

Perylene Polyphenylmethylsiloxanes for Optoelectronic Applications

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ABSTRACT: The incorporation of fluorescent organic dyes in an encapsulating matrix represents a route to generate stable and processable materials for optoelectronic devices. Here, we present a method to embed perylene dyes into a high refractive index (HRI) polysiloxane matrix applying an allyl functionalized perylene dye and hydrosilylation chemistry. In a first approach, the dye molecules were covalently integrated into the backbone of linear polyphenylmethylsiloxane chains. The fluorescent and liquid polymers were synthesized with molecular weights from 5660 up to 8400 g mol⁻¹. In a second approach, the dye itself was used as a cross-linking agent between linear polyphenylmethylsiloxane chains. These preformed fluorescent batch polymers are liquids with dye concentrations between 0.025 and 8 wt %. The applied synthetic methods incorporated the dye covalently into the polymer structure and avoided the crystallization of the dye molecules and thus the formation of excimers, which would reduce the optical emission. The resulting products can be easily

incorporated into curable commercially available HRI polyphenylmethylsiloxane resins. The formed materials are ideal LED encapsulants with a solid and flexible consistency, a uniform dispersion of the dyes, and adjustable mechanical properties, realized by changing the amount of perylene polymers. Further properties of the obtained materials are thermal stabilities up to 478 °C, quantum yields larger than 0.97, and high photostabilities. Thus, the covalent integration of dyes into polyphenylsiloxane structures represents a possible route for the stabilization of the organic dyes against the extreme irradiance and thermal conditions in LED applications. © 2019 The Authors. *Journal of Polymer Science Part B: Polymer Physics* published by Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2019**, *57*, 1062–1073

KEYWORDS: LED; optoelectronics; perylene; polysiloxane; silicone

INTRODUCTION Organic alternatives for inorganic rare earth containing conversion materials in light emitting diodes (LEDs) are an object of present research.^{1–4} In these applications, the organic dyes should substitute traditional rare earth containing conversion compounds, such as Y₃Al₅O₁₂:Ce³⁺, Lu₃Al₅O₁₂:Ce³⁺, CaAlSiN₃:Eu²⁺, (Ba,SrCa)₂Si₅N₈:Eu²⁺, or β-sialon:Eu²⁺.^{5–13} One of the major challenges in the targeted materials is the solubility and stability of the organic dyes in the matrix, which can be improved by a tailored design of the matrix polysiloxane. Organic dye-based converters are also attractive for clean and renewable energy generating applications, such as new efficient materials for photovoltaics and luminescent solar collectors (LSC). Quite stable and promising candidates for both types of applications are perylene diimide derivatives.^{14–20} The difference in the two mentioned applications are the irradiance conditions. While the irradiance in LEDs can be larger than 500 mW mm⁻², materials in photovoltaics and LSCs have only to withstand 100 mW cm⁻² under standard testing

conditions.^{21,22} Requirements for organic dyes and their matrices in these optoelectronic applications are high quantum yields as well as high thermal and photophysical stabilities, which are both necessary for improved lifetimes of the devices.^{2–4,23–29} Often used substrates for the integration of perylene dyes are poly(methyl methacrylates) and epoxy-based polymer materials.^{21,30–33} The physical or covalent integration of perylene diimide derivatives into various types of polymers can lead to improved materials properties.^{15,17,18,34–37} Examples for matrices in which the fluorescent dyes were already successfully incorporated are polystyrene and polydimethylsiloxanes.^{38–43}

The chemical inertness of polysiloxanes, their high thermal stabilities, high transparencies, and tunable refractive indices by side group substitution in combination with an incorporation of organic fluorescence dyes makes them excellent materials for an optimization with focus on dye stability.^{31–33} The integration of the commercially available perylene dye Lumogen®F Red

Additional Supporting Information may be found in the online version of this article.

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305 (LG305) into low refractive index (LRI) polysiloxanes for LSC applications revealed that the integrated light output of the samples correlates with an increased dye concentration up to 0.01 wt %.³⁰ At concentrations larger than 0.05 wt % the efficiency decreases significantly. The same results were found for the quantum yield (QY) of LG305 in another LRI polysiloxane for LED applications.¹ The QY started to decrease at LG305 concentrations ≥ 0.05 wt % due to the low solubility and consequent precipitation of LG305 in polydimethylsiloxanes. In our previous work, we were able to show that curable phenyl group containing high refractive index polysiloxanes (HRI) allow higher concentrations (≥ 0.3 wt %) of the dyes with constant high quantum yields and extended stabilities of covalently and non-covalently bonded perylene-based dyes.¹ One of the main reasons for this constant quantum yield and dramatically reduced crystallization is the separation of dye molecules due to the sterically demanding polymer matrix structure and due to the direct covalent bonding of the dye molecules to this structure.

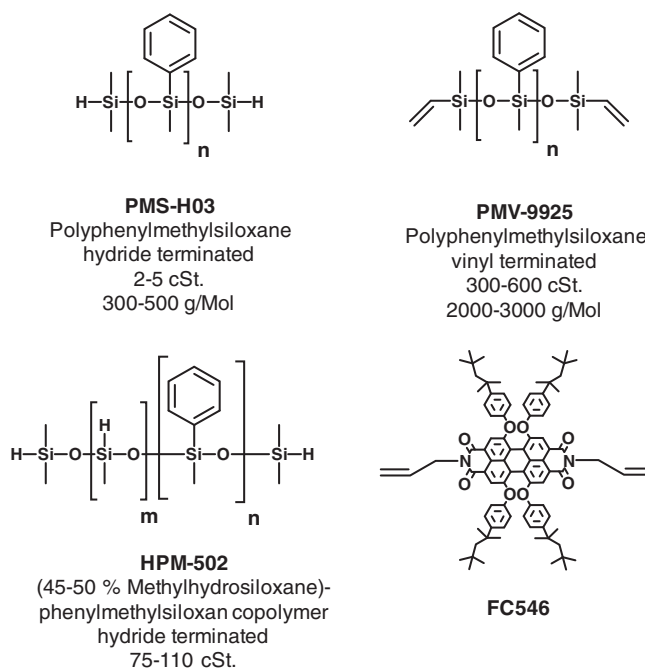
An integration of organic dye molecules into a linear polyphenylsiloxane backbone or cross-linked between polyphenylsiloxane chains separates the molecules locally. A subsequent covalent incorporation of these liquid perylene containing polymers into a heat curable polysiloxane resin leads to a solid and flexible material in which high dye concentrations can be incorporated and crystallization is inhibited. Additionally, increasing the phenyl group concentration or incorporating cross-linked siloxanes to a curable polymer resin can lead to enhanced gas barrier properties and thus decreases oxygen caused degradation phenomena.^{1,44,45} While linear and cross-linked polymers with perylene derivatives incorporated have already been published, the resulting materials are not suitable for a subsequent covalent integration into a curable matrix system by hydrosilylation.^{39,40,46,47}

In the presented study, the allyl group containing perylene diimide dye FC546 was used to synthesize two different perylene polysiloxanes with various dye concentrations in the backbone of a polymethylphenylsiloxane (PMPS) and cross-linked to the pendant hydride groups of a methylhydrosiloxane-phenylmethylsiloxane copolymer. Both polymer classes were synthesized by a platinum catalyzed hydrosilylation reaction. By changing the ratio of the hydride and vinyl terminated PMPS precursors the chain length was modified systematically. Subsequently, the liquid perylene polymers were covalently integrated in a thermally curable phenyl containing HRI polysiloxane resin.

