In situ polymerization monitoring of a diacrylate in an electrically conducting mesoporous nanoparticle scaffold

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ABSTRACT

The properties of nanoparticle–polymer composites strongly depend on the network structure of the polymer matrix. By introducing nanoparticles into a monomer (solution) and subsequently polymerizing it, the formation of the polymer phase influences the mechanical and physicochemical properties of the composite. In this study, semi-conducting indium tin oxide (ITO) nanoparticles were prepared to form a rigid nanoparticle scaffold in which 1,6-hexanediol diacrylate (HDDA), together with an initiator for photo-polymerization, was infiltrated and subsequently polymerized by UV light. During this process, the polymerization reaction was characterized using rapid scan Kubelka–Munk FT-IR spectroscopy and compared to bulk HDDA. The conductivity change of the ITO nanoparticles was monitored and correlated with the polymerization process. It was revealed that the reaction rates of the radical initiation and chain propagation are reduced when cured inside the voids of the nanoparticle scaffold. The degree of conversion is lower for HDDA infiltrated into the mesoporous ITO nanoparticle scaffold compared to purely bulk-polymerized HDDA.

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GRAPHICAL ABSTRACT

Introduction

The everyday use of composite materials consisting of a polymeric matrix and an inorganic filler is substantiating the relevance of advanced materials. Advanced functional composites increase the potential of their starting components toward unique and promising technical features and possibilities. [1] The preparation of nanoparticle–polymer composites (NPC) is a widely used approach to merge the functional properties of inorganic nanoparticles with polymer traits. [2] The particles offer characteristics like electrical or thermal conductivity as well as magnetic, photocatalytic or electro-optical activity. [3] Flexibility, low weight, transparency and chemical versatility are the contributing attributes of the polymer phase. [4] NPC materials are commonly prepared by dispersing nanoparticles in a polymeric matrix of either a monomer or thermoplastic. [5, 6] This approach has several disadvantages regarding material efficiency, percolation threshold and processing conditions. [7] A suitable class of inverse NPC is presented in this study in terms of the optical features and physical properties, enabling the material to be applied in optoelectronic devices or coatings.

Conductive NPC materials based on indium tin oxide (ITO) nanoparticles with the composition $\text{In}_{1.9}\text{Sn}_{0.1}\text{O}_3$ are applied in microelectronics, photovoltaics, batteries and displays. [8–10] Many different preparation methods are suggested for their use in

flexible NPC films, which lack the controlled structuration of the nanoparticle network. New preparation modes were recently reported to overcome the various limitations seen in conventional blending regarding the arbitrary distribution of nanoparticles in the polymer matrix, namely vapor condensation, capillary rise infiltration and ink-jetting. [6, 7, 11–14] One of these new methods is based on the preparation of a highly porous nanoparticle scaffold formed by flame spray pyrolysis (FSP) [15] and the infiltration of the pores with a photo-curable monomer. [16] In a second step, the monomer is photo-polymerized under preservation of the initial particle network, forming an inverse NPC. [7, 11] This process requires a suitable monomer that has a low viscosity, for the proper imbibition into nanopores, as well as a high transparency for applications in the optoelectronics industry. [17] Meeting these demands and featuring fast photo-polymerization and high cross-linking density, 1,6-hexanediol diacrylate (HDDA) was selected as the monomer to infiltrate the ITO nanoparticle layer. In the case of ITO nanoparticles scaffold formed by FSP, the particles are already interconnected by each other in the dry state and it could be shown that conductivity is even improved in the following steps which is a big advantage compared to the application of ITO containing formulations in wet chemical processes, like application of conventional ITO/monomer nanocomposites. [18] The films prepared in this study are electrically conductive, flexible and transparent. [11]

The deliberate control of material properties requires profound knowledge about the formation of individual composite phases and their interactions. [19] The properties of the NPC film depend on the restructuring effects during imbibition as well as the interplay between network formation and rearrangement during photo-polymerization. Imbibition into nanopores is a capillary force driven process, whereby Venkatesh et al. demonstrated that the viscosity of the imbibing liquid in the nanopores is different from the continuum physical properties of the liquid in bulk behavior. [20] The impact of monomer imbibition on the nanoparticle network formed by FSP and layer transfer is already well described by Schopf et al.; [16] however, the photo-polymerization of the acrylic monomer in the mesoporous scaffold still needs to be investigated in detail. Heretofore, research has directed its focus toward the impact of nanoconfinement on the polymerization of methacrylates and their derived compounds that form linear polymers. The chemistry and physics of the polymer phase and its formation change drastically under spatial constraints when the polymers are confined in nanopores and interact with the boundary. [21–26]

