

Novel Photoinitiator System for Simultaneous Physical drying and Free Radical Polymerization of Water-Borne Dispersions with Near-Infrared Excitation : (Dedicated to D.C. Neckers (1938-2022) and Y. Yagci (1952-2023) according to their achievements in photopolymer science)

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Novel Photoinitiator System for Simultaneous Physical Drying and Free Radical Polymerization of Water-Borne Dispersions with Near-Infrared Excitation

(Dedicated to D.C. Neckers (1938-2022) and Y. Yagci (1952-2023) according to their achievements in photopolymer science)

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Energy efficient processes in industry represent a key factor to realize a fast transition to renewable energy sources. In the coatings industry, oven technologies applied for drying and curing, mainly contribute to energy consumption. Substitution of these wasting technologies by near infrared radiation (NIR) in combination with a NIR-absorber represents a promising alternative to reduce the energy use. Here, combining of a NIR-LED with a heptamethine cyanine operating as absorber can significantly accelerate the drying process of a water borne coating as measured by Laser Speckle Imaging (LSI). The combination of cyanine and bis(tert-butyl)iodonium salts as radical initiator results in an initiation system that efficiently works in combination with a NIR-LED to dry the coating followed by crosslinking in the same step. photo-DSC and FTIR measurements confirmed the results obtained. The use of a water compatible photoinitiator system based on a cyanine with sulfonate groups and bis(tert-butyl)iodonium lactate as water soluble coinitiator opened the possibility to eliminate the cosolvent needed for film formation and to create a complete VOC free formulation.

Keywords: Water-borne Coatings, Near infrared, Drying, Curing, Cyanine, Iodonium Salt

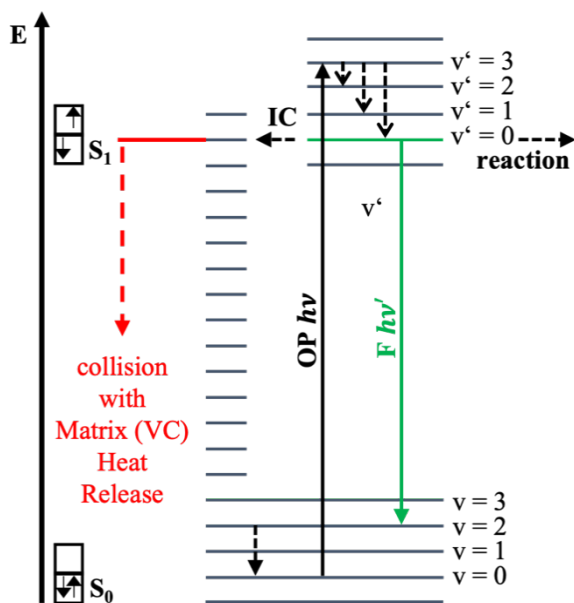
Nowadays, elimination of factors affecting climate change requires to consider renewable energy sources and their use in high-energy consuming production lines. This demand would be easier to achieve with a significant lower request of energy by enabling energy-efficient processes. In the coating industry, substitution of conventional oven technologies for drying and curing with high demand on energy address to enable energy saving technologies; that is efficient radiation technologies fitting into these goals. Although radiation curing technologies have been already well established

[1-4], conventional oven processes have been still widely used [5, 6]. Therefore, there exists a need to develop alternatives to make the transition easier feasible.

Cyanines may receive a certain operational part to solve these issues. They are very efficient light absorber molecules with an odd number of methine groups [7-9]. For example, heptamethine based cyanines exhibit strong absorbance. These compounds usually possess very high extinction coefficients; that is $>10^5 \text{ M}^{-1}\text{cm}^{-1}$. An additional vinyl group in the methine chain results in a

bathochromic absorption shift of the absorption maximum of about 100 nm known as the 100 nm rule [9].

Exposure of the cyanine with a suitable light source results in one-photon absorption (OP). Excitation promotes the molecules ground state (S_0) into the first excited state (S_1). The latter can radiatively deactivate by fluorescence (F) or non-radiatively by internal conversion (IC). Here, a higher vibrational level of the ground state couples with the lowest vibrational level of the S_1 resulting in formation of a very hot state assigned to the S_0 . Collision of this hot state with matrix molecules results in transfer of the excessive energy to the surrounding matrix. This released heat can operate in physical processes such as melting of powders [5, 10-13]. On the other hand, vibrational relaxation cannot be seen as the major non-radiative reaction pathway because the very hot molecule would burn during this stepwise deactivation procedure. Until today, the description for generation of heat in such processes has been poorly explained in literature. Scheme 1 shows the proceeding processes. The main deactivation in heptamethine cyanines typically proceeds nonradiative with a yield of > 80% with respect to the absorbed energy [14-17]. Fluorescence occurs as minor event [4].