EXPERIMENTAL

Materials

Polyphenylmethylsiloxane hydride terminated (*PMS-H03*, Gelest Inc., Morrisville, PA), polyphenylmethylsiloxane vinyl terminated (*PMV-9925*, Gelest Inc.), (45–50% methylhydrosiloxane)-phenylmethylsiloxane copolymer hydride terminated (*HPM-502*, Gelest Inc.), the platinum carbonyl cyclovinylmethylsiloxane complex (*Ossko-Catalyst*, 1.85–2.1% Pt in vinylmethylcyclosiloxane, Gelest Inc.) and the commercially available, curable *OE6630* polysiloxane resin [Dow(1), Dow Corning Inc., Midland, MI] were used as received without any further purification



SCHEME 1 Structures, names, abbreviations, and important properties of the polymer and dye precursors.

(Scheme 1). The Dow(1) two component resin contains a Si-H and a Si-vinyl component.¹ It is thermally curable by thermal treatment of the mixed components. The curing process is a platinum catalyzed hydrosilylation. The allyl functionalized organic dye FC546 was provided by BASF SE and was also used as received. The synthesis of FC546 was already published in a previous work.¹ FC546 contains *N,N'*-diallyl units which permit a covalent integration into the polysiloxane backbone or network *via* hydrosilylation. Four 2,4,4-trimethylpentan-2-yl phenoxy units in *bay position* were introduced to increase the solubility in the phenyl containing polymers and in organic solvents like toluene (Scheme 1). The emission maximum is detected at 602 nm ($16,611\text{ cm}^{-1}$), the excitation maximum is detected at 574 nm ($17,421\text{ cm}^{-1}$) in toluene (Fig. S1). A local excitation maximum is detected at 450 nm ($22,222\text{ cm}^{-1}$) caused by the substituents in bay position. The precursor's purity was characterized by NMR and FTIR spectroscopy (Figs. S2-S10).

Instrumentation

Fourier transformed infrared spectra (FTIR) were recorded in total reflectance mode on a Vertex 70 spectrometer (Bruker Corporation, USA) from $4500\text{--}400\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} increment and 10 scans averaged. UV-vis transmission measurements were performed on a Lambda 750 instrument (Perkin Elmer Inc., USA) equipped with a 100 mm integration sphere from 700 to 350 nm with a 2 nm increment and 0.2 s integration time. Fluorescence spectroscopy was performed applying a FluoroMax 4 Spectrofluorometer (Horiba Scientific, Japan) with an excitation wavelength of 450 nm and an emission wavelength of 630 nm. The absolute photoluminescence quantum yields and the emission spectra were measured in a Quantaaurus C11347-11 integration sphere setup (Hamamatsu Photonics, Japan) with a

xenon high-pressure lamp and a multichannel analyzer at 450 nm excitation wavelength. NMR spectra were recorded with an Avance III 300 MHz spectrometer and an Avance III HD 400 MHz spectrometer (Bruker Corporation, USA) at 300.13/400.13 MHz for ^1H NMR and at 59.63/79.49 MHz for ^{29}Si NMR. All NMR samples were prepared in chloroform-D (CDCl_3). SEC measurements were performed with concentrations of 2 g l^{-1} sample in THF applying a PSS-SDB-1000 Å and a PSS-SDB-100000 Å column with 1 ml min^{-1} and a RI-Shodex and a UV-Waters 2487 detector. In a further experiment, we applied a setup with sample concentrations of 4 g l^{-1} in THF using a PSS-SDV-1000 Å or a PSS-SDV-10000 Å column with 1 ml min^{-1} and a RI-SECURITY² and a UV-SECURITY² detector. Thermogravimetric measurements were carried out with a TG209 F1 Libra thermomicrobalance (Netzsch-Gerätebau GmbH, Germany) applying a heating rate of 10 K min^{-1} up to 250 or 800°C with gas flux of N_2/O_2 of 20 ml min^{-1} each. Differential scanning calorimetry was performed with a Netzsch DSC 204 F1 Phoenix calorimeter with aluminum crucibles with pierced lids under nitrogen (100 ml min^{-1}) with a heating rate of 5 K min^{-1} from -40 to 400°C . Hardness measurements were performed using a Sauter HBA-100 Shore A durometer (Sauter GmbH, Germany). A self-constructed fiber coupled 450 nm wavelength illumination system with 710 mW LEDs ($6 \times \text{LDW5SN}$) was used as irradiation source for photostability experiments.

Quantum Yield and Self-Absorption Coefficients

For the quantification of dye stability and efficiency after the integration of the perylene polymers to a curable polysiloxane resin the absolute quantum yield of all solid samples has been measured before and after curing, as well as after a post-curing procedure. In these experiments, solid samples ($7 \times 7 \times 1 \text{ mm}$) were measured in an integration sphere setup in reflectance mode with an excitation wavelength of 450 nm. From the quantum yield emission spectra the self-absorption coefficients were determined. Therefore, a cured sample of Dow(1) with a very low concentration of FC546 (15 ppm dye by weight) with virtually zero self-absorption was prepared. The emission spectra of the samples were scaled by a fit to the zero self-absorption spectrum leading to a normalization in an area, which is not effected by self-absorption. The quality of the fit was verified by Pearson's chi squared test. The procedure was already described in literature in more detail.^{1,48,49}

Preparation

The covalent integration of FC546 into the polymer backbone (P-FC546 series) was performed by mixing phenylmethylpolysiloxane PMS-H03 and PMV-9925 in variable ratios before adding the dye (Scheme 1). The cross-linking integration of FC546 into HPM-502 (OPSB-FC546 series) requires no premixing (Scheme 2). A stock solution of FC546 was used (0.1 wt %, toluene) to add a defined amount of dye to the polymers ($m(\text{polymer} + \text{dye}) = 500 \text{ mg}$ for each sample). Toluene was added to increase the total volume of solvent to 5 ml. Ossko-catalyst was diluted (0.18% Pt in xylene) and added (2 ppm Pt[0] referred to the product mass) to the mixture which was stirred at 100°C for 24 h. Afterwards the solvent was removed under reduced

pressure. The liquid products are denominated P-FC546 for the linear polymers and OPSB-FC546 for the cross-linked polymers.

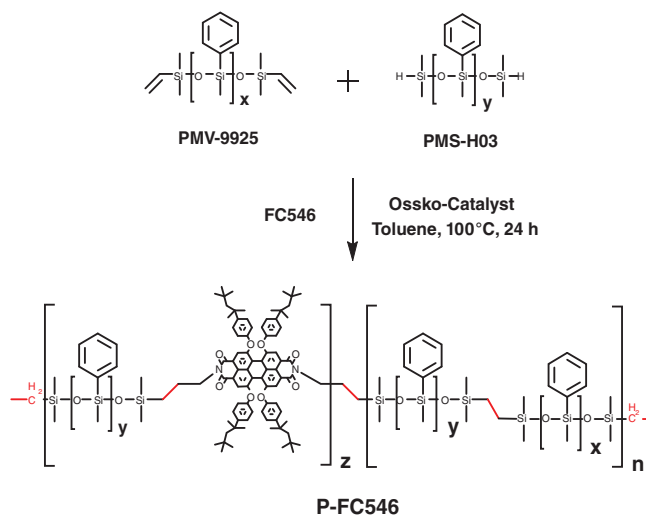
For the subsequent integration of P-FC546 or OPSB-FC546 into the Dow(1) resin the two Dow(1) components A and B were pre-mixed as specified by the manufacturer (4/1). The perylene containing polymers were added to the mixture respectively and gas was removed under reduced pressure (4 mbar, >30 min) before casting the mixture into PTFE ($30 \times 10 \times 1 \text{ mm}$) or aluminum molds ($8 \times 2 \text{ mm}$). The samples are denoted by the name of the commercial resin Dow(1), the respective dye integrated perylene polysiloxanes and the final dye concentration in the perylene polysiloxanes in % and in the cured resin in ppm by weight.