The effect of nanoconfinement on the polymerization of a cross-linking system was investigated theoretically by Lin et al., who showed that the reaction rate varied as a function of pore size and pore boundary distance. [27] In the case of soft boundaries formed during emulsion polymerization performed by Ballard et al., investigating the micro-emulsion polymerization of butylacrylate concluded that nanoconfinement primarily triggers intermolecular transfer reactions to the polymer causing gelation. [28] On the other hand, the radical polymerization reaction dynamics for highly cross-linking compounds (e.g., HDDA) in nanocavities have not yet been elucidated.

The formation process of the ITO nanoparticle HDDA composite must be well understood in order to predict and adjust the properties of the material. As shown in our previous work, during the polymerization of the diacrylate monomer, the nanoparticle network rearranges such that the conductivity is increased by one order of magnitude. [11] This observation raises the question as to how the cross-linking of the monomer might impact the restructuring of the nanoparticle scaffold under the shrinkage forces that occur. The promising features of

the NPC film are related to the polymerization kinetics of the polymer under the scaffold's nanoconfinement, i.e., the final degree of conversion changes the thermomechanical properties. [29] The specific system of ITO nanoparticles and HDDA monomer presented here is optimized by adjusting the irradiation parameters to reach a high final degree of conversion for optoelectronic, flexible thin films for use in consumer goods and electronic devices.

Therefore, to shed light on the interactions between both composite phases, the polymerization of HDDA inside an ITO nanoparticle layer was investigated using in situ diffuse reflection Fourier transform infrared spectroscopy (DRIFT) and analyzed with the Kubelka–Munk theory to calculate the reaction velocity constants. [30] The conductivity changes caused by the polymerization process were observed and related to the impact of the nanoparticle scaffold on the polymerization reaction to understand the increase in conductivity during network formation. The polymerization reaction for the system was analyzed based on the model of Goodner and Bowman for the thin-film polymerization of HDDA. [31] For consistency, the results for the polymerization of the pure phase in a thin film were referenced against other HDDA studies that underwent different photo-initiation treatments but showed the same reaction kinetics, e.g., in dynamic photo-calorimetry scans with other photo-initiators. [32–34]

Experimental section

Synthesis and preparation

Materials

Indium(III) acetylacetonate (98%, Strem Chemicals, Germany) and tin(II) 2-ethylhexanoate (95%, Sigma-Aldrich, Germany) were used as precursors with toluene (VWR Chemicals, Germany) and xylene (VWR Chemicals, Germany) as solvents. 1,6-hexanediol diacrylate (technical grade 80%, Laromer® HDDA, BASF, Germany) was utilized as the monomer for infiltration with bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (BAPO, OmniCure 819, IGM Resins, Netherlands) as the radical photo-initiator.

Particle synthesis

The ITO particles were synthesized using flame spray pyrolysis (FSP) [35] and collected on a glass fiber filter (Pall, Type A/E, 247 mm diameter) at a distance of 60 cm above the nozzle. The precursor solutions were composed of 0.1 M indium(III) acetylacetonate and 0.1 M tin(II) 2-ethylhexanoate dissolved in toluene and xylene, respectively. To synthesize the ITO particles, both solutions were mixed at a ratio of 1:19, fed to a nozzle with a flow rate of 5 ml/min, and dispersed with an O₂ gas flow of 5 L·min⁻¹. The spray was ignited with a support flame of CH₄ (1.5 L·min⁻¹) and O₂ (3.2 L·min⁻¹). The details of the process and setup were published previously. [18]

Layer preparation

Glass slides (Microscopic Glass Slides, VWR, Germany) were used as support substrates. For the spectroscopy samples, 50 nm chromium and 75 nm gold were deposited on the glass slides with a sputter coater (EM ACE600, Leica, Germany). Samples for SEM and EDX experiments were prepared by laminating ITO nanoparticles on plain polished glass slides. The particles were transferred from the glass fiber filter to the glass slides via a lamination process at ambient temperature and a lamination pressure of 3.5 MPa, as described in detail in Schopf et al. [36] The obtained ITO layers were dried at 120 °C in a vacuum furnace for 12 h below 50 mbar to remove atmospheric contaminants.

