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Quantifying Dual-Color Photopolymerization in Xolography via Raman Spectroscopy

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ABSTRACT

Xolography is a volumetric 3D printing technology utilizing two different wavelengths of light to produce objects with micrometer resolution and excellent surface quality within minutes. Dual-color photoinitiators (DCPIs) are crucial for spatial control of polymerization. However, their performance has mainly been assessed indirectly by evaluating printed objects. In this study, we present a methodology using in situ Raman spectroscopy to characterize the dual-color curing response of a representative spiropyran-based DCPI in a methacrylate-based resin composition. A dual-wavelength irradiation setup has been developed to monitor the degree of curing (DoC) as a function of the applied light doses, providing quantitative, real-time insights into bond conversion and polymerization kinetics, as well as enabling the Xolography process window to be derived. The DCPI exhibited a contrast of 89%, showing improved performance compared to first generation systems, while its efficiency was benchmarked against a benzophenone reference. Spatially resolved Raman mapping of volumetric test prints revealed DoC gradients ranging from 40% to 80% directly after printing. We demonstrate that subsequent posttreatments can eliminate these nonuniformities, increasing the DoC to > 90%. This approach provides a framework for evaluating novel dual-color photoinitiator systems, facilitating the rational design of resins, illumination protocols and optimized configurations for volumetric 3D printing.

1 | Introduction

Volumetric 3D printing is advancing additive manufacturing by overcoming limitations inherent to conventional layer-based techniques, such as inhomogeneous materials due to interface defects, surface quality limitations without post-processing procedures, the need for support structures, and long fabrication times [1–8]. Among the different volumetric approaches, Xolography has gained significant attention due to its ability to fabricate cm-sized hard plastics, flexible elastomers, biocompatible hydrogels, and precursors for glass and ceramic parts with resolutions down to 5 μm within minutes [3, 7, 9–11].

Xolography employs dual-color photoinitiators (DCPIs) to induce local polymerization inside a confined monomer volume upon excitation by intersecting light beams of two different wavelengths [9]. As illustrated in Figure 1a,b, a UV light sheet (λ_1) promotes the DCPI from the dormant state A to the active state B. An orthogonally positioned projector generates the second wavelength (λ_2) in the visible range and projects sectional images of the 3D model onto the plane of the UV light sheet. The DCPI converts to the initiating state C at the intersection points of both wavelengths, which locally triggers and confines radical photopolymerization. By moving the light sheet through the vat and synchronized projection of slice images, the desired 3D object is fabricated. The continuous printing process generates

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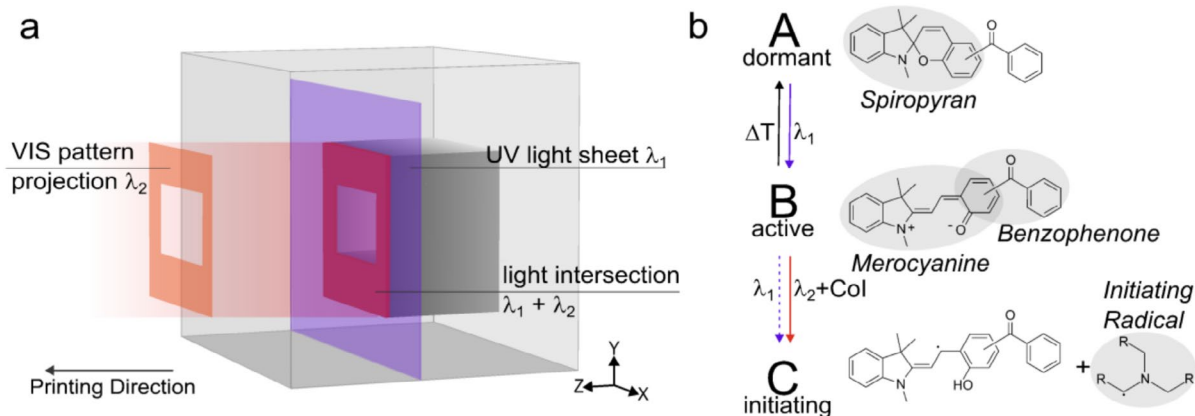


FIGURE 1 | (a) Schematic of the dual-wavelength volumetric photoactivation concept. (b) Reaction path illustrating the sequential activation mechanism (solid lines) and the undesired, competing single-wavelength initiation pathway (dashed line).

homogeneous materials with optical-grade surfaces making this process attractive for rapid optics prototyping [3, 7–12]. Another active area of research is the production of soft hydrogel-based scaffolds for bioprinting applications, as the fragile and sensitive cell-laden objects are created directly in the volume without shear-force [13–15].

The current DCPIs used in Xolography combine a spiropyran photoswitch with a benzophenone photoinitiator moiety. As depicted in Figure 1b, the absorption of UV light (λ_1) induces the ring opening of the spiropyran (A), converting it to the corresponding merocyanine isomer (B) that absorbs light in the visible range. If λ_2 is not present, the molecules thermally revert back to the dormant spiropyran state. Absorption of λ_2 by the intermediate merocyanine excites the benzophenone unit that in combination with an amine-based co-initiator leads to generation of radicals (C) via a Norrish Type II mechanism [3, 10, 16–20].

After removal of the printed object from the cuvette and washing away adhering residues of uncured material using solvents, the so-called green state can be postcured to enhance final mechanical, optical, and thermal properties of the fabricated part [14, 21–24].