RESULTS AND DISCUSSION

New polysiloxanes were synthesized by covalent attachment of the perylene dye to different polymer precursors. In the first precursor, the allyl-modified dye molecules were integrated linearly into the polymer by hydrosilylation with α,ω -Si-H-group containing polysiloxanes. The second precursor polymer was prepared by cross-linking the polysiloxane chains with the dye molecules by hydrosilylation of pendant Si-H groups in the linear polymer chains. Both methods result in liquid polymer structures in which the integrated dye molecules are separated from each other, which cause a reduced possibility of stacking phenomena, excimer formation, and solubility problems in the final polysiloxanes matrix. The influence of the various bonding modes as well as the final polymer structure on the dye properties was studied.

Linear Perylene Polysiloxanes

The linear polysiloxanes were prepared by using a hydride terminated polyphenylmethylsiloxane (PMS-H03) and a vinyl terminated polyphenylmethylsiloxane (PMV-9925). Applying a



SCHEME 2 Synthesis of P-FC546 perylene polysiloxane by hydrosilylation of a vinyl and a hydride terminated precursor. The FC546 dye is part of the polymer backbone due to missing pendant hydride groups. [Color figure can be viewed at wileyonlinelibrary.com]

platinum catalyst the terminated Si-H and Si-vinyl groups start to form C-C single bonds leading to longer chains. By adding small amounts of the FC546 dye, the dye can also react in the hydrosilylation reaction and thus, was also incorporated into the formed polymer backbone (Scheme 2).

Cross-linked Perylene Polysiloxanes

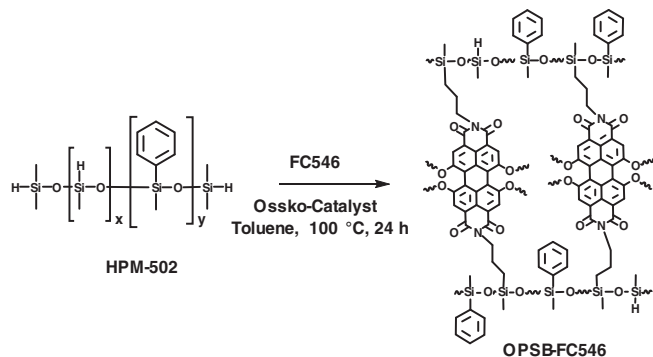
We investigated a second route to incorporate the FC546 dye covalently in a liquid polysiloxane. In this case, a polymethylhydrosiloxane-phenylmethylsiloxane copolymer with pendant and terminal hydride atoms was used as precursor (HPM-502). Applying a platinum catalyst the Si-H groups start to form C-C single bonds with the dye molecules (Scheme 3).

Due to the pendant Si-H groups, the precursor polymer chains can be cross-linked with each other. The resulting products are still liquid and denoted as OPSB-FC546. In these studies, only one polymer precursor was used and allowed the systematic investigation of the effect of dye concentration. The synthesized polymers are denoted with OPSB-FC546 X% with X = 0.05, 0.1, 1, and 8. The highest concentrated sample with 8 wt % dye covalently incorporated was only prepared for a better detection in IR and NMR spectroscopy.

Precursor Incorporation in Curable Polysiloxane Resin

The synthesized perylene polysiloxanes are not suitable for a direct use in optoelectronics because they are still liquids. Optoelectronic suitable solid materials were obtained by a subsequent addition of the polymers to a thermally curable, two component polysiloxane resin incorporating 100 ppm dye in the final cured sample (Fig. 1). In applications in which high temperatures are predominant at working conditions, polysiloxane resins are subject to post-curing processes.

This is the reason why the absolute quantum yield and the hardness (Shore A) of the samples were determined for both cases, directly after preparation of the samples and after a post-curing process (200 °C, 48/120 h). The corrected quantum yields and the self-absorption coefficients were calculated from the absolute quantum yield emission spectra, respectively (see Supporting Information).^{1,48,49}



SCHEME 3 Synthesis of OPSB-FC546 perylene polysiloxane by hydrosilylation of a polysiloxane with hydride pendant and terminated groups with FC546. The FC546 dye is cross-linking the polymer chains.

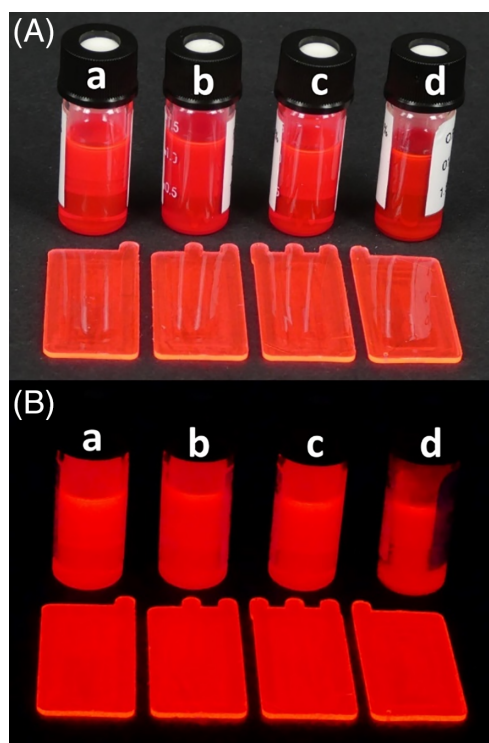


FIGURE 1 (A) Image of the liquid perylene polysiloxanes (a) P2-FC546, (b) P3-FC546, (c) P4-FC546, and (d) OPSB-FC546 0.1% and casted specimen of the same precursor polymers mixed with the OE6630 resin and cured subsequently for 4 h at 150 °C below. (B) Samples shown in (A) excited with a 450 nm light source. [Color figure can be viewed at wileyonlinelibrary.com]

Under working conditions, the local temperature at the light emitting InGaN chip of a LED for example can reach up to 150 °C and the irradiance can reach values $>500 \text{ mW mm}^{-2}$ (at $\lambda = 450 \text{ nm}$). The dye-incorporated matrices need to withstand these extreme conditions to ensure a long and stable performance. For a simulation of these working conditions a variety of cured samples was exposed to light (450 nm, 710 mW LEDs (6 × LDW5SN) and other samples were exposed to high temperature (200 °C, air) for several hours. Transparency measurements by optical spectroscopy can detect a change in color, which is usually caused by dye degradation due to light exposition. The influence of the thermal treatment was determined by measuring changes in quantum yield. Additionally changes in the cured polymer resin structure due to the incorporation of the perylene polymers were investigated by thermogravimetric (TG) and differential calorimetric measurements (DSC).

Chain Length Variation of Linearly Incorporated Dye Polymer with Constant Dye Concentration

By changing the hydride to vinyl ratio of the precursors with a constant dye concentration of 0.1 wt % chain length of the perylene polymers were modified. The nomenclature of the samples was chosen to differentiate between the samples

TABLE 1 Composition of the different samples with the FC546 dye in the PX-FC546 polymer

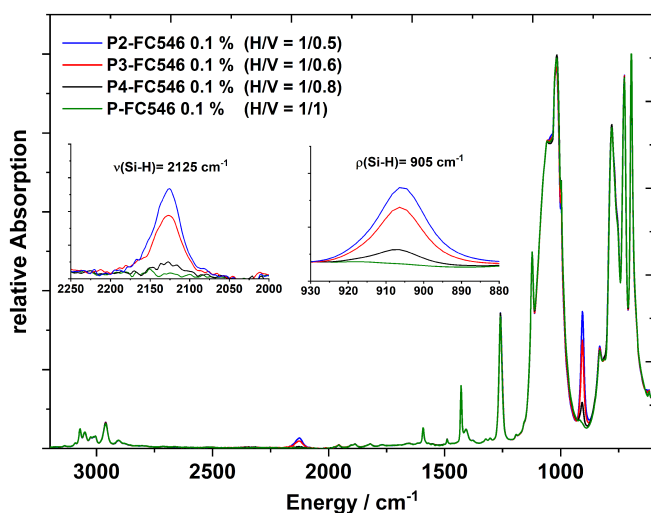
	n(PMS)/		m(PMS)/g	m(PMV)/g	c(FC546)/wt %
	PX-FC546 0.1%	n(PMV)			
5	1/1	0.0689	0.4310	0.1	
4	1/0.8	0.0833	0.4166	0.1	
3	1/0.6	0.1052	0.3947	0.1	
2	1/0.5	0.1212	0.3788	0.1	

(Table 1). SEC, FTIR, and ^1H NMR spectra were measured directly after the synthesis. The FTIR spectra show the anticipated vibration bands for phenyl containing polysiloxane type polymers (Fig. 2).^{50–53}

Specific aromatic vibration bands due to phenyl side groups at 3045, 3070 [$\nu(\text{C-H})_{\text{AR}}$]; 1488, 1429 [$\nu(\text{C}=\text{C})_{\text{AR}}$]; and 725, 694 [$\delta(\text{C-H})_{\text{AR}}$] cm^{-1} can be detected next to the silicon oxygen vibrations at 1014, 1048, and 1120 cm^{-1} [$\nu(\text{Si-O-Si})$].