Filling of pores and photo-polymerization

HDDA was mixed with 1 wt.-% of the radical photoinitiator to allow for photo-polymerization after imbibition. A drop of the solution was applied onto the reference substrate and thinly spread out to achieve a homogeneously wetted surface of approx. 10 µm thickness. The particle layer was infiltrated with a defined volume of 10 µL with a piston-driven air displacement pipette (Research 2.5, Eppendorf, Germany) for in situ IR spectroscopy. Polymerization was conducted with UV irradiation (OmniCure S2000, Lumen Dynamics, Canada) at a source distance of 65 mm with an ambient temperature nitrogen flush of 3.3 L·s⁻¹ to obtain an oxygen-free reaction atmosphere. The irradiation intensity was set to 20, 50 and 100% lamp power. The irradiation was

always maintained in continuous mode during IR scanning for at least 120 s. During the irradiation, the temperature was constantly monitored at the rear side of the glass slide. Therefore, a type K thermocouple was attached at the bottom of the glass slide during the reaction. Figure 1 illustrates the steps in the layer-to-layer process including particle layer formation.

Characterization

Electron microscopy

Scanning electron microscopy imaging (SEM) was performed with a Leo1530 (Gemini, Zeiss, Germany) with an acceleration voltage of 5 kV. Samples were pre-sputtered on the surface for SEM using a platinum palladium layer to prevent electrical charging. Fracture planes were freshly created by cracking the glass support slide immediately prior to the examination.

EDX

The chemical compositions of the electrodes were evaluated using an SEM (Supra 40, Zeiss, Germany) equipped with an EDX detector (XFlash 6/30, Bruker and an active detector area of 30 mm²). The step size for the line scan was 0.1 µm. To avoid charging, the electrodes were sputtered with gold using a sputter coater (K550, EMITECH) for 40 s at a current of 20 mA prior to scanning.

IR-spectroscopy

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed with a diffuse reflectance unit (Praying Mantis A528/Q, Harrick, USA) installed in an XSA module (Bruker Optics, Germany) and coupled to a VERTEX 80 FT-IR spectrometer (Bruker Optics, Germany). The polymerization reaction was traced using rapid scanning in interleaved time-resolved (TRS) acquisition mode on a liquid nitrogen cooled mercury cadmium telluride (LN-MCT) detector. Details of the spectrometer settings are presented in the Supporting Information. Data acquisition and evaluation were performed with an OPUS 7.8 (Bruker Optics, Germany). Spectra were automatically integrated with fixed integration windows. Normalization of the vinyl stretch

Figure 1 Representation of the processing steps. **1** Synthesis of ITO particles via FSP and collection on glass fiber filters. **2** Transfer of the nanoparticles onto the substrate via lamination. **3** Defined liquid drop application on the layer and subsequent

imbibition with the monomer solution containing the photo-initiator. **4** Polymerization of the imbibed monomer to form a nanoparticle–polymer composite film with an in situ IR scan.

($\tilde{\nu}_1 = 1637\text{cm}^{-1}$, $\tilde{\nu}_2 = 1620\text{cm}^{-1}$) and vinyl out-of-plane ($\tilde{\nu} = 814\text{cm}^{-1}$) modes was done against the carbonyl stretch vibration ($\tilde{\nu} = 1735\text{cm}^{-1}$). The conversion curves were normalized against equilibrium intensities prior to UV irradiation and partially smoothed using the Savitzky–Golay method. The conversion curves were averaged after multiple repeated polymerization processes for the corresponding parameters and sample types, respectively. Data reduction with averaging over individual runs was performed with OriginPro 2020 (OriginLab, Northampton), as exemplarily shown in Figure S1 in the Supplementary Material.

Raman microscopy

Raman mappings were recorded with a SENTERRA II Raman microscope (Bruker Optics, Germany) in chemical imaging mode. The wavelength of the excitation laser was selected as 785 nm at a power output of 1 mW. 50×1000 was selected for the focus lens, and the magnification was set to $20 \times$ with 32 scan points per axis with a spot size of $20 \mu\text{m}$.

Optical microscopy

Microscopic images were taken with an upright light microscope (Axio Zeiss Imager A1 with AxioCam MRn, Germany). Sample illumination and measurement were performed in reflection mode.

Magnifications varied from 25 to $200 \times$; scale bars are indicated in the micrograph images.