A major challenge in Xolography research lies in establishing a direct correlation between the applied light dose and the resulting DoC. Several processes influence this relationship, including the light transmission of the resin, the absorption properties of the photoinitiator, the intramolecular physical and photochemical processes involved, the generation of radicals in combination with the coinitiator, and the reactivity of the resin mixture. Here we use Raman spectroscopy, which is a powerful, nondestructive method for in situ monitoring of photopolymerization [25–29]. Compared to infrared spectroscopy, Raman measurements offer higher spatial resolution and greater sensitivity to vibrational modes relevant to (meth)acrylate conversion [25, 30–31]. By tracking specific Raman bands, both the DoC and the polymerization rate can be quantified in direct relation to the light doses applied, enabling deeper insights into the interaction between photoinitiator systems and resin formulations [4, 21, 27].

The resins used in this study are highly cross-linked (meth)acrylates, specifically designed to balance viscosity, reaction kinetics, and resulting mechanical properties. These formulations differ from conventional stereolithography (SLA) and dental resins in terms of both monomer composition and choice of photoinitiator. To further advance volumetric 3D printing technologies it is essential to improve photoinitiator design as well as to optimize resin formulations, and for this purpose a detailed understanding of each stage in the dual-color initiation process is key. Despite recent progress in Xolography, no standardized metrics exist for evaluating parameters such as the efficiency and contrast of DCPIs and the employed resin compositions. While Raman spectroscopy cannot capture every aspect of the underlying photochemical processes, it provides robust, quantitative information on bond conversion and polymerization kinetics in real time, making it an indispensable tool to investigate curing behavior during printing on the molecular structure level.

In this study, we present a methodology for extracting such structural information using in situ Raman spectroscopy combined with quantitative analysis based on a modified Gompertzian fit function. We propose an experimental framework to assess DCPI performance both temporally and spatially, and to validate it by comparing an example dual color photoinitiator (DCPI 2001) in a (meth)acrylate system with a single-wavelength benzophenone photoinitiator as a reference. As the system operates by a well-established Norrish Type II mechanism, we intentionally focus on the resulting polymerization kinetics rather than looking into the initial photochemical steps of radical generation. This approach provides a practical basis for refining initiator selectivity, adjusting resin compositions, and developing illumination strategies tailored to volumetric 3D printing in general and Xolography in particular.

2 | Results and Discussion

2.1 | Resin Matrix and Reference System

For this investigation, we selected a resin composition that is commonly employed in Xolography-based 3D printers to fabricate polymeric parts. The resin is primarily composed of a mixture

of urethane dimethacrylate (UDMA) and ditrimethylolpropane tetraacrylate (DiTMPTA) as the main polymerizable components. Additionally, it contains the spiropyran-photoswitch-based DCPI 2001, the co-initiator N-methyldiethanolamine (MDEA), and SiO_2 nanoparticles serving as a rheology modifier.

To evaluate the performance of DCPI 2001, we used benzophenone (BP) as a reference photoinitiator mainly for two reasons: (1) BP is part of the DCPI molecular structure responsible for radical generation; therefore, the photochemistry and the resulting photoinitiation and polymerization mechanism in the same resin matrix are expected to be comparable. (2) The study is conducted using a UV curing wavelength of 375 nm, as this is a standard laser diode wavelength used in the Xolography 3D printing process. BP exhibits residual absorbance at 375 nm that is of the same order as DCPI 2001 in the resin.

2.2 | Photoinduced Switching, Initiation and Bleaching of the DCPI

The light-dependent behavior of the DCPI is critical for understanding its performance. To assess this, UV/vis absorption spectra were recorded under dark conditions and UV illumination before and after postcuring (Figure 2).

Under dark conditions DCPI 2001 is in its dormant state and displays a strong absorption band below 400 nm. Upon UV exposure, the spiropyran turns into the metastable merocyanine form that exhibits a broad absorption band centered at 604 nm which enables visible-light absorption of the DCPI. The spectrum of this active state also shows an increased UV absorption around 400 nm which is the cause for the undesired competing single-wavelength channel for curing. By irradiation with both wavelengths radical polymerization is initiated, and the resin hardens forming the green state. The absorption band of the remaining DCPI molecules with its maximum at 604 nm disappears due to thermal relaxation of

the DCPI. Concurrently, a secondary band emerges around 470 nm, corresponding to a DCPI photoproduct integrated into the polymer network which is also fluorescent [9]. Final illumination at 455 nm after postprocessing leads to photobleaching of the colored species, resulting in a colorless, nonfluorescent material with low residual absorption in the visible wavelength range and therefore the final objects appear nearly transparent.

2.3 | Monitoring of Polymerization via In Situ Raman Spectroscopy

Raman spectroscopy enables the detection of specific molecular vibrations, which are sensitive to the structural changes occurring during polymerization [30, 31]. Since each vibrational mode corresponds to a distinct Raman band and specific vibrations decrease in intensity as polymerization progresses, the crosslinking of monomers can be quantified by tracking the attenuation of characteristic peaks [21, 27]. To monitor the curing process, a Raman spectroscopy system (WITec Alpha 300) was coupled with a custom-developed irradiation system utilizing a 375 nm UV diode laser for in situ measurements. The chosen Raman excitation wavelengths were 532 and 633 nm, which both lie outside of the absorption band of the photoinitiator in its dormant state. Further details of the experimental setup and parameters of the measurements are described in Section 4. Figure 3 illustrates the exemplary evolution of Raman spectra during UV-induced curing of the resin containing DCPI 2001.

