid of neopentyl glycol a decrease of fluorescence by 4%, thus distinctly smaller compared to the activation experiment (b), was observed (Figure 5c). Additional control experiments of PEI without sensor verify that intrinsic fluorescence properties of the matrix are unaffected by experimental conditions, therefore thermal influences on PEI matrix are excluded and suitability of Stil-3 within PEI was demonstrated.

3. Conclusion

Two different sensor molecules, Stil-3 and Stil-4, were successfully embedded within a poly(styrene divinylbenzene) resin PS/DVB. Sensor response and detection were proven under accelerated conditions by conversion of the virgin trifluoroacetyl form into the hemiaminal after exposure to *n*-butylamine solution, demonstrating the usability of the chosen detection system in the solid-state. Function of the sensor system was demonstrated for poly(ester imide) PEI specimen in both, solution and thermal experiments, thus providing a powerful tool for tracking the thermal long-term degradation of poly(ester imide) impregnating resins for coils in electric engines. In future work, we will further investigate the in situ activation of Stil-3 and Stil-4 under engine-working conditions, in which PEI samples release the required analyte neopentyl glycol by thermal degradation and consequently trigger hemiacetal formation. In

total this inline detection system allows the continuous monitoring of PEI degradation as it happens in, e.g., all commercial electric engines, where wire-enamels based on PEI are used for insulation—a big step toward their reliable function.

4. Experimental Section

Reagents and Chemicals: All chemicals were purchased from commercial suppliers and, except the following, used without further purification. Poly(ester imide) resin PEI was provided by ELANTAS GmbH. Styrene was destabilized by washing with a solution of NaOH (10 wt%) and drying over Na₂SO₄ before usage. Adsorber material Amberlite XAD-4 was washed thoroughly with distilled water and acetone before the adsorber column was charged. AIBN was recrystallized from methanol at 50 °C before usage.

Instruments and Methods: UV-vis absorbance spectra of dissolved sensor molecules were recorded on a Perkin Elmer UV-VIS Lambda 365 spectrometer. For solution experiments typically a stock-solution of either 1 mg Stil-3 or Stil-4 in 1 mL dioxane was prepared. The required amount of stock-solution was transferred into a cuvette and was filled up to 3 mL using dioxane. For solid-state measurements, the spectrometer was equipped with a Lambda 365 Integrating sphere. Fluorescence spectra of both, dissolved and embedded sensor molecules, were recorded on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer, detector voltage was set to 500 V. For solution experiments, first the analyte was transferred into a cuvette and dissolved in dioxane. Afterward the required amount of the stock-solution containing Stil-3 respectively Stil-4 was added and the fluorescence measurement was started immediately after sensor addition. ¹H NMR-, ¹³C NMR-, and ¹⁹F NMR spectra were recorded either on an Agilent Varian Gemini 200 (400 MHz) or on an Agilent Varian Unity Inova (500 MHz) spectrometer at 27 °C. Chemical shifts (δ) were given in parts per million (ppm) and were referred to the solvent signal of CDCl₃ (7.26 ppm (¹H NMR), 77.0 ppm (¹³C NMR)). Values of coupling constants *J* are given in hertz (Hz). HPLC measurements were performed on a VWR Hitachi

Chromaster on an Atlantis T3 (5.0 μm , 4.6 mm $\times$ 250 mm) C18 reversed column, using a flow rate of 0.8 mL min^{-1} , an injection volume of 10 μL and UV-vis detection. For sample preparation HPLC-solvent was used with sample concentrations of 1 mg mL^{-1} . ESI-TOF MS measurements were performed on a Bruker Daltonics microTOF spectrometer, using direct injection with a flow rate of 180 $\mu\text{L h}^{-1}$ in either positive or negative mode. For sample preparation HPLC-grade solvent was used with sample concentrations of 0.5 mg mL^{-1} and without addition of salt. For HPLC/ESI-TOF MS coupling a sample concentration of 1 mg mL^{-1} was used. 10 μL were injected on the column and a flow rate of 0.5 mL min^{-1} was used. A TripleTOF 6600–1 mass spectrometer (AB Sciex) was used for high-resolution mass spectrometry, which was equipped with an ESI-DuoSpray-Ion-Source (operated in positive ion mode) and was controlled by Analyst 1.7.1 TF software (AB Sciex). The ESI source operation parameters were as follows: ion spray voltage: 4500 V, nebulizing gas: 60 p.s.i., source temperature: 450 $^{\circ}\text{C}$, drying gas: 70 p.s.i., curtain gas: 55 p.s.i. Data acquisition was performed in the MS¹-ToF mode, scanned from 100 to 2500 Da with an accumulation time of 50 ms.