Scheme 1. Simplified photophysical processes of the electronic states of cyanines (redrawn from [18]).

Furthermore, the S_1 of the photoexcited cyanine can react in an oxidative mechanism with an acceptor if the free enthalpy of the photoinduced

electron transfer (PET) results in negative values. The oxidation potential of the cyanine and the reduction potential of the iodonium cation drive this system in the right direction by excitation at 860 nm [4]. The PET results in efficient bleaching of cyanine with minor possibility of electron back transfer. PET leads to reduction of the iodonium cation. The respective $Ar_2I\cdot$ radical fast decomposes in an iodine arene and the respective aryl radical. The latter efficiently initiates radical polymerization. This work mainly focused on radical polymerization. Here we focus only on radical polymerization because processing proceeded in water.

As already described, heptamethine cyanines efficiently absorb near-infrared radiation [4]. Deactivation mostly proceeds nonradiative while collision with matrix molecules leads to a huge temperature increase of the surrounding matrix. In other words, excitation of these compounds with a light source emitting a suitable emission wavelength (diode Laser or light emitting diodes) can lead to an increase of several hundred degrees Celsius of the matrix in a short time frame depending on heat capacity of the system, heat flow conditions, irradiation intensity, concentration, and thickness.

Accordingly, experiments approved the possibility to use this heat generated for the drying of aqueous coating dispersions. This was also claimed in a recent patent application [19]. Nevertheless, observation of the physical drying process applying photonic sources instead of ovens does not appear as trivial. Water often interferes the signal taken to analyze the process of lot. Thus, a defined thickness needs to be established with a sample has no coverage on top. Furthermore, high spatial and temporal resolution can be seen as additional parameters together with a defined relative humidity of the surroundings. Thus, an airflow needs to be realized complementing the setup to get reliable data from those drying experiments. Increasing temperature of the sample should not significantly interfere the signal. In addition, opaque/pigmented systems should not show major issues during the measurement. Nevertheless, thickness appears as an additional important parameter because it may affect diffusion of volatile components such as water/solvent while penetration of absorbed light into the film depicts a further point controlled by the absorption of the cyanine by Lambert-Beer's Law.

These criteria represent big obstacles for methods

such as real-time infrared spectroscopy (RT-FTIR), rheology measurements, magnetic resonance imaging (MRI), optical microscopy or classical gravimetric techniques.

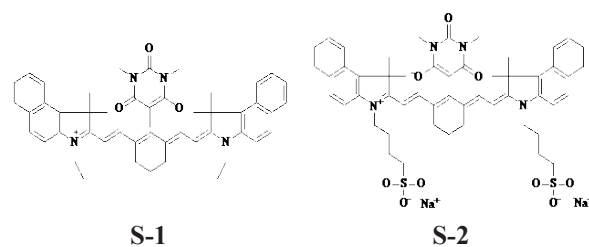
Laser Speckle Imaging (LSI) represents a suitable technique meeting all these criteria. It was introduced in the early 1980's to map the retinal blood flow as studied by multiple scattering photons [20]. In this work, LSI was applied to collect scattered light of pigment particles (TiO_2) added to study temporal and spatial changes proceeding upon exposure with a coherent emitting 532 nm laser. This source generates a speckle image resulting in a 2D interference pattern. The information available from such experiments where speckle images were generated (see SI for an example) relate to the instantaneous position of the pigment particles [20]. The scattered light and its propagation in the sample possesses a significant higher speed compared to the particle movement. This movement completely proceeds randomized after a small number of scattering events. The information provided by the speckle image relates therefore to the instantaneous position of the pigment particles. Consequently, spatial comparison of the speckle intensities within the image of another speckle intensity after a certain delay or lag time, namely τ , results in an intensity fluctuation available from the measurement. As a result, this quantity gives information about the dynamics and mobility of pigment particles within the coating over experimental time t . Equation 1 shows the relation between these parameters helping to understand the complex spatial dynamics. It appropriately fits the obtained data to an exponential decay function $g_1(t, \tau)$:

$$g_1(t, \tau) = \exp(-\gamma[\tau/\tau_0(t)]^{\alpha(t)}) \quad (1)$$

The value γ relates to an experimental numerical constant which was defined elsewhere [21]. The most important parameters are the characteristic relaxation time $\tau_0(t)$ to define the drying process. This can be seen as a quantity related to the viscosity of the drying coating solution on the substrate. Furthermore, the stretching/compressing exponent $\alpha(t)$ represents as a value for the type of motion of the particles. Here, $\alpha < 0.5$ indicates sub-diffusive dynamics while values of $\alpha = 0.5$ relate to Brownian/diffusive dynamics. Values of α appearing above this number are caused by super-diffusive processes approaching ballistic motion.

Three different samples were analyzed during the drying; that is the neat coating, the coating comprising cyanine **S-2**, and the coating comprising the cyanine **S-2** processed with near-infrared

irradiation (NIR). The sample comprising **S-2** and with no processing of NIR radiation was brought to the experiment to evaluate if the laser of the LSI affects somehow the measurement of the sample. This is relevant because the cyanines possess notable absorption in the visible region although it is lower compared to the absorption in NIR. Nevertheless, most cyanines possess a minimum of absorption at the emission wavelength of the Laser (532 nm). In the case of cyanine **S-2**, the extinction coefficient at 532 nm was $2500 \text{ M}^{-1} \times \text{cm}^{-1}$ in water which is around 17 times lower compared to the absorption maximum at 795 nm ($43080 \text{ M}^{-1} \times \text{cm}^{-1}$). This ratio can be larger for other cyanines. Thus, the laser intensity was kept as low as possible. Here, the laser operated with 25 mW to keep excitation of **S-2** as low as possible by the green laser.



Nevertheless, the measurement denoted a small impact of the laser resulting in a shift of $\tau_0(t)$ to about 84 s while $\alpha(t)$ had an offset of 87 s (see blue and black data points Fig. 1). The first kink at t_1 in the $\tau_0(t)$ refers to the concentration. It relates therefore close to the packing of the scattering particles resulting in a constant mobility. As expected, a faster drying could be observed in the sample with 0.2 wt% **S-2** applying NIR radiation as shown by the red data points in Fig. 1. The first kink t_1 appeared at 287 s significant earlier compared to a value of 1329 s of the same sample without NIR radiation (●). This confirmed faster drying of at least 1042 s of the coating comprising absorber **S-2** after processing with NIR radiation. Interestingly, there was a small decrease of $\tau_0(t)$ to about 35 s in the sample dried with NIR (●), which did not proceed in the other samples. Possibly, this indicates a decrease in viscosity because of a rapid heating on a molecular level caused by absorption of NIR radiation during exposure. After a small decrease at the beginning, a rapid increase of viscosity was observed resulting in a value of 287 s where $\tau_0(t)$ starts to decrease again. This rapid increase related to water evaporation. It referred to the close packing followed by the deformation of the binder particles due to the capillary pressure [22]. In the capillaries formed, the TiO_2 particles were likely to be drawn downward toward the substrate as drying continues. This led to a temporary increase in mobility. Also,

the value of $\alpha(t)$ increased, whereas the motion of the particles became more and more advective. Interestingly, there was a bigger time lag in the kink of $\tau_0(t)$ and $\alpha(t)$ in the radiation dried sample (●) which could indicate a skin formation on the surface due to the fast drying/strong absorption. Such events would be undesired. Nevertheless, also the kink of the $\alpha(t)$ value of the radiation dried sample (●) occurred already at 801 s compared to a value of 1248 s for the same sample without irradiation (●), which would still enhance the drying about 447 s / 7:27 min. In general, the increased temperature promotes film formation by increasing the mobility of the particles [22].

Physical dried coatings often exhibit a poor resistance against chemical or mechanical impacts. Therefore, chemical crosslinking with NIR radiation appeared as a further challenge of this type of water-borne coating. Conventional coatings of this type normally were dried in energy consuming convection ovens followed by consecutive curing UV-radiation in a two-step process [19]. Here we propose a process with NIR of physical drying and curing in just one step. This would substitute the energy consuming drying process as well as

hazardous UV-radiation.