The bands at 1410 cm^{-1} (vinyl CH_2 deformation) and 1644 cm^{-1} ($\text{C}=\text{C}$ stretch) significantly decreased, reflecting the consumption of reactive double bonds of the methacrylate functional units, while the band at 1729 cm^{-1} ($\text{C}=\text{O}$ stretch) broadens. In contrast, the band at 1455 cm^{-1} (CH_3 scissoring) remained constant throughout, as methyl groups do not actively participate in the polymerization process and retain their mobility and thus vibrational signature postcuring [27, 28, 30–34].

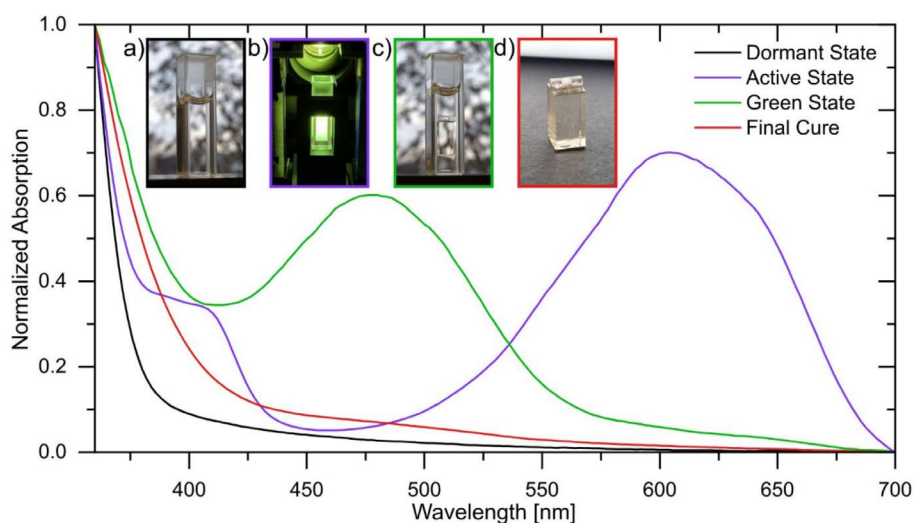


FIGURE 2 | UV/vis absorption spectra of critical states during the printing process: (a) Resin absorbance before illumination (dormant state), (b) spectrum recorded under in situ illumination with UV light (375 nm, active state), (c) spectrum recorded after illumination with UV light and curing of the material within the cuvette (green state), and (d) spectrum recorded after additional illumination with UV and vis light for postcuring the material. Insets show photographs of a cuvette during the different stages of the printing process.

The DoC was calculated according to Equation (1), using the stable 1455 cm^{-1} band as reference and monitoring the intensity decrease of the 1410 cm^{-1} peak.

$$\text{DoC}(t) = \left[1 - \frac{A_{1410}/A_{1455}}{A_{1410}(0)/A_{1455}(0)} \right] \times 100 \quad (1)$$

For determination of the peak area A , Raman spectra were baseline-corrected, followed by curve fitting of the respective bands with Gaussian functions and subsequent integration (see Section 4 for details).

Figure 4a,b depicts the DoC data and curve fits as a function of applied UV light doses for resins containing DCPI 2001 under single- and dual-color illumination and for the reference BP

photoinitiator under dual-color illumination. The light dose D in J cm^{-2} was calculated as the product of the applied UV irradiance ($E = 6.2\text{ mW cm}^{-2}$) and exposure time. The DoC curves reflect the mechanism of radical photopolymerization, which has been extensively studied in literature. The resins contain dissolved oxygen which initially quenches the radicals generated by the photoinitiator under illumination. This is reflected in the slow onset of crosslinking initiated by the DCPI until the UV dose exceeds about 0.2 J cm^{-2} . When the oxygen is consumed, the concentration of the produced radicals increases, the crosslinking of monomers is accelerated and the viscosity increases leading to gelation. In this phase bimolecular termination is only marginally affected, while propagation becomes dominant, causing the steep slope of the DoC curve. At this point the first derivative of the DoC curve fit, representing the polymerization

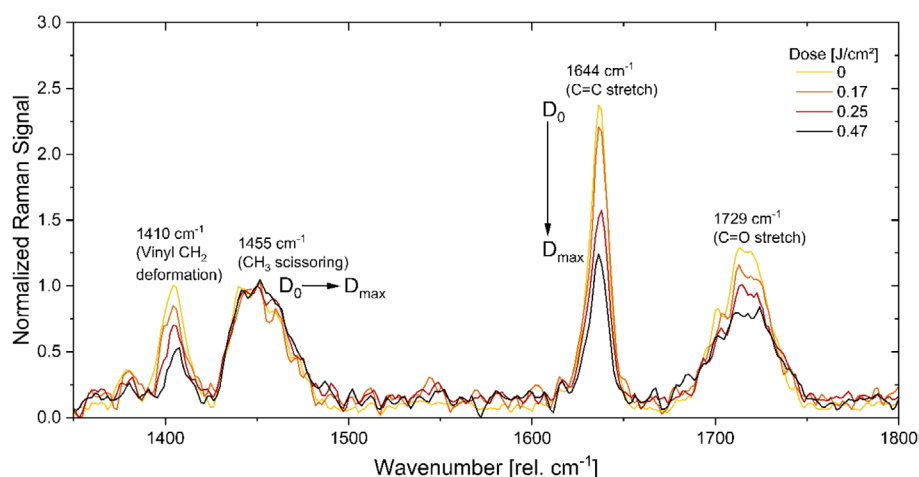


FIGURE 3 | Baseline-corrected and normalized Raman spectra (532nm excitation wavelength) showing the decay of characteristic vibration in the resin containing DCPI 2001 upon increasing 375 nm UV exposure.