TGA measurements were performed on a TGA Netzsch T210, using sample amounts of 5 mg. Measuring was done under a flow of nitrogen (20 mL min^{-1}) and a heating rate of 5 K min^{-1} . Thin-layer chromatography (TLC) was performed on either Merck silica gel 60 or Macherey–Nagel ALUGRAM ALOX N/UV254 sheets. Spots on TLC plates were visualized by UV light (254 or 366 nm) or by using the oxidizing agent “blue stain” consisting of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (2.5 g) and $\text{Ce}(\text{SO}_4)_2\cdot 4\text{H}_2\text{O}$ (1 g) dissolved in distilled water (90 mL) and concentrated H_2SO_4 (6 mL). For column chromatography either Merck Kieselgel 60 (230–400 mesh) or neutral aluminum oxide (Brockmann I Typ 507, 150 mesh) from Sigma Aldrich was used. For degradation experiments, PEI was cured in a teflon-mould (50 mm $\times$ 10 mm $\times$ 10 mm), yielding specimen with a weight of 5 g. PEI specimen were stored in a glass-tube which was placed in a sand-bath for continuously heating the samples at 200 and 220 $^{\circ}\text{C}$. The glass-tube was equipped with an adsorber column filled with Amberlite XAD-4 (50 g). By applying a constant flow of oxygen (4 mL min^{-1}), gaseous degradation products were flushed into the adsorber column and adsorbed degradation products were collected after 500, 1000, 3000, and 5000 h by washing the adsorption material thoroughly with acetone. Quantification of neopentyl glycole was done by ^1H NMR spectroscopy, using 1,3,5-trioxane as external standard.

Synthesis of 2,2,2-Trifluoro-1-(4-vinylphenyl)ethan-1-one 1: A two-neck flask was heated under vacuum and flushed with nitrogen three times. It was charged with Mg-turnings (1.82 g, 75.00 mmol, 1.50 eq.) and dry THF (50 mL) was added. Afterward 4-bromostyrene (6.50 mL, 50.00 mmol, 1.00 eq.) was added via syringe and the reaction was initiated by hand warmth. The reaction turned yellow and was allowed to cool down to room temperature and was stirred for 1 h. After addition of dry THF (5.00 mL) the reaction mixture was cooled down to -78°C . Ethyl trifluoroacetate (9.00 mL, 75.00 mmol, 1.50 eq.) was added dropwise via syringe and the reaction was allowed to run for 1 h at -78°C . After the solution was warmed up to 0 $^{\circ}\text{C}$ 1 M HCl (100 mL) was slowly added and the reaction mixture was extracted with ethyl acetate (3 $\times$ 100 mL). The combined organic phases were washed with brine and dried over MgSO_4 . The solvent was removed under vacuum and the crude product was purified by column chromatography using pentane / diethyl ether ($v/v = 50:1$) and isolated as a colorless oil (for ^1H -, ^{13}C -, and ^{19}F NMR spectra of all synthesized compounds see Figures S14 to S26 in the Supporting Information).^[38]

^1H NMR (400 MHz, CDCl_3 , δ): 5.49 (d, $J = 10.9$ Hz, 1H, H-1a), 5.96 (d, $J = 17.6$ Hz, 1H, H-1b), 6.79 (dd, $J = 17.6$ Hz, $J = 10.9$ Hz, 1H, H-2), 7.56 (m, 2H, H-4), 8.05 (m, 2H, H-5); ^{13}C NMR (100 MHz, CDCl_3 , δ): 116.9 (C-1), 118.7 (C-8), 126.9 (C-6), 129.2 (C-4), 130.7 (C-5), 135.6 (C-2), 144.7 (C-3), 180.1 (C-7); ^{19}F NMR (470 MHz, CDCl_3 , δ): -71.4 (s, 3F).

Synthesis of p-Iodo-N,N-dihexylaniline 2: A mixture of p-iodoaniline (3.79 g, 17.31 mmol), 1-bromohexane (8.50 mL, 10.00 g, 60.58 mmol, 3.50 eq.), N-ethyldiisopropylamine (10.34 mL, 7.83 g, 60.58 mmol), and dimethylformamide (15 mL) was stirred at 110 $^{\circ}\text{C}$ for 20 h. After cooling to room temperature, the reaction mixture was poured on 100 mL of distilled water and the product was extracted with chloroform