UV irradiance

The power output of the UV source (OmniCure S2000, Lumen Dynamics, Canada) was measured with a spectral radiometer (Sola-Scope 1, Solatell, UK). The irradiance was measured at the sample position inside the DRIFT sample environment of the IR spectrometer perpendicular to the incoming beam. The integration times for UV irradiance were 10, 20, 50 and 100 ms. The radiation power was measured at 1 nm binning from 250 to 425 nm and integrated over the entire spectrum. The background intensity was $80 \text{ nW}\cdot\text{cm}^{-2}$.

Conductivity

The electrical resistance was measured in a 2-point geometry against an internal reference with a digital multimeter (Keysight 34465A Truevolt, USA) with integration over 10 net power line cycles. To minimize the distortion effects of the particle layer during conductivity testing, the maximum output was limited to approx. $5 \mu\text{A}$, thereby preventing heating and restructuring. A constant contact resistance for all measurements between sample and probe was achieved with precision spring probe pins with fixed lateral pressure (1040-D-1.5 N-NI-2.4, Conrad Electronic, Germany). The internal lead resistance was

measured on a gold-sputtered glass slide. The plotted conductivity values represent static measurements with averaging over 30 s to achieve low statistical errors. Error bars represent multiple samples.

Results and discussion

ITO nanoparticle network

The properties of the FSP prepared ITO nanoparticles are well described elsewhere and were exemplarily justified in the SEM imaging of layers that were laminated onto reflective metal sputtered glass substrates. [18] Fig. 2a depicts the ITO nanoparticle layer and shows the porous network of nanoparticles. The layer thickness varied between 9 and 10 μm . The mean size of the nanoparticles was found to be centered at 5.9 nm, as already reported using TEM imaging and BJH analysis. [11] The nanoparticle layer

features high porosity, with a broad pore size and shape distribution (Fig. 2b). [16] The samples underwent gas physisorption measurements combined with the BJH method and t-method for porosity calculation, as well described by Schopf et al. [36] Although the nanoparticle network features a very high porosity of up to 85%, [11] the nanoparticle layer shows electrical conductivity in the range of sputtered bulk-type layers with $2.38 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$. This is proof of the percolating nanoparticle structure, as the conductivity arises from particle–particle contacts throughout the entire nanoparticle layer. The porous structure features pores and tunnels that have a tortuous geometry within the nanoparticle layer. [16] According to the theoretical models, the fractal units of the nanoparticle aggregates are hierarchically structured. [37] Thus, the pore structure allows the imbibition of the void network with a liquid, thus forming an interpenetrating co-continuous network

Figure 2 Scanning electron microscopy images of ITO nanoparticles laminated on the glass substrate. **a** Cross-sectional view of the fractal-hierarchical structured nanoparticle network. Bottom layer represents the glass substrate. **b** Magnification of **a**), visualizing the nanoparticle aggregates. **c** SEM image of the fresh

breaking edge of the NPC film on glass substrate after polymerization. Acrylate covers the nanoparticle scaffold completely with marginal surface excess. **d** Magnification of the breaking surface in **c**) showing a void-free, interpenetrating, co-continuous composite phase.

of the ITO nanoparticles and the imbibed monomer/polymer matrix phase.

Formation and structure of the nanocomposite

After pretreating the nanoparticle layers in a vacuum to remove the adsorbed volatiles, such as water, the samples were infiltrated with highly cross-linking HDDA and the photo-initiator BAPO, which is commonly used as a Type I initiator for the photopolymerization of acrylates without the need for an activator. [38] The defined imbibition of the monomer-initiator solution into the particle layer was followed by UV polymerization to form a *p*HDDA-ITO composite. The prepared NPC film is flexible, transparent and electrically conductive, as reported recently. [11] Recently reported DMA results showed a decrease of the storage modulus of the NPC film ($G' = 290$ MPa) compared to the pure polymer film by factor 5 showing a reduction of the film's stiffness. [11] The optical characteristics of the sample, which also determine the absorption of UV light and suitability for spectroscopic analysis, were investigated via UV/Vis and Raman spectroscopy. Since the nanoparticle scaffold shows the hierarchical structural elements over a broad aggregate size range [16], a strong diffuse scattering of light in the samples is present over a broad wavelength range. [39]

Due to the strong diffuse scattering caused by the nanoparticles, the quality of the spectra was too low for a detailed quantitative evaluation of the formed polymer. The diffuse scattering of the composite was

observed in a Raman microscopy experiment. The Raman technique was unsuitable to perform a time-dependent experiment at high scanning speeds as the scattering at nanoparticle aggregates strongly reduces the reflected beam collimation and sensitivity of the Raman scattering (Supplementary Material Figure S5). [40]