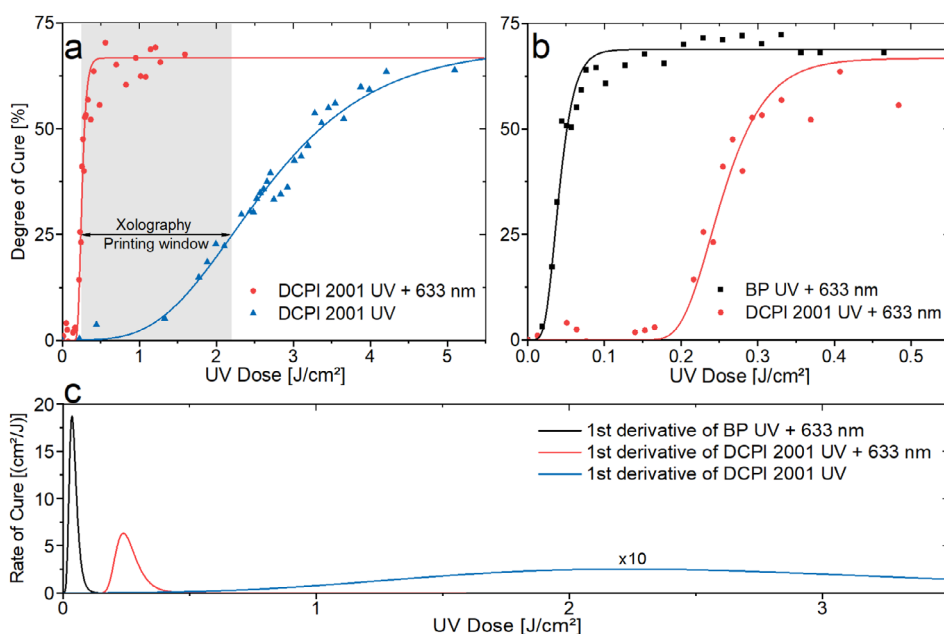


FIGURE 4 | (a) DoC curves of resin containing DCPI 2001 under UV-only and dual-color illumination for contrast evaluation. (b) DoC curves of resin containing DCPI 2001 under dual-color illumination in comparison to reference resin containing BP for efficiency analysis. (c) Rate of polymerization for the studied resins determined from the first derivative of the DoC fit curves. The curve for DCPI 2001 under UV-only illumination was magnified by a factor of 10 for better visibility.

rate, reaches its maximum as shown in Figure 4c. As crosslinking density rises, the system transitions into a glassy state, where monomer and radical mobility is severely reduced. The polymerization rate declines, and the DoC curve gradually levels off, approaching the final DoC [2, 4–6, 21, 24]. We found final crosslinking degrees of approximately 70% which corresponds to the values reported for dental resins with comparable compositions [35–37].

2.4 | Degree of Cure Kinetics and Xolography Printing Window

Both detailed and simplified models have been proposed to describe free-radical photopolymerization kinetics, including mechanistic approaches proposed by Kamal or Avrami, as well as phenomenological fits [2, 4, 6, 38–39]. While mechanistic models provide detailed insights, they typically require extensive parameterization and are sensitive to experimental boundary conditions. In this study, we chose a modified Gompertz function from Schmitt et al., which has previously been shown to capture the sigmoidal conversion behavior of multifunctional (meth)acrylates with high accuracy [6]. We adapted the mathematical form to fit the DoC curves, the expression is shown in Equation (2):

$$\alpha(D) = \alpha_{\max} e^{-e^{k(D_s - D)}} \quad (2)$$

where D is the applied light dose, $\alpha(D)$ is the DoC at dose D , $\alpha_{\max}$ is the asymptotic maximum conversion, D_s denotes the dose at which the rate of polymerization is maximal (inflection point), and k characterizes the curve steepness. This choice enables robust extraction of these key process parameters from experimental data without overfitting. The model is not intended to represent the full mechanistic complexity of the curing process but rather to provide a standardized phenomenological framework for comparative analysis of different initiators and illumination protocols.

The fitted conversion curves in Figure 4a,b along with their first derivatives in Figure 4c clearly illustrate the four characteristic stages of the free-radical photopolymerization process, particularly in samples with slower curing kinetics, such as those exposed to UV-only illumination. The fit quality was assessed using the coefficient of determination R^2 . The best agreement was observed for resin containing DCPI 2001 under UV-only illumination with an R^2 of approximately 0.98, reflecting the model's strength to describe gradual, slow curing behavior. Slightly lower fit quality was observed for resins containing DCPI 2001 and BP under dual-wavelength illumination, with R^2 values around 0.97 and 0.96, respectively.

Table 1 presents the extracted parameters for quantitative evaluation. All three curves reach a similar maximum DoC of around $\alpha_{\max} = 70\%$, suggesting that while the type of initiator and illumination regime influence the reaction rate, they do not affect the final crosslinking degree. The BP system exhibits the steepest slope k , meaning that it has the highest reactivity. Conversely, the DCPI 2001 system under UV-only illumination displays the most delayed onset and gradual kinetics.

TABLE 1 | Fit parameters and coefficient of determination for the experimental data.