Two additional vibration bands according to the Si-H bond at 2125 cm^{-1} [$\nu(\text{Si-H})$] and 905 cm^{-1} [$\rho(\text{Si-H})$] are also present. These bands can be used to differentiate between the samples. At a PMS/PMV ratio of 1/1 no Si-H vibrations can be detected while a decreasing vinyl concentration leads to an increasing number of unreacted Si-H groups. This agrees with the assumption that a higher concentration of the hydride terminated PMS-H03 leads to a higher concentration of Si-H terminated reaction products and to lower chain lengths.

An increase of molecular weight (M_w) compared with the precursor polymers are caused by the hydrosilylation reaction. The stepwise increase of the ratio of the hydride and vinyl terminated precursor polymers leads to an increase of M_w as expected (Table 2). The product elugrams show that there are still traces

**FIGURE 2** FTIR spectra of P-FC546 and the PX-FC546 - 0.1% series with $x = 2, 3, 4$. [Color figure can be viewed at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com)]**TABLE 2** Molecular weight M_w and polydispersity index D for various polymers

Sample	$M_w/\text{g mol}^{-1}$	D
PMS-03	420/400 ^a	1.1
PMV-9925	2500/2500 ^a	2.4
P4-FC546 0.1%	8400	1.9
P3-FC546 0.1%	6080	1.7
P2-FC546 0.1%	5660	1.7

^a M_w taken from the manufacturer data sheet.

of unreacted polymeric educts. The polydispersity is larger than 1.7 but very similar for all measured samples and in the same range like other polysiloxanes synthesized by hydrosilylation or ring-opening polymerization with values from 1.2 to 3.5.^{54–57}

The ^1H NMR spectra show all anticipated chemical shifts of the polymers at 7.86–6.88 (m, Phenyl-H) and 0.62 – –0.26 ppm (m, Si-CH₃) (Fig. S11). Additionally, small signals of the incorporated dye can be detected at 1.37 (s, FC546) and 0.79 ppm (s, FC546) next to impurities at 2.00 (s), 1.55 (s, water), and 1.27 ppm (s). The intensity of the chemical shift at 4.76 ppm according to the hydrogen atom in the Si-H group is decreasing from P2-FC546–0.1% to P5-FC546–0.1% due to the decrease of unreacted Si-H groups. This result corresponds with the FTIR data shown before. The spectroscopic data and chromatographic data prove the successful synthesis of linear polymers with different chain length and the covalent integration of FC546.

Variation of Dye Concentration in Linear Dye Incorporated Polymers with Equal Chain Length

The influence of the polymer chain length and the covalent bonding of the dye was investigated by maintaining the hydride to vinyl ratio of the precursors constant (1/0.5 [P2-FC546]) and increase the dye concentration from 0.025 to 1 wt % stepwise (Table 3). The FTIR spectra show the anticipated vibration bands for phenyl containing polysiloxane type polymers as described and assigned in the section before (Fig. 3).^{50–53}

The two vibration bands according to the Si-H bond at 2125 cm^{-1} [$\nu(\text{Si-H})$] and 905 cm^{-1} [$\rho(\text{Si-H})$] show a decrease of intensity, which is an indication of the covalent incorporation of

TABLE 3 Composition of the different samples with the FC546 dye in the P2-FC546 polymer

P2-FC546 X %	m(FC546)/mg	n(FC546)/ μmol	c(FC546)/%
0.025	0.125	0.097	0.025
0.05	0.25	0.194	0.05
0.1	0.4	0.388	0.1
0.25	1	0.971	0.25
0.5	2.5	1.941	0.5
1.0	5	3.883	1.0

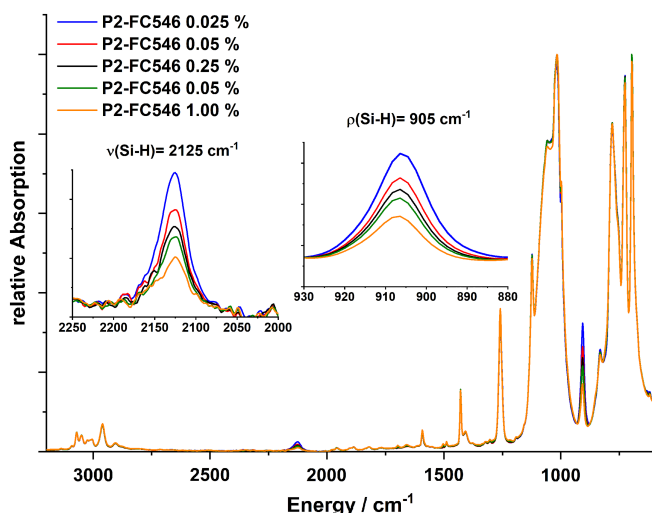


FIGURE 3 FTIR spectra of the P2-FC546 - X% series with X = 0.025, 0.05, 0.25, 0.5, and 1.0. [Color figure can be viewed at wileyonlinelibrary.com]

the FC546 dye molecules into the polymer backbone by the hydrosilylation reaction. If there were no attachment to the polymer, the intensity would be equal for every sample.

The decrease of hydride vibration bands intensity is directly correlated to the increase in dye concentration. As a result, a higher dye concentration should also lead to slightly longer polymer chains if the dye is not attached as an end group. By comparing the SEC data, no systematic changes in chain lengths can be detected due to the change of dye concentration (Table S9), which is most likely based on the low concentration of the dye and the possibility of attaching it as a polymer end group. Due to the high concentration of 1% dye in the sample P2-FC546 all chemical shifts of the incorporated FC546 dye can be detected in a much better resolution than in the lower concentrated sample P2-FC546 0.1% discussed before. FC546 shows two specific chemical shifts for the allyl functionalization caused by the methylene (5.12 ppm, 2H) and methine protons (5.93 ppm, 4H) (Fig. S10). Due to the covalent integration by hydrosilylation these shifts are not detectable in the perylene polymer anymore, which also verifies the covalent bonding to the polymer backbone (Fig. S12).

Cross-linking of Polymer Chains by Variations in Dye Concentration

By reacting the allyl groups FC546 with polymers with pendant hydride groups a cross-linked perylene polymer is formed

TABLE 4 Composition of the different samples with the FC546 dye in the OPSB-FC546 polymer

Sample	m(FC546)/mg	n(FC546)/ μ mol	c(FC546)/%
OPSB-FC546 - 0.1%	0.5	0.38	0.10
OPSB-FC546 - 1.0%	5.0	3.88	1.00
OPSB-FC546 - 8.0%	40.0	31.06	8.00

(Table 4). The total mass of the polymer and the added dye was 500 mg for each sample, except for the high concentrated sample OPSB-FC546-8.0%, where the dye was weighted and directly added to the polymer instead of using a stock solution (see section 2). The FTIR spectra reveal the anticipated vibration bands for phenyl containing polysiloxane type polymers as described and assigned in the section before.⁵⁰⁻⁵³ The two vibration bands according to the Si-H bond at 2160 cm^{-1} [$\nu(\text{Si-H})$] and 900 cm^{-1} [$\rho(\text{Si-H})$] show no change of intensity at lower dye concentrations. At the highest concentration of 8% a significant increase occurs, due to the covalent attachment of the dye to the polymer structure (Fig. 4).