Here the heptamethine cyanines operate as a sensitizer to reduce iodonium salts resulting in formation of free radicals to initiate free radical polymerization (FRP)[15, 16]. In the first step, an already known photoinitiator system used for 100% systems [15,16] was modified to obtain initiating components facilitating their use in a water-borne coating. Butyldiglycol was added as cosolvent. The initiator system contains the cyanine S-1 and an iodonium salt with different counter ions such as nitrate (NO_3), a perfluorinated aluminate (ALU), tetraphenylborate (BPh₄), hexafluoro-phosphate (PF₆), Bis(trifluoromethanesulfonyl)-imide (NTf₂) and lactate (LAC). Bis-(4-methyl-phenyl)-iodonium was only used as cation for the nitrate counter anion (Table 1). The remaining experiments used bis(tert-butyl)iodonium salts. The use of the cosolvent was necessary to solve the cyanine S-1 and most of the iodonium salts.

The reactivity of the formulations was determined from the peak in the exothermic signal of the photo-DSC (Fig. 2). Surprisingly the iodonium salt with the lactate anion appeared as the most reactive coinitiator. This was counter intuitive

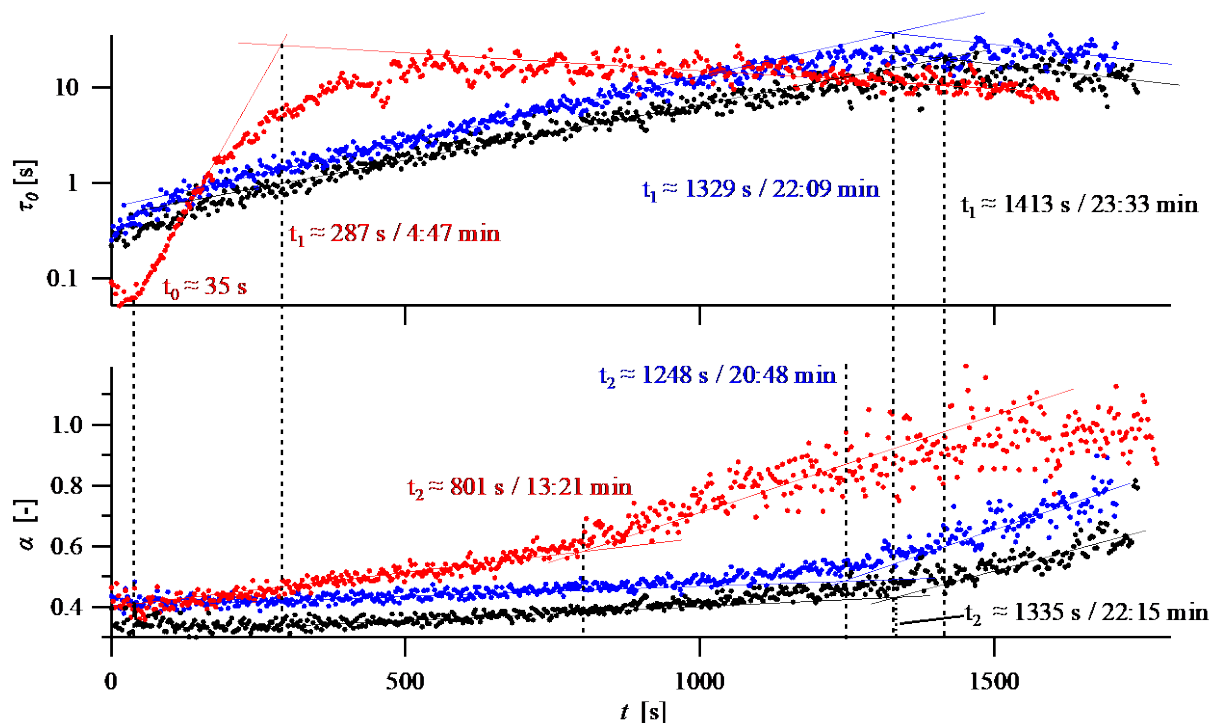


Fig. 1. Physical drying observed by Laser Speckle Imaging (LSI). τ_0 : relates to viscosity, α : type of motion of the particles ($\alpha < 0.5$ indicate sub-diffusive dynamics, $\alpha = 0.5$ indicate Brownian motion, $\alpha = 1$ indicate ballistic motion) – kink in either τ_0 or α marks phase transition - (●) 0.2 wt% S-3/with NIR ($\lambda_{\text{max}}=820$ nm, $E \approx 200$ mW/cm²), (●) 0.2 wt% S-2/no NIR (●) pure Coating/no NIR