	DCPI 2001 + UV	DCPI 2001 + UV + 633 nm	BP + UV + 633 nm
$\alpha_{\max}$ (%)	69.11	66.72	68.84
D_s (J cm ⁻²)	2.225 ± 0.040	0.239 ± 0.004	0.036 ± 0.001
k (cm ² J ⁻¹)	1.00 ± 0.07	25.79 ± 3.69	74.21 ± 8.96
R^2	0.98	0.97	0.96

Figure 4a compares the performance of DCPI 2001 under UV-only versus dual-wavelength exposure. An ideal DCPI does not initiate photopolymerization under single-wavelength illumination. However, due to the presence of a competing activation channel in DCPI 2001, it generates radicals even under UV-only illumination. We studied this undesired effect by exposing the resin to an UV irradiance of $E = 6.2 \times 10^{-3} \text{ W cm}^{-2}$ over several time intervals, corresponding to an increasing UV light dose, and performing Raman measurements in between. As the blue curve in Figure 4a shows, significant polymerization occurs when the applied light dose exceeds 1 J cm^{-2} . The conversion curve is shifted rightward and displays a markedly reduced slope, indicating a slower polymerization rate.

Under dual wavelength exposure, the irradiance of the second wavelength ($\lambda_2 = 633 \text{ nm}$) was intentionally set to a much higher value ($E = 12.7 \times 10^6 \text{ W cm}^{-2}$) compared to the UV irradiance ($E = 6.2 \times 10^{-3} \text{ W cm}^{-2}$). This ensures that all DCPI molecules excited by UV light are efficiently driven into the initiating state, thereby favoring the dual-color activation channel over the undesired UV-only pathway. As a result, the DoC curve under dual-wavelength conditions exhibits a rapid onset, with significant curing occurring at light doses above 0.2 J cm^{-2} . The curve shows a steep slope and the corresponding rate of cure peaks at $R = 6.3 \text{ cm}^2 \text{ J}^{-1}$, demonstrating the high reactivity of the system when both wavelengths are effectively utilized.

From the comparison of the DoC curves for the DCPI under the single and dual-color illumination, the process window for Xolography 3D printing (Figure 4a) can be estimated. This window is critically dependent on the differential photosensitivity between the two illumination modes. The upper limit of the process window is defined by the single-wavelength exposure. To prevent unintended curing in undesired areas, the applied UV dose D must not exceed the critical gelation threshold. This threshold is set as the dose D_s that leads to the maximum polymerization rate in the UV-only curve, which corresponds to a DoC of approximately 25%. Consequently, the maximum permissible dose is defined to be $D_{\max} = 2.23 \text{ J cm}^{-2}$. The lower limit of the process window, conversely, is defined by the minimum dose required for effective solidification under dual-color irradiation. The minimum effective dose $D_{\min}$ is defined as the D_s value for the two-color curve, resulting in $D_{\min} = 0.24 \text{ J cm}^{-2}$ [40–42].

The specific process window for the current resin is significantly larger compared to the first generation DCPI in a PETA based resin, which was approximated to work between 0.27 and 0.81 J cm^{-2} [3].

We further compared the benzophenone-based initiator system (BP) with the DCPI 2001 in the same resin matrix (Figure 4b). For this purpose, the optical density of BP at the UV illumination wavelength (375 nm) has been matched to the value of the DCPI 2001 which is about $OD = 0.3$ as shown in Figure S3. This ensures that an equal number of UV photons are absorbed along the 2 mm thick sample cell. From the graph it becomes evident that BP requires a UV dose of approximately 0.02 J cm^{-2} to initiate polymerization, while DCPI 2001 requires a significantly higher UV dose of around 0.2 J cm^{-2} . Additionally, the slope of the BP conversion curve is slightly steeper than that of DCPI 2001. These results show that DCPI 2001 is less efficient than BP in terms of the number of radicals generated in relation to the number of UV photons absorbed. The reasons for this difference in efficiency are a significant energy loss in the DCPI due to the thermal relaxation of the active merocyanine back to the dormant spiropyran and differences in the reaction rates for the intermolecular photoelectron transfer to the co-initiator.

2.5 | Contrast and Efficiency of the DCPI

To enable direct quantitative comparison, we derived two performance metrics: The contrast parameter C , quantifying the suppression of single-wavelength initiation, and the relative efficiency η_{rel} , comparing the light dose required to reach the same DoC against a reference system. By applying the proposed modified Gompertzian function, the fit parameters can be used to assess these metrics. The contrast parameter is calculated using Equation (3). Detailed derivations are provided in [Supporting Information](#).

$$C = 1 - \frac{D_s^{UV+VIS\infty}}{D_s^{UV}} \quad (3)$$

Here, the numerator represents the dose required to achieve 37% (e^{-1}) of the maximum conversion α_{max} , which is equivalent to a DoC of around $\alpha = 25\%$, under dual-wavelength exposure, with visible light in excess, while the denominator refers to the dose under UV-only exposure. This also reflects the estimated Xolography process window. A contrast value of $C = 1$ implies that no polymerization occurs under UV light alone, indicating an ideal dual-color effect. Conversely, $C = 0$ signifies that visible light has no additional effect, indicating the absence of a dual-color effect.