(3 $\times$ 50 mL). The combined organic phase was washed with distilled water (2 $\times$ 75 mL) and dried over Mg_2SO_4 . The obtained oil was purified by flash chromatography on silica gel using hexane/ethyl acetate (19:1 = v/v) as the eluent, yielding **2** as a yellow liquid.^[39]

^1H NMR (400 MHz, CDCl_3 , δ): 0.89 (t, $J = 6.7$ Hz, 6H, H-1), 1.30 (m, 12H, H-2 + H-3 + H-4), 1.54 (m, 4H, H-5), 3.21 (m, 4H, H-6), 6.40 (m, 2H, H-9), 7.42 (m, 2H, H-10); ^{13}C NMR (100 MHz, CDCl_3 , δ): 14.2 (C-1), 22.8 (C-2), 27.0 (C-4), 27.2 (C-5), 31.9 (C-3), 51.2 (C-6), 75.5 (C-11), 114.2 (C-9), 137.8 (C-10), 147.8 (C-8).

Synthesis of 4-Bromo-4'-(dihexylamino)stilbene 3: A mixture of **2** (9.00 g, 23.40 mmol), 4-bromostyrene (3.78 mL, 5.31 g, 29.25 mmol, 1.25 eq.), palladium diacetate (57.78 mg, 0.261 mmol, 0.011 eq.), tri-*o*-tolylphosphine (150.84 mg, 0.495 mmol, 0.021 eq.), and triethylamine (19.26 mL, 138.06 mmol, 5.90 eq.) was dissolved in dry DMF (30 mL) and refluxed at 115 $^{\circ}\text{C}$ under nitrogen. To the cooled solution water and chloroform were added and the aqueous layer was extracted with chloroform (3 $\times$ 50 mL). The combined organic layer was washed with distilled water (3 $\times$ 75 mL) and dried over Mg_2SO_4 . The crude product was purified by column chromatography on silica gel using hexane/chloroform (2:1 = v/v) as the eluent and afterward was recrystallized from methanol yielding **3** as a yellow solid.^[39]

^1H NMR (400 MHz, CDCl_3 , δ): 0.91 (m, 6H, H-1), 1.32 (m, 12H, H-2 + H-3 + H-4), 1.59 (m, 4H, H-5), 3.28 (m, 4H, H-6), 6.61 (d, $J = 8.9$ Hz, 2H, H-9), 6.77–7.02 (m, 2H, H-11 + H-12), 7.31–7.43 (m, 6H, H-10 + H-14 + H-15); ^{13}C NMR (100 MHz, CDCl_3 , δ): 14.2 (C-1), 22.8 (C-2), 27.0 (C-4), 27.4 (C-5), 31.9 (C-3), 51.2 (C-6), 111.8 (C-9), 120.0 (C-17), 122.4 (C-11), 124.2 (C-10), 127.5 (C-12), 128.0 (C-13), 129.8 (C-15), 131.7 (C-16), 137.5 (C-14), 148.2 (C-8).

Synthesis of 4-Trifluoroacetyl-4'-(dihexylamino)stilbene Stil-3: 3 (250.0 mg, 0.55 mmol) was dissolved in 5 mL of dry tetrahydrofuran and cooled to -78°C using methanol/liquid nitrogen as the cooling agent. To the stirred solution was added a 1.6 M solution of butyllithium in hexane (387.5 μL , 0.65 mmol, 1.10 eq.) and stirring was continued for 30 min. Then, ethyl trifluoroacetate (70.0 μL , 0.85 mmol, 1.03 eq.) was added and the solution was stirred for another 60 min. The solution was warmed up to room temperature, 1 mL of methanol was added and, subsequently, 20 mL of diethylether. The orange solution was washed once with 3 mL of 1 M hydrochloric acid, 3 mL of a sodium bicarbonate solution and twice with 15 mL of distilled water. After drying over Mg_2SO_4 and evaporation to dryness, the orange oil was purified by flash chromatography on silica gel using hexane/dichloromethane ($v/v = 4:1$) as the eluent, yielding **Stil-3** as orange crystals.^[39]