The UV/Vis spectrum of the NPC emerging from the particle scaffold structure is shown in Fig. 3a. The plain *p*HDDA shows neither absorption nor scattering above the 400 nm wavelength, as reported elsewhere. [11] The total reflection was measured for the plain sample as well as the sample inside an Ulbricht sphere to extinguish specular reflection component and to analyze the diffuse fraction of the reflected light. It emerged that the majority of reflection occurs as an off-specular diffuse light (red line) with more than 50% scattering contribution.

The transparency for such ITO layers is in the same order as data that were recently reported for thin films of between 5 and 10 μm thickness. [41] Fig. 3b depicts the light microscopy image of an intentionally partially infiltrated and polymerized NPC film. The light side of the micrograph depicts the infiltrated and polymerized composite phase, whereas the unfilled nanoparticle layer is still visible on the dark side of the image. The fibrous media remains from the particle collection filter. The diffuse light scattering changes significantly after the imbibition and polymerization of the acrylate. The internal structure of the NPC film was investigated and compared to the nanoparticle layer using SEM. Figure 2c shows the structure of the composite. Images were taken of

Figure 3 **a** UV/VIS spectrum of ITO-*p*HDDA composite film. Total reflection (black line) was corrected for the specular component with an Ulbricht sphere (red line), showing that the diffuse scattering in the integrating sphere is dominant. **b** Light

microscopy image of the partially infiltrated ITO nanoparticle layer from the top view. The left side shows the excess of the monomer on top of the nanoparticle layer.

the sample cross section along a fracture edge. Based on the electron micrograph analysis, no inhomogeneity, voids or cluster formation could be detected. Figure 2d clearly shows the embedded nanoparticles in a continuous polymer phase. In this co-continuous phase, the initial nanoparticle network still persists after the imbibition and polymerization and does not segregate under polymer addition.

The SEM images only reveal structural information along the fracture plane and give limited information about the material gradients. To analyze the chemical composition, EDX scans were recorded of the sample. These samples were not pre-sputtered with Cr/Au to reduce spectral artifacts and line superposition in the EDX scans from chromium and gold. The EDX line scan in Fig. 4 (additional scan in Supplementary Material Figure S3) was taken perpendicular to the glass surface from top to bottom (green arrow in the SEM section). The SEM section below the EDX data denotes the scanning region inside the sample. The original SEM image can be found in Figure S2 in the Supplementary Material. From scan points zero to approx. 30, the excess of acrylate on top of the film is identified due to the high carbon content (63.6 wt.-% of carbon in monomer, calculated based on the molar masses). The composition of the pure ITO was validated previously and it is ensured that the carbon present in the composite is not caused by chemisorption of atmospheric carbon. Previous EDX investigations of Naatz et al. show that the carbon present in pure TiO_2 layers due to chemisorption is about one order of magnitude below the amount of

carbon present in the composites. [12] The carbon content (at.-%) in the composite is about 50% in the previous investigation, matching our current EDX results, while the pure polymer shows a carbon content of about 80 at.-%. The pure ITO has been characterized intensively in previous investigations of Kemmler et al. [18] Hence, we believe that the EDX data clearly indicate the homogeneous distribution of polymer within the composite. The neglectable presence of ambient carbon compared to polymer carbon content in the nanoparticle scaffold was also described in Naatz et al. [42] In the middle range, a consistent distribution of carbon, indium, oxygen and tin can be detected. Based on this, a homogeneous imbibition along the lateral axis can be verified for the NPC films. The finite increments of concentration at the phase borders occur from the size of the measurement spot for the EDX scan, and thus, the atom concentration is smudged around the phase borders. The increase in oxygen and silicon at around $\Delta x = 13 \mu\text{m}$ marks the glass substrate. The overall structure of the co-continuous phase network is homogeneous. The NPC films show no areas of phase enrichment or depletion. Hence, the nanoparticle scaffold prepared via the FSP process exhibits high structural stability, not least because of the high compression during the lamination process. The high stability of the laminated nanoparticle layer and the imbibition process allows for a defined tailoring of the percolating nanoparticle scaffold. [16]

Figure 4 EDX line scan with the concentrations of the elements of interest along the z axis of the NPC film with a total scan length of 16 μm . Δx is the displacement from the scan origin. The scale reaches from top (origin) to bottom (16 μm). The green arrow

shows the scanning direction of the EDX analysis in the SEM section. The corresponding full-aspect SEM images are shown in the Supplementary Material Figure S2.