For the DCPI 2001 the contrast parameter was calculated to be 0.89. Compared to the DCPI used in Ref. [3] with a calculated value of 0.67, it shows a significantly improved dual-color effect for the generation of radicals but an undesirable photoinitiation pathway still exists under single wavelength UV irradiation. Indeed, the UV/vis absorption spectra revealed that the DCPI in the active state absorbs the first UV wavelength which is the root cause for the competing photoinitiation channel. One way to improve selectivity and minimize unwanted curing is to reduce the strength of the absorption band of the merocyanine state at 400 nm or to shift the short-wave absorption band further into the visible range. Tailoring the absorption spectrum of the merocyanine form and leaving the spiropyran absorption spectrum unchanged requires molecular refinement of the photoinitiator system.

The relative efficiency η_{rel} of the DCPI can be calculated using Equation (4), which compares the light dose required to achieve 95% of the maximum conversion α_{max} between a reference and a test material, under the assumption that both systems exhibit a similar α_{max} .

$$\eta_{\text{rel},95\%} = \frac{D_{\text{s,ref}} + 3k_{\text{ref}}^{-1}}{D_{\text{s,test}} + 3k_{\text{test}}^{-1}} \quad (4)$$

The choice of the DoC used for curve comparison is important, as the distance between curves is not constant throughout the curing process. Literature on different (meth)acrylates shows varying conversion degrees of the green state, with values in the range of 20%–80% [35–38, 43–44]. Our experiments on green states yielded conversion degrees in the range of 40%–80%. The 95% conversion threshold was chosen to ensure full formation of the green state, providing a basis to compare how efficiently different initiators transition a resin from the dark state to the green state.

Using this approach, the relative efficiency of dual wavelength illuminated DCPI 2001 compared to benzophenone was determined to be 22.5% which suggests that DCPI 2001 requires a fourfold to fivefold higher UV energy dose to achieve the same DoC. This observed relative efficiency should not be interpreted as a general property of this DCPI, but as a benchmark against a well-characterized single-wavelength initiator. Furthermore, if both systems are measured under identical experimental conditions and follow the same polymerization mechanism, the relative efficiency can further be used to estimate the radical yield of the test material, assuming the radical yield of the reference material is known.

The choice of BP as a reference photoinitiator in this study is justified by its structural similarity to the radical-generating moiety of DCPI 2001 and its similar absorbance at 375 nm, which makes direct comparison under the employed illumination conditions possible. However, it must be emphasized that BP represents a single-wavelength system, whereas the DCPI relies on sequential dual-color activation. As such, the efficiency comparison presented here reflects the relaxation pathways ($B \rightarrow A$) that leads to a loss of absorbed light energy.

Comparing relative efficiencies across different resin compositions may prove especially useful for the future selection and optimization of formulations in volumetric 3D printing. As far as volumetric 3D printing applications are concerned, the thermal relaxation channel of the DCPI is essential for enabling the production of extended objects. Although shortening the thermal relaxation time of the DCPI allows for faster printing, this comes at the expense of efficiency. Careful design of the molecular structure of DCPI ensures that these conflicting objectives are balanced.

2.6 | Spatially Resolved Green State and Degree of Cure in the Final Object

While global parameters such as contrast and efficiency give valuable insight into initiator performance, the spatially resolved uniformity of polymerization can provide information about the volumetric 3D printing process itself. To investigate local

variations in curing behavior, we printed rectangular blocks with a size of 7 mm × 13 mm × 7 mm ($X \times Y \times Z$) using a commercial volumetric “Xube” 3D printer (see Section 4 for details). Blocks were cut in half using a razor blade and cross-sectional Raman mapping was performed on the blocks in both green state and post-cured state, covering all three principal planes as shown in the Figure 5 top panel. Measurement points were spaced 1 mm apart and a preillumination Raman spectrum of DCPI 2001 served as a 0% cure reference for determining the DoC, results are shown in the bottom panel of Figure 5.

The Raman mapping of the green state revealed DoC values between 29.5% and 83.2%. During the fabrication process the UV light sheet moves through the resin container in the printing direction and applies a UV light dose of 2 J cm^{-2} to the whole resin volume defined by the laser irradiance and printing speed. According to Figure 4a this value secures that the dual color curing process achieves maximum conversion for the green state while keeping the crosslinking due to single wavelength UV photoinitiation in unwanted areas below the gelation point.

When considering the spatial variations, 5%–10% higher degrees of curing were observed along the sides of the XY plane compared to the center, and 20% higher DoC were found at the bottom of the sample compared to the top, as seen in Figure 5a. Two factors explain these variations: (1) The volumetric 3D printer radiates a UV light sheet into the cuvette from opposite sides to compensate for the exponential Lambert–Beer absorption of light and achieve homogenous excitation of the resin volume. Based on simulations of the light sheet intensity distributions by Regehy et al., the difference in intensity between the center and the sides of a 1 cm cuvette with a resin optical density of approximately 0.3 is between 1% and 2% for such a double-sided UV illumination [3]. This calculation assumes Gaussian laser beams with perfect beam shape, characterized by a beam propagation

parameter $M^2 = 1$. The UV diode lasers used to generate the light sheet exhibit a reduced beam quality factor, so an intensity fall-off from cuvette windows to center in the range of 5%–10% is realistic. The intensity loss translates to lower absorbed UV light doses toward volume center, thereby generating fewer radicals. This behavior is reflected in the observed decreasing DoC values from side walls to center, consistent with the recent numerical framework by Salajeghe et al. predicting such conversion gradients within the printed volume [45]. (2) The higher DoC values at the bottom of the cuvette could be attributed to undesired reflections of light by the bottom glass window.