This missing intensity change of the Si-H vibration at low dye concentrations according to a covalent integration of FC546 is caused by the very high concentration of Si-H units in the polymer chain. In the synthesis of the P-FC546 polymers, the hydride terminated PMS-H03 contains two Si-H units per molecule. In the HPM-502 that is used for the OPSB-FC546 synthesis contains 45-50% of the polymer's silicon atoms attached to a pendant hydride atom. A reaction with a small amount of FC546 does not change the signal intensity significantly and measurable.

The ^1H NMR spectra of the sample OPSB-FC546-8.0% shows every anticipated chemical shifts of the polymer and the FC546 dye except the methylene and methine protons of the allyl groups of the dye. As described before, FC546 shows two specific chemical shifts for the allyl functionalization caused by the methylene (5.12 ppm, 2H) and methine protons (5.93 ppm, 4H). The HPM-502 polymer reveals no chemical shifts in this area. By just mixing an unspecific amount of FC546 and HPM-502, the sum spectrum of the corresponding chemical shifts can be observed (Fig. 5). After the hydrosilylation reaction of 8 wt % of FC546 with HPM-502 (OPSB-FC546 8% is formed), the methylene and methine proton chemical shifts of FC546 allyl groups disappeared and a new shift for the formed methylene proton of the C-C single bond is observed (1.49 ppm, 4H).

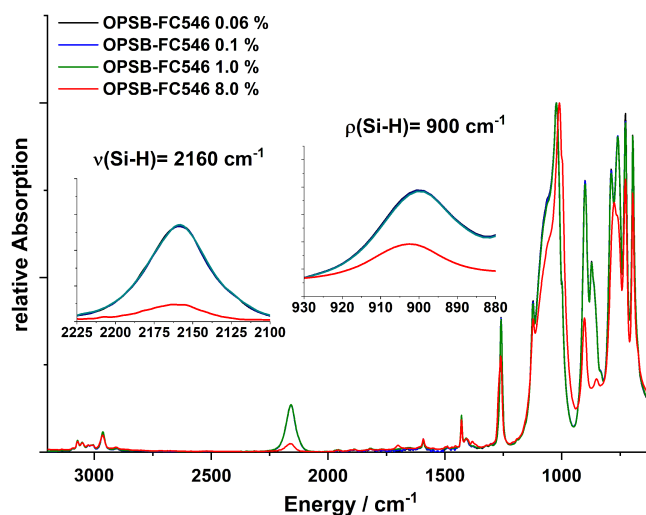


FIGURE 4 FTIR spectra of the OPSB-FC546 - X% series with X = 0.06, 0.1, 1.0, and 8.0. [Color figure can be viewed at wileyonlinelibrary.com]

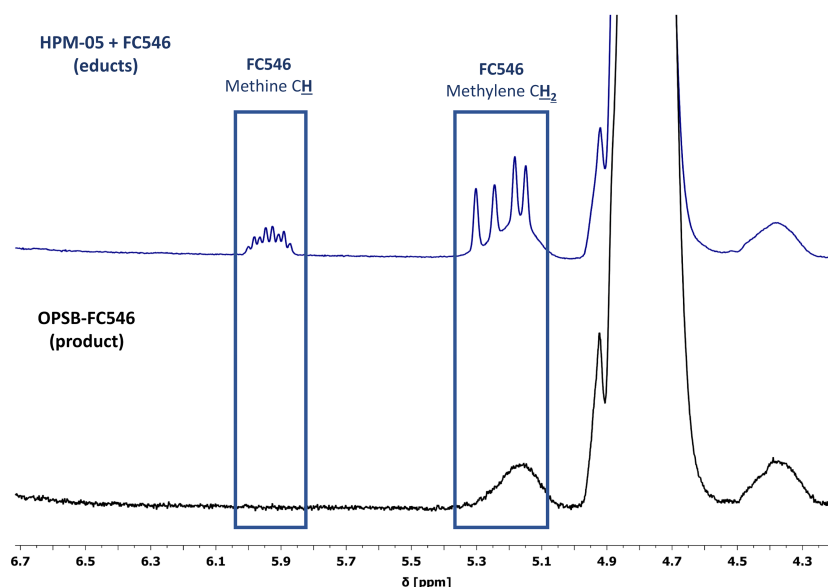


FIGURE 5 ^1H NMR spectra of OPS-B-FC546 8% before and after the hydrosilylation reaction measured in chloroform-D. [Color figure can be viewed at wileyonlinelibrary.com]

From the ^1H NMR spectra the percentage of phenyl groups was calculated for a quantitative comparison. Compared with the P-FC546 series with 38% phenyl groups the OPSB-FC546 samples contain only 29%. This is also caused by the high concentration of methylhydrosiloxane units of 45–50% in the OPSB-FC546 samples.

The SEC is calibrated with linear polystyrene standards. This leads to a significant inaccuracy by determining cross-linked polysiloxanes. Nevertheless, we tried to determine the M_w of one of the OPSB-FC546 samples exemplarily. The SEC of the linear OPSB precursor polymer shows M_w values of 1400 g mol^{-1} and a polydispersity index of 4.1. The OPSB-FC546–0.1% sample shows an M_w value of $13,470 \text{ g mol}^{-1}$ and a polydispersity of 3.1 (SEC data and elugrams are part of the Supporting Information). The M_w of this OPSB-FC546–0.1% sample increases significantly (~ 10 times). This is another indirect proof of the expected cross-linking properties of FC546 when it is reacted to polymers with pendant hydride groups.

Integration of Perylene Polysiloxanes to a Curable Resin

A selection of the prepared perylene polysiloxanes were added to a commercially available, two component polysiloxane resin (Dow Corning OE6630 [Dow(1)]). Subsequently, the mixtures were cured according to the supplier's temperature profile to form solid samples containing 100 ppm dye, respectively. For the Dow(1)PX-FC546 0.1% - 100 ppm series with a constant dye concentration the amount of perylene polysiloxane added to the resin is 10 wt %. For the other perylene polymers with different dye concentrations incorporated the amount was adjusted to get 100 ppm dye in the cured samples (Table 5). The perylene polymers are completely mixable with the two Dow(1) components without any haze or precipitation. At working conditions in optoelectronic devices, especially in LEDs, high temperatures up to 200°C affecting cured polysiloxane resin and the incorporated dyes by inducing a post-curing process. This is why the absolute quantum yield and the hardness (Shore A) of the samples were determined directly after preparation of the samples and after a post-curing process (200°C , 48/120 h). For a further characterization of changes in

TABLE 5 Composition of the cured polymers from Dow(1) component A and the perylene polysiloxane precursors

Sample	m(Dow(1)-A)/g	m(Dow(1)-B)/g	m(Peryl. Polys.)/g	Phosphor conc./ppm
Dow(1)PX-FC546 0.1% - 100 ppm (X = 2, 3, 4, 5)	0.720	0.180	0.10	100
Dow(1)P2-FC546 0.025% - 100 ppm	0.480	0.120	0.40	100
Dow(1)P2-FC546 0.05% - 100 ppm	0.640	0.160	0.20	100
Dow(1)P2-FC546 0.25% - 100 ppm	0.768	0.192	0.04	100
Dow(1)P2-FC546 0.5% - 100 ppm	0.784	0.196	0.02	100
Dow(1)P2-FC546 1.0% - 100 ppm	0.792	0.198	0.01	100
Dow(1)OPSB-FC546 0.05% - 100 ppm	0.664	0.166	0.17	100
Dow(1)OPSB-FC546 0.1% - 100 ppm	0.720	0.180	0.10	100
Dow(1)OPSB-FC546 1.0% - 100 ppm	0.792	0.198	0.01	100

TABLE 6 The degradation temperatures T_{95} of the samples

Sample	$T_{95}/^{\circ}\text{C}$
Dow(1)	465
Dow(1)FC546 - 100 ppm	468
Dow(1)P2-FC546 0.025% - 100 ppm	433
Dow(1)P2-FC546 0.05% - 100 ppm	450
Dow(1)P2-FC546 0.1% - 100 ppm	474
Dow(1)P2-FC546 0.5% - 100 ppm	472
Dow(1)P2-FC546 1.0% - 100 ppm	470
Dow(1)P3-FC546 0.1% - 100 ppm	469
Dow(1)P4-FC546 0.1% - 100 ppm	472
Dow(1)OPS-B-FC546 0.1% - 100 ppm	478

the resin structure due to the incorporation of the perylene polymers FTIR spectra were measured and thermogravimetric as well as calorimetric measurements were performed.