Figure 5 Reaction pathway and reaction constants for the polymerization reaction of HDDA with BAPO as an initiator. **a** Type I photo-initiator decomposition reaction of BAPO with velocity constant k_d as suggested by Ruhland et al. [43] **b** Chain propagation reaction of HDDA.

Reaction mechanism

Figure 5 presents the reaction scheme for the bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (BAPO) initiated homo-polymerization reaction of HDDA. The concentration of focal species of interest are the initiator [I], initiator radicals [I•], double bonds [N_V], monomer [M] and reactive radical oligomer chains [$\lambda_R\bullet$]. The species are labeled correspondingly in the reaction scheme. The corresponding reaction velocities for the steady-state approximation of the radical polymer concentration are $v_d = k_d[I]$ for the dissociation, $v_i = 2fk_i[I]$ for the initiation, with f as the photo-initiator efficiency coefficient, $v_p = k_p[M][I\bullet]$ for the chain propagation reaction, and $v_t = -k_t[\lambda_R\bullet]^2$ for the termination. The reaction rate constants are k_d for the photo-dissociation, k_i for the initiation, k_p for the propagation and k_t for the termination.

Rate of Conversion

The physical properties of the polymer vary depending on whether it is prepared in bulk phase or as an imbedded co-phase in the nanoparticle scaffold's

Figure 6 DRIFT spectrum of HDDA showing all spectral features of interest. C = O stretch ($\tilde{\nu} = 1735 \text{ cm}^{-1}$) and C = C stretch ($\tilde{\nu}_1 = 1637 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 1620 \text{ cm}^{-1}$) bond vibrations as well as C = C out-of-plane (op) vibration ($\tilde{\nu} = 814 \text{ cm}^{-1}$) are labeled.

voids. The quick polymerization process of HDDA in thin films ($t_1/2 \cong 0.5 - 3 \text{ s}$) in this study was investigated using a rapid scan IR technique to access the kinetic parameters for the polymerization reaction. A representative static diffuse reflection FT-IR (DRIFT) spectrum measured with the Kubelka–Munk conversion is shown in Fig. 6. The photo-initiator decays via UV-induced α -cleavage of the benzoyl-phosphineoxide bond, enabling the initial radical formation [I•] (Fig. 5). This dissociation is a first-order reaction depending on the UV light absorption at the extinction maximum for the excitation and the photo-initiator efficiency ϕ , which defines the ratio of the reaction starting radicals. The reaction of the HDDA polymerization is governed by the heterolytic photo-dissociation, initiation, chain propagation and termination of radicals. For the discussion, a free radical polymerization reaction model based on the study of Iedema et al. was chosen. [44] Based on various simplifications of this theory, a function was defined to fit the reaction rate constants against the measured degree of conversion $\chi_V(t)$. The time dependency of the degree of conversion represents the effective polymerization speed. The derivation of the fit function is explained in the appendix. The fit function was used to calculate the reaction parameters; however, to prove the approximations in place for this study, the original Iedema model [44] was simulated and compared with the newly developed fitting

routine. Particularly steady-state conditions were thus proven and the simplifications in the appendix verified, as described later.

For the quantitative analysis of the polymerization reaction speed, the photo-initiator decay must be characterized according to its absorption rate and radical starting efficiency. For this, the photoreaction parameters were deduced according to Ruhland et al., to investigating the initiation reaction of BAPO in a liquid acrylate monomer. [43] The corresponding physical values are presented in Table 2. The light intensity of the UV source was varied for the recordings of the Kubelka–Munk intensity of the diffuse IR reflection. For this, the samples were laminated onto reflecting gold-coated glass slides to analyze multiple scattering trajectories at the nanoparticle bodies in the polymeric matrix in diffuse reflecting FTIR spectroscopy. [45] The UV source intensity was controlled via a power output setting, and the absolute irradiance at the sample position was measured for kinetic data evaluation (Supplementary Information Figure S6). The UV source shows a significant discontinuity at very low power settings, as shown in Figure S6. According to the irradiance flux dependence on the source, [46] the minimum power output was set to 20%, equal to $35.6 \text{ W} \cdot \text{m}^{-2}$, and increased to the maximum up to 100%, resulting in $177.4 \text{ W} \cdot \text{m}^{-2}$. In situ temperature monitoring showed a significant increase during irradiation and polymerization. As the sample was constantly flushed with ambient temperature