As shown in Figure 5b,c, a polymerization gradient along the Z-axis was detected in both the YZ and XZ planes, with a higher final conversion observed in regions printed earlier in the fabrication process. This effect originates from the finite thermal relaxation time of the active state of the DCPI, which enables the photoinitiator to continue absorbing visible light after the UV light sheet has passed. Due to the continuous nature of the vis projection and the fast termination by abrupt projector shutdown upon reaching the final layer, the printing regions experience different total vis exposure times. Earlier printed regions benefit from a prolonged total exposure to the vis light projection, maximizing the conversion of the long-lived active DCPI molecules. In contrast, the last printed regions only receive vis light up until the moment of projector shutdown, resulting in a sudden termination of the ongoing polymerization and, consequently, a lower final DoC.

Postcuring involves a combination of intense UV light exposure and heat (see Section 4) to reach final cure and thus, improve mechanical properties of the printed objects. This procedure significantly reduced spatial heterogeneities within the sample as shown in Figure 5d–f reaching DoC values of up to 99%. Only a slight variation remained, with the top region of the object exhibiting a ~5% higher DoC, possibly due to stronger exposure to

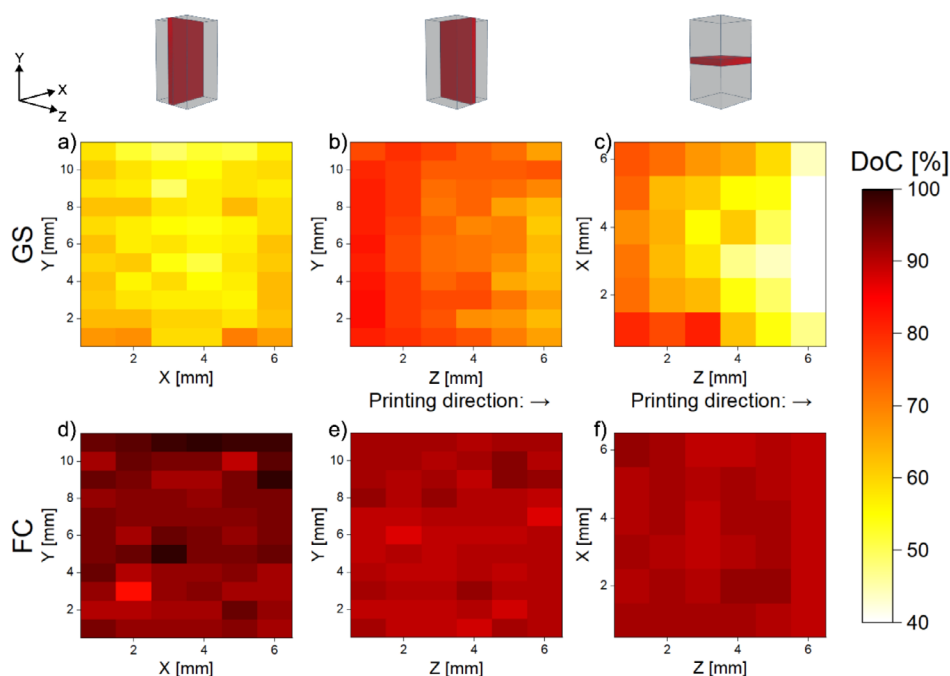


FIGURE 5 | (a–c) Spatially resolved degree of cure for printed green state objects (GS). (d–f) Spatially resolved degree of cure for postprocessed final cured objects (FC).

heat in the oven during the postcuring process. Due to the additional thermal curing, the final DoC was significantly higher than that achieved by UV light only.

3 | Conclusion

In this work, we have presented a quantitative framework for evaluation and targeted optimization of DCPIs in volumetric 3D printing. In situ Raman spectroscopy enables the extraction of efficiency and contrast parameters, providing reproducible benchmarks for initiator systems and resin formulations. Complementary UV/vis analysis supports the photophysical interpretation and points to strategies to minimize side-channel activation in future molecular designs.

The methodology further allows to direct compare of resin formulations, considering green state as well as final cure performance. Nevertheless, resin optimization must also address viscosity, optical transmission, shelf life as well as long-term stability and mechanical properties of the printed objects. Relative efficiency may serve as an indirect measure of radical yield by referencing systems with known yields, offering an accessible route to fundamental initiation metrics via Raman spectroscopy.

The observed elimination of spatial inhomogeneities in DoC mapping indicates that secondary curing steps can compensate for initial nonuniformities. However, this does not diminish the relevance of initiator selectivity and illumination strategies, as the green state DoC distribution directly reflects fundamental curing kinetics during printing. Inhomogeneities arising at this stage can affect feature fidelity, interlayer adhesion and mechanical properties prior to postprocessing, which may not be fully recoverable. Optimizing DCPI performance and light delivery therefore remains essential, with postcuring serving as a complementary, but not substitutive, strategy to achieve uniform and high-quality final parts. Future improvements in light delivery, such as grayscale modulation or predictive exposure models, could further enhance curing uniformity and precision.

Although demonstrated here for a specific spiropyran-based DCPI in a UDMA/DiTMTPTA resin, the methodology is in principle broadly applicable to other initiators and resin formulations. In situ Raman spectroscopy provides direct access to bond conversion kinetics independent of the specific photoinitiator chemistry, while the derived metrics (contrast and efficiency) are defined relative to internal references and can thus be transferred across systems. Future work will extend this framework by incorporating further Raman line shape analysis, additional DCPIs and resin matrices with different optical densities, viscosities or functionalities to establish universal benchmarking criteria for volumetric printing.