Quantum Yield and Heat Treatment

The Dow(1)PX-FC546 0.1% - 100 ppm and the Dow(1)P2-FC546 X% - 100 ppm samples show no significant changes in the quantum yield (QY) compared with the quantum yield of the prepolymer samples (Fig. 6). This was expected because the dye concentration is low (100 ppm) and equal in every cured sample.

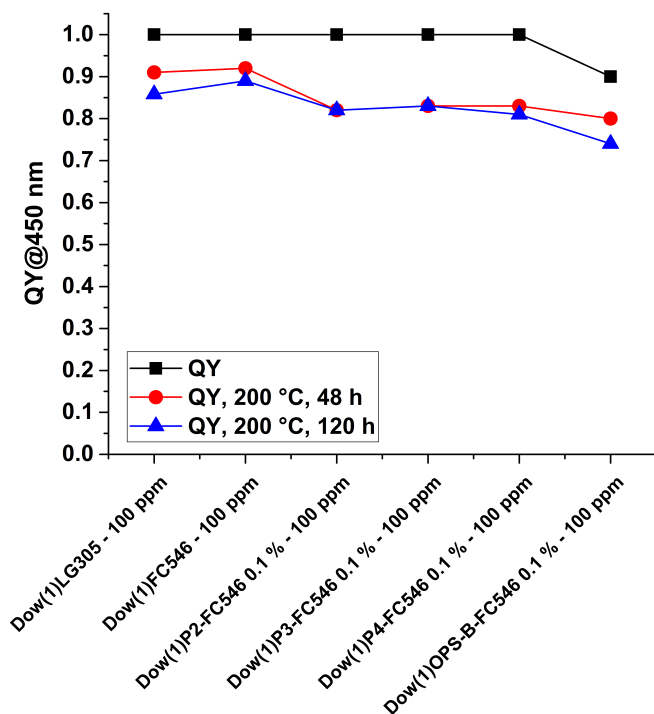


FIGURE 6 Absolute quantum yield of the cured Dow(1) samples with the PX-FC546 0.1% or the pure dye incorporated measured with an excitation wavelength of 450 nm directly after the synthesis, as well as after a first (200 °C, 48 h) and a second heat treatment (200 °C, 72 h). [Color figure can be viewed at wileyonlinelibrary.com]

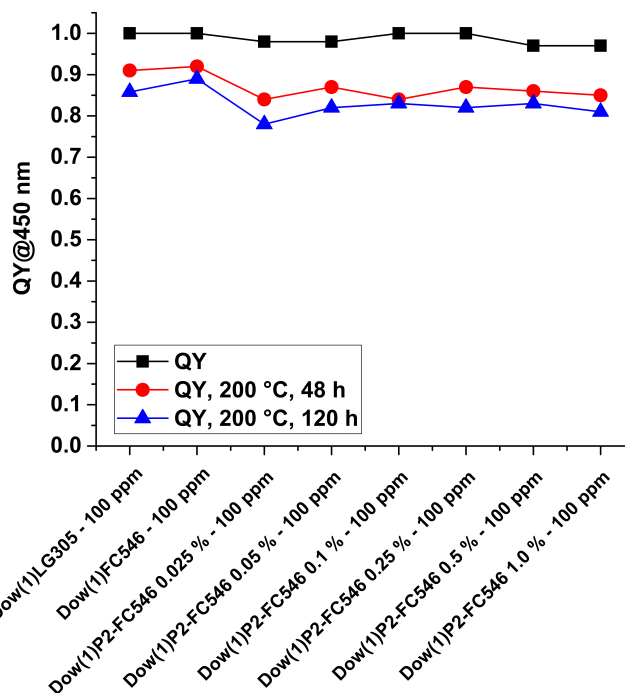


FIGURE 7 Absolute quantum yield of the cured Dow(1) samples with the P2-FC546 X% series or the pure dye incorporated measured with a excitation wavelength of 450 nm directly after the synthesis, as well as after a first (200 °C, 48 h) and a second heat treatment (200 °C, 72 h). [Color figure can be viewed at wileyonlinelibrary.com]

The differences in dye concentrations of the perylene polymer precursors do not affect the final QY either. In previous results, we already showed that the influence of the dye concentration to the QY in phenyl containing polysiloxanes is insignificant compared with only methyl containing polysiloxanes. This can be explained by the high solubility of the dye caused by a closer physicochemical compatibility of sterically demanding perylene molecules to phenyl containing polymers.¹

The QY is above 0.97 for all samples. Neither the chain length of the perylene polysiloxane nor the concentration of the bonded dye molecules shows significant influences to the QY (Fig. 7).

The Dow(1)OPSB-FC546 X% - 100 ppm samples show a decrease in QY correlated to the increase of dye concentration from 0.95 (X = 0.05%) to 0.875 (X = 1%). In the P-FC546 compounds polymer chains separate the dye molecules. π - π -Interactions of dye molecules leading to quenching effects are less probable in these samples. Furthermore, the high concentration of phenyl side groups leads to a sterically shielding and of the dye units as shown in a previous paper.¹

In the OPSB-FC546 polymers, the separation of the FC546 dye molecules is influenced by distribution of silicon hydride units. The molecules can be attached to directly neighboring silicon atoms, which would increase the possibility of dye-dye interactions. This is more probable with an increasing dye concentration as reported for perylene bridged ladder polysiloxane, synthesized by polycondensation, where an increased π - π stacking interaction

at high concentrations is caused by the direct localization of the molecules next to each other.⁴⁷ As a consequence, a decrease in quantum yield is possible.

Again, we believe that the phenyl groups in the Dow(1) matrix decrease the π - π stacking probability of single dye molecules.^{1,58,59} The phenyl units are able to interact with incorporated dyes core. The separation of the dye molecules and the dilution leads to a quantum yield increase. The QY of the isolated OPSB-FC546 1.0% (QY = 0.452) is 1.93 times lower compared with the diluted Dow(1)OPSB-FC546 1.0% - 100 ppm (QY = 0.875) sample. The QY of all measured samples decreased after the first post curing heat treatment (48 h, 200 °C). The highest decrease was detected for the Dow(1)PX-FC546 0.1% - 100 ppm series $\geq 18\%$.