because this anion did not perform well in 100% systems with a less polar matrix [16]. Additionally, it opens the possibility of eliminating the co-solvent, as the iodonium salt with lactate has good compatibility with aqueous solutions. This leads to formulation with less VOC. The iodonium nitrate was not analyzed more in detail because ion exchange processes as well as precipitation was expected to interfere the experiment. Therefore, the focus was put on the iodonium lactate. Furthermore, the cyanine requests also a sufficient water solubility to improve the compatibility in the system processed. This can be achieved by introduction of sulfonate groups in the side chain or at the indolium rings. Consequently, the cyanine **S-1** was substituted resulting in **S-2**. This reduced the reactivity of the system (Fig. 3), which can be explained by the lower extinction coefficient of **S-2** in butyldiglycol ($45788 \text{ M}^{-1}\text{cm}^{-1}$ at $\lambda_{\text{max}} = 799 \text{ nm}$). For comparison, **S-1** exhibited a significant larger extinction coefficient in organic surrounding ($198480 \text{ L}\cdot\text{cm}^{-1}\text{mol}^{-1}$ at $\lambda_{\text{max}} = 794 \text{ nm}$). Consequently, **S-2** absorbs less radiation/energy compared to **S-1** based on the same molar amount explaining the lower reactivity. Replacement of the remaining cosolvent butyldiglycol by water led to a small decrease of the reactivity.

Table 1. Structures of the nitrate, aluminate and tetraphenylborate iodonium salts.

Name	Cation	Anion
NO3		NO_3^-
ALU		
BPh4		

In summary, we report the successful drying and simultaneous curing of a waterborne coating with near infrared (NIR) and a photoinitiator system based on a heptamethine cyanine (**S-2**) and iodonium lactate (IS-LAC) being dynamically measured using Laser Speckle Imaging. With this approach the physical drying can be accelerated, and high double bond conversion are achievable.

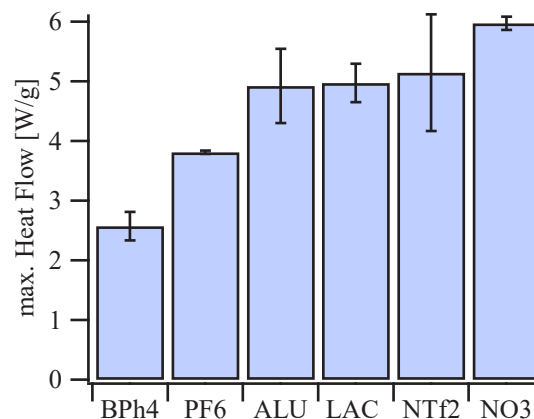


Fig. 2. Max reactivity of different Ionium-Salts in combination with **S-1** measured by photo-DSC with NIR radiation ($\lambda_{\text{max}} = 820 \text{ nm}$, $E \approx 200 \text{ mW/cm}^2$) - the error bars show the standard deviation ($n = 2$).

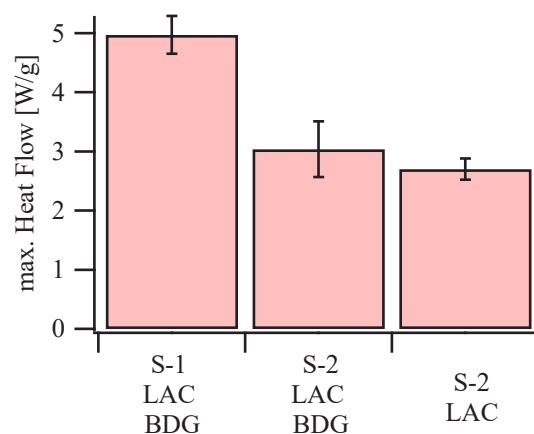


Fig. 3. Max reactivity of different photoinitiator system in combination with and without the cosolvent butyldiglycol (BDG) measured by photo-DSC with NIR radiation ($\lambda_{\text{max}} = 820 \text{ nm}$, $E \approx 200 \text{ mW/cm}^2$) - the error bars show the standard deviation ($n = 2$).