^1H NMR (400 MHz, CDCl_3 , δ): 0.91 (t, $J = 6.8$ Hz, 6H, H-1), 1.33 (m, 12H, H-2 + H-3 + H-4), 1.60 (m, 4H, H-5), 3.30 (m, 4H, H-6), 6.64 (d, $J = 8.9$ Hz, 2H, H-9), 6.91 (d, $J = 16.2$ Hz, 2H, H-12), 7.22 (d, $J = 16.2$ Hz, 2H, H-13), 7.42 (d, $J = 8.8$ Hz, 2H, H-10), 7.57 (d, $J = 8.5$ Hz, 2H, H-15), 8.01 (d, $J = 7.9$ Hz, 2H, H-16); ^{13}C NMR (100 MHz, CDCl_3 , δ): 14.2 (C-1), 22.9 (C-2), 27.0 (C-4), 27.4 (C-5), 31.9 (C-3), 51.2 (C-6), 111.5 (C-9), 121.3 (C-7), 125.9 (C-12), 128.6 (C-13), 130.9 (C-15), 134.0 (C-16), 146.1 (C-14), 148.9 (C-8), 179.8 (C-18); ^{19}F NMR (470 MHz, CDCl_3 , δ): -71.1 (s, 3F); UV-vis (dioxane): $\lambda_{\text{max}}(\epsilon) = 440$ nm (26 500). HR-MS (See Figure S29 in the Supporting Information, M–H⁺ (460,2817) and M–H₂O–H⁺ (478,2933)).

Synthesis of 1-[4-(2-[4-(2-(4-Dihexylaminophenyl)-vinyl]-phenyl)-vinyl)-phenyl]-2,2,2-trifluoroethanone Stil-4: A two-neck flask was heated under vacuum and flushed with nitrogen three times. Then **3** (2.00 g, 4.52 mmol, 1.15 eq.), **1** (788.64 mg, 3.94 mmol, 1.00 eq.), and dichlorobis-(triphenylphosphine)-palladium(II) (74.66 mg, 0.10 mmol, 0.027 eq.) were dissolved in triethylamine (15.00 mL, 108.00 mmol, 27.4 eq.) and dry DMF (16.00 mL). The reaction mixture was stirred at 115 $^{\circ}\text{C}$ for 16 h. The solution was allowed to cool down and water (50 mL) was added. The aqueous layer was extracted with DCM (3 $\times$ 50 mL) and the combined organic layers were washed with distilled water (3 $\times$ 100 mL). After the organic layer was dried with MgSO_4 the solvent was removed under vacuum and the crude product was purified by column chromatography on neutral Al_2O_3 using hexane/ethyl acetate ($v/v = 2:1$) as the eluent, yielding **Stil-4** as red crystals.^[34]

^1H NMR (400 MHz, CDCl_3 , δ): 0.91 (m, 6H, H-1), 1.33 (m, 12H, H-2 + H-3 + H-4), 1.60 (m, 4H, H-5), 3.29 (m, 4H, H-6), 6.62 (d, $J = 8.9$ Hz, 2H,

H-9), 6.90–7.31 (m, 4H, H-12 + H-13 + H-18 + H-19), 7.40 (d, $J = 8.8$ Hz, 2H, H-10), 7.51 (m, 4H, H-15 + H-16), 7.64 (d, $J = 8.5$ Hz, 2H, H-21), 8.07 (d, $J = 7.9$ Hz, 2H, H-22); ^{13}C NMR (100 MHz, CDCl_3 , δ): ^{19}F NMR (470 MHz, CDCl_3 , δ): -71.2 (s, 3H); UV-vis (dioxane): $\lambda_{\text{max}}(\epsilon) = 438$ nm (42 700). HR-MS (See Figure S30 in the Supporting Information, M–H⁺ (562,3280) and M–H₂O–H⁺ (580,3387)).

Preparation of Model Resin PS/DVB and Sensor Embedding: The required amount of dye **Stil-3** or **Stil-4** (dye concentrations between 0.125 mg g^{−1} PS/DVB up to 0.5 mg g^{−1} PS/DVB were used) was dissolved in the reaction mixture of styrene, divinylbenzene (4 mol% referred to styrene), and AIBN (1 mol% referred to styrene). The reaction mixture was transferred into a teflon mould (25 mm × 10 mm × 2 mm) and was stored in an oven at 78 °C for 3 h. During the curing process the teflon mould was covered with a watch glass to reduce the evaporation of styrene. After 3 h the polymer was obtained as a transparent, glass-like specimen.

Preparation of PEI Specimen and Sensor Embedding: PEI is a two-component system and was prepared according to the manufacturing protocol, by mixing both components in a 50/50 (w/w) ratio. The required amount of dye **Stil-3** or **Stil-4** (dye concentrations between 0.125 mg g^{−1} PEI resin up to 2 mg g^{−1} PEI resin were used) was dissolved in the mixture, which subsequently was transferred into a teflon mould (25 mm × 10 mm × 2 mm) and curing was done by storing the teflon mould within a petri-dish in an preheated oven at 80 °C for 50 min, followed by 5 min at 140 °C. After cooling down, the specimen was removed from the mould, having a transparent, yellowish/brownish appearance.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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