After the second heat treatment (72 h, 200 °C) the decrease of QY is not significant for all samples. The slightly higher methyl group concentration of the OPSB-FC546 polymers has no impact on the temperature stability. The influence of the post-curing heat treatment to the dye-dye interaction or to the structural integrity of the dye molecules and the significantly higher dye stability in the Dow(1) matrix compared with the covalently or non-covalently bonded perylene dyes in curable non-phenyl containing polydimethylsiloxanes was discussed in former studies.¹

The incorporation of the FC546 dye in a perylene polysiloxane before adding it to a curable polysiloxane resin does not change the dyes properties responsible for the high QY compared with a direct integration. The measured QY, the corrected QY, the self-absorption coefficients, and the emission spectra from the QY-measurements ($\lambda_{\text{ex}} = 450 \text{ nm}$) are part of the Supporting Information. The self-absorption

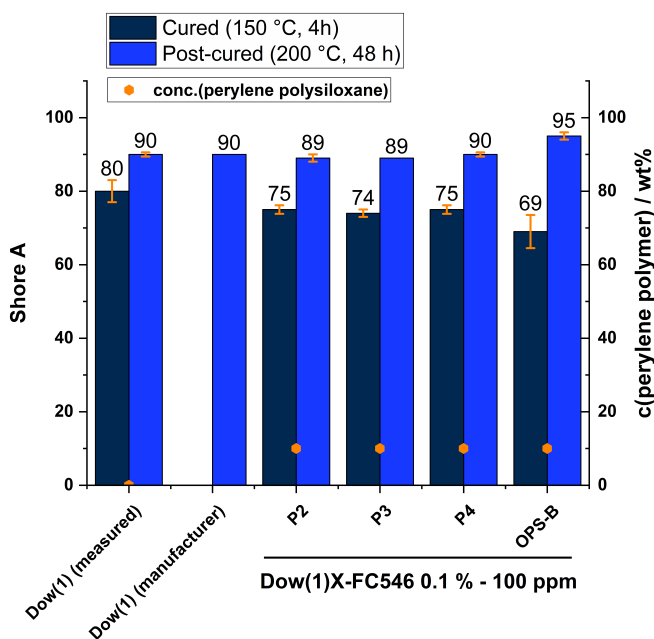


FIGURE 8 Shore A values of the cured Dow(1) samples with the linear perylene polymers PX-FC546 0.1% and OPS-B FC546 0.1% incorporated compared to the pure cured Dow(1) resin. [Color figure can be viewed at wileyonlinelibrary.com]

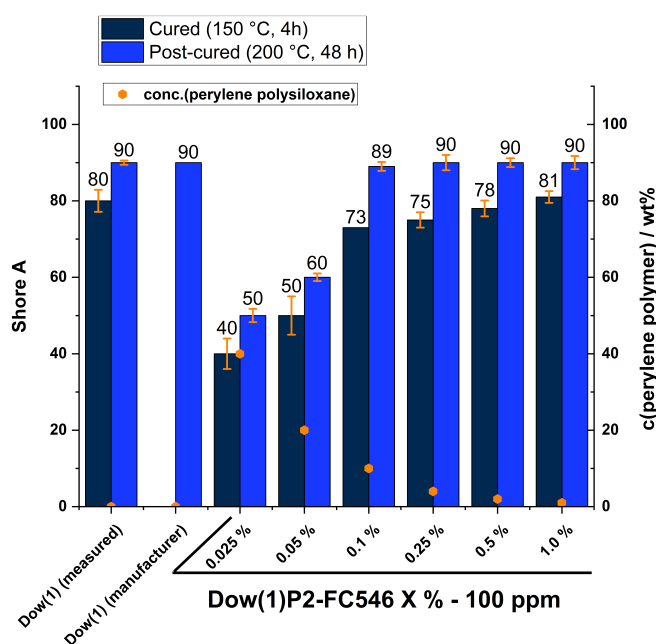


FIGURE 9 Shore A values of the cured Dow(1) samples with the linear perylene polymers P2-FC546 X% incorporated compared with the pure cured Dow(1) resin. [Color figure can be viewed at wileyonlinelibrary.com]

coefficient was calculated by using the emission spectra of a very low concentrated sample with virtually zero self-absorption (Dow(1)FC546-15 ppm) as described in literature.^{1,48,49}

FTIR, Hardness, Thermal, and Calorimetric Investigations

Due to the addition of the perylene polysiloxane to the Dow(1) resins components a change in structure, respectively, material properties are expected. The stability of the cured materials was studied by detecting the T_{95} value in the TGA. To evaluate the different materials state of degradation the temperature at which the samples possess 95% of their original mass is defined as T_{95} value. Therefore, larger T_{95} values reveal higher thermal stability of the materials.

The mixing proportions, given by the manufacturer were retained, but the total number of polymer chains and reactive groups is increased by the perylene polysiloxane addition. By measuring the hardness of the cured samples directly after the curing procedure and after the additional post-curing process (120 h, 200 °C), conclusions about mechanical changes can be made (Fig. 8). The hardness of the Dow(1)PX-FC546 0.1% - 100 ppm series is not affected by the addition of 10 wt % of perylene polysiloxane compared with the pure Dow(1) sample (Shore A = 90). The Dow(1)OPSB-FC546 1% - 100 ppm sample shows a slight increase of hardness (Shore A = 95). The Dow(1)P2-FC546 X% - 100 ppm series show an increase of hardness with an increase of perylene polymer concentration (Fig. 9). The trend in hardness directly correlates with the thermogravimetric data and the degradation temperatures of the post-cured samples, respectively (Table 6).

All samples show a high T_{95} degradation temperature above 433 °C. The T_{95} of all samples with dye concentrations larger than 0.1 wt % dye in the perylene polysiloxane slightly higher than the pure Dow(1) matrix with an insignificant deviation of 6 °C (468–474 °C).

The lowest T_{95} values were measured for the Dow(1) P2-FC546 0.025% - 100 ppm (433 °C) and Dow(1)P2-FC546 0.05% - 100 ppm (450 °C) samples. The highest T_{95} value was observed for the Dow(1)OPS-B-FC546 0.1% - 100 ppm sample (478 °C). Comparable cross-linked structures like perylenediimide-bridged ladder polysiloxanes show lower T_{95} values of 430 °C.⁴⁷ The increases of hardness and degradation temperatures are not caused by the higher dye concentration but by the higher amount of perylene polysiloxane added to the Dow(1) matrix.

The hydride and vinyl terminated Dow(1)P2-FC546 polymers widen the actually closer-meshed network of the pure Dow (1) matrix (>10 wt %), which leads to a more flexible and less stable structure. Whereas the already cross-linked OBSB-FC546 perylene polysiloxane, with its additional pendant hydride atoms, is cross-linking the Dow(1) matrix furthermore, even in small amounts, which explains the increase of hardness and thermal stability. Additionally, due to the increased polymer and hydride concentration in the Dow(1)P2-FC546 X % - 100 ppm samples, respectively, the manufacturers curing conditions are insufficient, which makes a post-curing process necessary. This can be shown by FTIR of the samples. The vibration bands according to the Si-H bond at 2125 cm^{-1} [$\nu(\text{Si-H})$] and 905 cm^{-1} [$\rho(\text{Si-H})$] are still present in the cured samples. No Si-H vibrations can be detected in the post-cured samples. The polymers are completely integrated into the resins structure (Figs. S16-S17).