nitrogen, it is assumed that no heat spots occurred during the reaction time. The impact of temperature on the polymerization kinetics was investigated very intensively by other groups. [22, 31, 44] As the heat flux from the polymer layer onto the substrate cooled with current nitrogen stream exceeds the heat formation during photo-polymerization, we consider the polymerization heat in this particular sample design as neglectable. The reaction rate depends on the diffusions coefficients and viscosity of the solution as well as the rate constants and free volume parameters. In general, an increase in the reaction temperature also increases the reaction rate.

Figure 7 shows two contour plots for the Kubelka–Munk spectra of the neat polymer film (Fig. 7a) as well as the composite film (Fig. 7b) during the UV light-initiated reaction. The strongly pronounced bands are identified as C = O stretch ($\tilde{\nu} = 1735 \text{ cm}^{-1}$) and C = C stretch ($\tilde{\nu}_1 = 1637 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 1620 \text{ cm}^{-1}$) vibrations, according to peak positions in reference studies. [47] From these contour plots, a vast decrease in the C = C vibrational modes during polymerization is visible. The integral of the double-bond peaks is used to calculate the degree of conversion by referencing against the stable strong mode of the C = O vibration. [48] The final intensity of the vinyl stretch vibration bands still reveals remaining intensity induced by the unreacted vinyl bonds of either confined monomer molecules or frustrated radical centers in the oligomers, which lack the spatial dynamics to continue the chain propagation or transfer reaction

Figure 7 Representative 3D contour plots of spectroscopic regions of interest for **a** the HDDA film and **b** the ITO layer infiltrated with HDDA. Intensities for the C = O stretch vibration are cropped at the upper intensity scale limit for better visibility.

Bond vibrations of interest, carbonyl stretch for referencing, and vinyl stretch for conversion analysis are labeled in the contour plots. The UV source power was set to 20% with a total irradiation time of 120 s.

trajectory. The higher the degree of conversion, the lower the mobility of the monomers and the macro-radicals due to gelation.

At a certain degree of conversion, the radicals and the monomers no longer react and the polymerization reaction stops due to vitrification, which is the case after a maximum of 60 s, depending on the investigated species, when integral intensity changes become insignificant. This point is defined as the final degree of conversion $\chi_{V\max}(\tau \rightarrow \infty)$. The lower degree of conversion of the infiltrated nanoparticle film may also be the result of the normalization procedure as the spectra of the composite are highly disturbed with inhomogeneous background intensity. The C = C absorption band of the liquid monomer was related to the absorption band of the solid polymer, even though the state of aggregation has an impact on the interaction between the molecules in the electromagnetic radiation. The chemical structure of the monomer contained in the nanoparticle scaffolds is another aggravating factor due to its inherent vinyl group. Even though the nanoparticle layers are photo-cured after the imbibition step, complete polymerization of the monomer is impossible due to its double-functionalized moieties yet closed reaction volume boundaries. In contrast to previous findings of the degree of conversion in ITO-HDDA-NPC, where FT-Raman spectroscopy was employed and full conversion was assumed from the Raman experiments [11], the present study clearly shows a significant remainder of vinyl groups in the IR spectrum. This also emphasizes the scattering and sensitivity issues of the Raman technique dealing

with nanoporous media, complicating the quantitative significance of the spectra. [39]

The degree of conversion as a function of reaction time τ is presented in Fig. 8 for the polymer and the composite at different lamp power settings. In addition to the stretch vibrations, the vinyl out-of-plane vibration at ($\tilde{\nu} = 814\text{cm}^{-1}$) was also analyzed regarding the degree of conversion (Fig. 6). This is due to the partial interference of particle scattering and thus, the broadening of the strong carbonyl stretch vibrational mode, e.g., the carbonyl stretch mode is superimposed onto the vinyl stretch vibrations. Figure 8a shows the first 120 s of the polymerization reaction after starting the UV irradiation. For all experiments in this study, the UV light source was switched on during the entire spectral recording period. Dark reaction processes in free radical polymerization are not in the scope of this work as it is believed that the auto-acceleration from the Trommsdorff effect is neglectable. [49] In all cases, the rapid increase in the degree of conversion at the beginning of the reaction seems very steep.