4 | Materials and Methods

4.1 | Resin Composition

The resins used in this study were formulated to enable highly cross-linked polymer networks suitable for volumetric printing. Table 2 summarizes the compositions for the DCPI 2001 and BP

TABLE 2 | Resin formulations used in this study including additives. All values in wt%.

	DCPI 2001	BP
UDMA	80	80
DiTMTPTA	15	15
MDEA	5	5
DCPI 2001	0.04	—
BP	—	0.16
SiO ₂	0.75	0.75

containing resin systems. Resins were mixed using a Hausschild DAC 600.2 VAC-P speedmixer at 2000 rpm for 5 min, transferred into COC cuvettes with 10 mm path length and centrifuged in order to remove entrapped air bubbles before printing.

4.2 | UV/vis Absorption Spectra

Absorption spectra were recorded on a Cary50 UV/vis spectrometer using semimicro COC cuvettes with 10 mm path lengths at 25°C. Baselines were recorded using ethyl acetate. Samples were illuminated within the spectrometer using a UV LED (375 nm, Thorlabs #M375L4) as well as vis LEDs (455 nm, Thorlabs #M455L4). For UV/vis spectra of the resin formulations, see Figure S3.

4.3 | Sample Preparation for In Situ Raman Measurements

Resin samples were prepared by placing a 2 mm thick metal ring with an inner diameter of 10.5 mm between two glass coverslips and filling the cavity with resin.

4.4 | Volumetric 3D Printing and Postprocessing of Samples for Raman Imaging

Six rectangular samples (7×13×7 mm) were printed using the DCPI 2001 resin in the 375 nm “Xube” at 1.5 mm min⁻¹ with a light dose of 20 mJ mm⁻². After printing, green state samples were washed sequentially in TPM (tripropylene glycol monomethylether) and ethanol, followed by drying in a ventilated oven for 5 min at 80°C. Final cure samples underwent additional washing using a solution of 2% TPO-L (ethyl trimethylbenzoyl phenylphosphinate) in ethanol, followed by identical drying. UV postcuring was performed in a UV chamber (Rapidshape RSCure) for 10 min using argon as protective gas and additional thermal annealing was performed in a ventilated oven at 110°C for 30 min. Two cuboids each were cut either at X = 3 mm, Y = 6 mm, or Z = 5 mm.

4.5 | In Situ Raman Setup

Raman measurements were performed using a confocal WITec Alpha 300 Raman microscope and a Zeiss 10× NA = 0.2

objective. The sample was positioned on a 10×10 cm computer-controlled motorized XYZ stage.

Two WITec excitation lasers were used in this study: one with a wavelength of 532 nm and one emitting at 633 nm. Both lasers were operated at an output power of 10 mW.

Scattered light was directed into the grating-based UHTS 300 spectrometer, offering a 3700 cm⁻¹ spectral range with a resolution of approximately 2.5 cm⁻¹. The Raman signal was detected using a thermoelectrically cooled DU970N-BV EMCCD camera, operating at a temperature of -60°C to minimize dark current and improve signal-to-noise ratio.

An external 375 nm iBeam Smart375S UV laser was integrated into the Raman setup. A lens system consisting of four plane mirrors and a plano convex lens ($F=25$, N-BK7) expanded the beam to a diameter of approximately 10 mm directed it onto a dichroic mirror (cut-on wavelength 445 nm) at a 45° angle above the sample holder. This configuration enabled illumination of the entire sample, while simultaneously allowing Raman signal acquisition.

Calibration of the laser sources was performed using a PM100D power meter equipped with an S130VC sensor head (Thorlabs). For UV laser power calibration, a mirror was moved up 5 mm to accommodate the power sensor placed underneath the sample holder. This ensured that the power was measured at the same location where the sample would later be positioned.

4.6 | In Situ Raman Measurement Protocols and Data Analysis

UV illumination was applied for a predefined duration to deliver a controlled dose, followed by a 30 s pause to allow relaxation of the active state of the DCPI. During dual-wavelength illumination, the 633 nm Raman laser was continuously applied at 10 mW to promote efficient transition of UV-activated molecules into their reactive state. All Raman spectra were acquired with an integration time of 10 s.

Control experiments were conducted to confirm the dependence on the specific photoinitiation system, which operates by a classical Norrish Type II mechanism. For these tests, the resin was formulated omitting either the photoinitiator or the entire initiating system. These samples were processed under identical conditions as described above, albeit with extended exposure times of up to 15 min, and showed no photopolymerization (see Figure S1).

For spatial Raman imaging the samples were measured with the 532 nm Raman laser at 10 mW focused on the surface of the sample. The measurement points were spaced 1 mm apart, with 66 points over the surface of the XY and YZ planes each, and 36 points over the surface of the XZ plane.

In some instances, samples exhibited significant fluorescence following UV exposure, which interfered with Raman signal quality. To mitigate this, photobleaching was induced by activation of the Raman laser, accelerating the relaxation of residual excited states.

All Raman spectra were analyzed using OriginPro 2025. Baseline correction was performed using automatic asymmetric least squares smoothing, followed by Gaussian peak fitting and integration of the band areas as described in Figure S2.

Fitting of the Gompertzian function was done using the Levenberg Marquardt iteration algorithm in OriginPro 2025.

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Conflicts of Interest

Martin Regehly and Stefan Hecht are co-founders of xolo GmbH.

Data Availability Statement

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

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Data S1:** pol9064749-sup-0001-Supinfo.pdf.