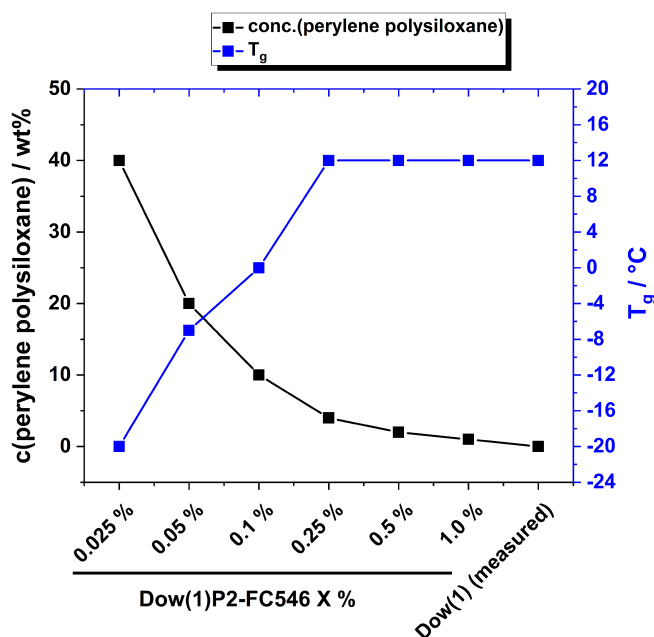


FIGURE 10 T_g values of the of the cured Dow(1) samples with the perylene polymers or the pure dye incorporated. [Color figure can be viewed at wileyonlinelibrary.com]

This interpretation agrees with the DSC data of the post-cured samples. The glass transition temperature (T_g) is directly correlated to the cross-linking degree of the polymer structure. Less cross-linked polymer chains lead to a decrease of the T_g value.^{60–63} The lowest T_g and the lowest cross-linking degree consequently was measured for the Dow(1)P2-FC546 0.0025% - 100 ppm sample in which the highest amount of perylene polysiloxane is incorporated. A decrease of perylene polysiloxane concentration leads to an increase of T_g and cross-linking as expected (Fig. 10). All DSC measurements and T_g values are part of the Supporting Information.

As a result, the incorporation of the linear perylene containing polymers to a curable polysiloxane resin can be used to incorporate high concentration of organic dyes to the resin. At the same time, the hardness of the cured material, predefined by the manufacturer can be tuned and adjusted to a given purpose by changing the amount of linear polymer added to the resin without losing the high thermal stability of >400 °C. The change in hardness and T_{95} is a consequence of a decrease of cross-linking caused by the incorporation of the perylene polymers to the resin and was verified by DSC measurements. The high thermal stability and the adjustable flexibility make these materials very interesting for different molding, grafting, or dispensing methods valid for manufacturing optoelectronics or LSCs.

Photostability

The photostability of the FC546 dye is directly correlated to the decrease in absorbance caused by irradiation. Therefore, five samples were exposed to a high power density 450 nm light source with 710 mW LEDs (6 × LDW5SN, 0.45 mA [max.: 0.7 mA]) in a remote setup to evaluate their photostability under LED working conditions. The absorbance of the samples was

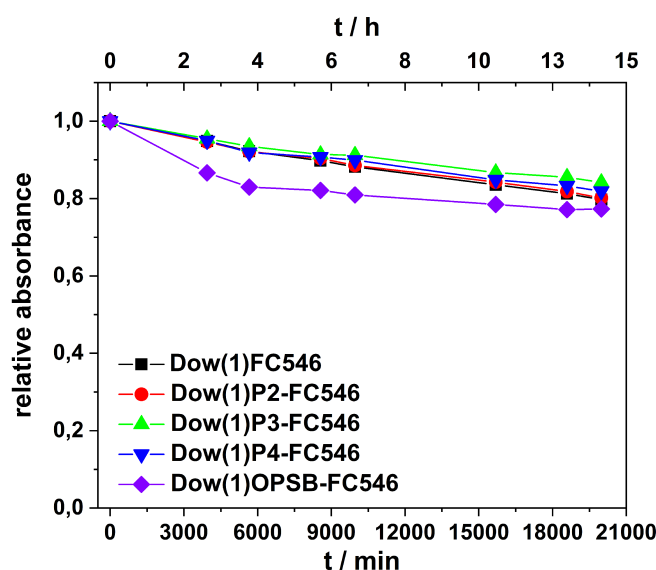


FIGURE 11 Relative absorbance of Dow(1)FC546 - 100 ppm, the Dow(1)PX-FC546 0.1% - 100 ppm series (X = 2, 3, 4) and Dow(1)OPSB-FC546 at different times measured during a light exposure with 450 nm light source. [Color figure can be viewed at wileyonlinelibrary.com]

determined periodically during the light exposure for 14 days by UV-vis spectroscopy with an integration sphere setup. Related to the absorbance at 450 nm the relative absorbance was calculated. A direct correlation between the dye degradation due to the exposure can be illustrated and compared by these values. The complete absorbance spectra for all measured samples are part of the Supporting Information (Figs. S43-S47).

For all samples, a decrease of absorbance occurs (Fig. 11). The decrease of the Dow(1)PX-FC546 0.1% - 100 ppm series is equal to the decrease of the Dow(1)FC546-100 ppm reference sample with the dye directly incorporated to the Dow(1) resin. Whereas the absorbance of the Dow(1)OPSB-FC546 0.1% - 100 ppm sample shows a larger decrease in the beginning of the irradiation. After a few days of irradiation, it approximates to the other samples relative absorbance. These results reveal that the photostability of the synthesized perylene polysiloxanes is not increased compared with a direct incorporated pure dye into a curable phenyl containing silicone resin. The slightly larger decrease of the absorbance of the cross-linked OPSB-FC546 sample at the beginning of the irradiation is not representative. The total number of methyl groups in this polymer is increased (Table 5) but the change in absorbance is not so significant compared with pure methyl containing polysiloxanes with equal dyes incorporated.¹

Assuming a further linear decrease of absorbance for all samples a decrease of 50% of initial absorbance is expected after 40 days. This is still considerably less than the lifetime of commercially available high performance LEDs with inorganic conversion phosphors. For other optoelectronic applications, the irradiance, respectively, the power density of the exposed light is lower. For example, in solar cells a total irradiance of 100 mW cm^{-2} is used under standard testing conditions.^{21,22} Considering the experimental setup for the irradiation the estimated irradiance is $\sim 700 \text{ mW cm}^{-2}$. Because the degradation of the dye directly correlates with the irradiance a much higher photostability for LSCs or solar cell applications is expected. A further investigation of the applicability in these kinds of applications is not part of this publication for operational reasons.

CONCLUSION

The *N,N'*-diallyl functionalized perylene diimide FC546 was used to synthesize two different classes of perylene polysiloxanes for a subsequent integration in a curable phenyl containing polysiloxane resin. First, the dye was incorporated into the polymer backbones of phenylmethylpolysiloxanes forming P-FC546 compounds. By changing the ratio of the hydride and vinyl terminated PMPS precursors and holding the dye concentration constant (0.1 wt %) samples with different chain length were synthesized. A second series with different dye concentrations was realized as well. Another polymer was prepared with the dye cross-linked to pendant hydride groups of a methylhydrosiloxane-phenylmethylsiloxane copolymer called OPSB-FC546. Both polymers were synthesized by a platinum catalyzed hydrosilylation reaction. The highest dye concentration covalently incorporated was 8 wt %. The formation of different

polymers and the covalent integration of the dye were proven by spectroscopic methods. Much higher dye concentrations can be realized compared with other polysiloxane substrates without precipitation and without using organic solvents due to the integration of the dye into the polymer structure. The perylene polysiloxanes were integrated into a phenyl containing HRI polysiloxane resin. The absolute quantum yield of the derived samples is >0.97 and is decreased slightly by a subsequent post-curing process. The hardness of the samples does not change for small amounts of the linear P-FC546 polymers added to the resin. An increased amount causes a tunable decrease of hardness, due to a widened network. At the same time the thermal stability decreases quantified by the T_{95} degradation temperature, which is still very high with $>430 \text{ }^\circ\text{C}$ for all samples. These changes in hardness and degradation temperature are a consequence of a decrease of cross-linking caused by the incorporation of the perylene polymers to the resin and was verified by DSC measurements. Applying the cross-linked OPSB-FC546 polymer as a batch polymer in the final resins leads to a slightly increase of hardness and thermal stability, due to the higher cross-linking ability caused by pendant Si-H groups. The measured photostability of the dye is very high for a radiation with an estimated radiance of $\sim 700 \text{ mW cm}^{-2}$ at 450 nm wavelength compared with other organic fluorescence materials but still considerably less than the lifetime of commercially available high-performance LEDs with inorganic conversion phosphors. For significantly lower radiance applications like LSCs or solar cells a high application potential is expected.

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