Experimental Section

More details about the materials used, the coating formulation as well as the measurement setups can be found in the supporting information.

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Supporting Information

Novel Photoinitiator System for Simultaneous Physical drying and Free Radical Polymerization of Water-Borne Dispersions with Near-Infrared Excitation

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Coating Formulation:

The coating for LSI and for the curing measurements were prepared according to the following Table and homogenized by a SpeedMixer from Hauschild. The curable polyurethane acrylate dispersion was provided as Lux 260 by Alberdingk & Boley, The TiO₂-Dispersion was provided as K-9900 by Kronos, the thickener Rheobyk-425, the defoamer BYK-025 and the wetting additive Rheo-BYK-UV3530 were provided by BYK-Chemie GmbH. The cyanine S-1 and S-2 were provided as S2265 and S2283 from FEW Chemicals. Two of the Bis(4-tert-butylphenyl)iodonium salts were purchased as S2617 (aluminate) from FEW Chemicals and as B2380 (hexafluorophosphate) from TCI Chemicals. The other (lactate, ntf2, tetraphenylborate) as well as the Bis(methylphenyl)iodoniumnitrat were prepared in our lab according to T. Brömme, *Untersuchungen zur NIR-sensibilisierten radikalischen Photopolymerisation in multifunktionellen Monomeren*, 2016, University Duisburg-Essen, PhD Dissertation.

Type	Amount [%]
curable Polyurethanacrylate	58
TiO ₂ dispersion (50%ig)	19
Water	19
Rheology Additive	1
Defoamer	1
Wetting Additive	1
Cyanine	x
Iodonium Salt	y
	100%

Drying Time - LSI

The prepared coatings were coated with a four-way film applicator from Erichsen with 180 µm on glass plates. The sample was irradiated with a NIR-LED from Phoseon Technology with an emission maximum of 820 nm and approx. 200 mW/cm² in the LSI setup. The sample chamber was closed and flushed with nitrogen and held constant at approx. 45% relative humidity. The laser of the laser had an emission at 572 nm with 500 mW. We reduced the intensity to 25 mW through a transmission of only 5%. The LED light was filtered out by a Band Pass color filter (FGB37S). The field of view (FOV) was set to 150 x 150 with 500 fps.

Conversion - ATR FTIR

The prepared coatings were coated with with a four-way film applicator from Erichsen with 180 µm on microscope slides from VWR and put into an inert-box from Addix. The chamber was then flushed with nitrogen and the samples were irradiated with the NIR-LED (820 nm and approx. 1 W/cm²). After 1, 2, 5, 10 and 20 min samples were measured by ATR-FTIR (Vertex 80 by Bruker) and the conversion was calculated by the depletion of the C=C signal with respect to the C=O signal as internal reference (Equation 1).

$$\text{conversion [\%]} = \left(1 - \frac{Abs_{C=C, \text{ cured}} \cdot Abs_{C=O, \text{ dried}}}{Abs_{C=O, \text{ cured}} \cdot Abs_{C=C, \text{ dried}}}\right) \cdot 100 \quad (1)$$

Reactivity Measurement - Photo-DSC:

For the reactivity measurements with the photo-DSC the sampled were prepared only with the curable polyurethane acrylate dispersion provided as Lux 260 by Alberdingk & Boley as and water. The photo-DSC is based on the Q2000 DSC by TA Instruments with a self-made shutter system and a light fiber connection for incorporating the LED light. The NIR-LED from Phoseon Technology with an emission maximum of 820 nm were used with an irradiance of approx. 200 mW/cm². All samples were heat to 60°C for 15 min to evaporate the water. After that the sample is kept on 30°C and irradiated for 15 min. The used dry sample mass was between 2-3 mg for each measurement.

Type	Amount [%]
curable Polyurethanacrylate	36.2
Water	63.8
Cyanine	x
Iodonium Salt	y
	100%

Extinction coefficient - UV-VIS:

To obtain the extinction coefficient for every cyanine and solvent four different concentrated solutions are prepared and measured with the UV-3600 i Plus spectrometer from Shimadzu. The extinction is then plotted against the concentration and fitted with a linear regression. From the slope the extinction coefficient can be obtained.