Figure 9b shows the maximum of the first derivative of the degree of conversion $d\chi_V/dt$ within the first second of the reaction time. In the case of the pure monomer, the rate is much higher than for the composite cases. The oscillation of the values for the ITO layer is due to the interaction and uncontrolled scattering of UV light with the particles and the photo absorption. However, as expected, the rate of conversion quickly decreases with time once the vitrification of the polymer is achieved. Figure 8b shows the double-logarithmic magnification of the radical

Figure 8 **a** Degree of conversion χ_V of acrylate vinyl bonds for different lamp power settings for pure acrylate and the infiltrated ITO films. Degree of conversion was calculated for either C = C

stretch (s) or the C = C out-of-plane (op) vibration. **b** Double-logarithmic inset of the reaction progress within the first 20 s of irradiation time.

Figure 9 **a** Free volume fraction development during the reaction process calculated with equation 14 as a function of $\chi_V(t)$. **b** First derivative of the degree of conversion against reaction time.

start at low degrees of conversion. Clearly, χ_V is highest for the pure polymer with the steepest slope as well as the degree of conversion at a given τ . The HDDA curves manifest two almost linear regions of the curve slope, with an inversion of slope at approximately 0.62 s. This indicates that two different processes occur on different time scales. In the beginning, radical species are formed until they reach steady-state concentration. Subsequently, the diffusion-controlled chain propagation with decrease in reaction rate dominates the kinetics. Furthermore, this suggests that the process of polymerization can be described as power functions in the respective region of the reaction time. For the neat HDDA, the slope decreases from 1.9 to 0.09 after the inflection point. The polymerization of the monomer in the voids is limited in existing reacting partners due to the phase boundary of the ITO scaffold. The confinement impacts the effective number of reaction partners as well as the effective diffusion inside the void. As expected from this spatial confinement effect and as confirmed by the TGA measurements for the *p*HHDA film versus the ITO-*p*HHDA composite [11], the degree of polymerization is lower in the case of the composite. Yao et al. explained these findings through confined residual acrylate moieties that are no longer able to reach reacting partners once gelation takes place inside the scaffold's nanovoids; meanwhile, the diffusion of either monomer molecules or light oligomers is entropically hindered, leading to a lower degree of polymerization due to dangling chain ends. [50] The adverse impact of added nanoparticles onto the reaction kinetics of photo polymerizing monomers leads to a reduced final degree of conversion for the filled polymer. [51, 52] Cho et al. showed that the conversion rate and final degree of conversion decrease with increase

in nanoparticle concentration. However, these findings correspond to arbitrarily distributed particles in the polymeric matrix. [53]

Figure 7 allows a qualitative direct comparison of the rate of conversion for the polymer compared to the nanocomposite. The drop of intensity for the HDDA film (Fig. 7a) occurs within a few seconds, until only a slow decrease in remaining vinyl stretch vibration intensity is seen. However, in the case of the polymerization in the nanoparticle scaffold (Fig. 7b), the slope of intensity decline of the vinyl stretch vibration is much lower compared to the pure polymer film. This might be due to various reasons. For the presented system of a highly densifying cross-linker, Fig. 8 proves that the final degree of conversion and the rate of conversion are smaller for the NPC film than in the bulk phase, as also reported by Salsamendi et al. [54] The reduced rate of conversion in the ITO scaffold can be correlated to the optical properties of the ITO. As ITO is an electro-optical material, it interferes with the incoming UV light, partially absorbing a significant amount of photons and thus undergoing electronic excitations as the ITO layers show an absorption maximum at 320 nm, as measured by Thirumoorthi et al. [41]

It is possible that the electronic excitation in the scaffold interacts with the free-radical polymerization reaction; for example, radical collision with the ITO particle walls may annihilate the reactivity of the active radicals since partial charge transfer at the interphase between ITO and an organic layer is well established. [55] Additionally, the nanoparticle agglomerates and aggregates are scattering centers for any incoming light. [53] The diffuse scattering occurs not only for the IR beam, but also in regard to the illumination with UV light. The optical effect of the photo-absorption of the nanoparticle scaffold should be noticeable in a photo-initiator efficiency

Table 1 Results of fitting parameters of function equation 32 for the degree of conversion vs. reduced data and the corresponding uncertainties for the different irradiation powers and materials. Significance of the fit result is represented by the t value

System	Radiation power	Vibration mode	Symbol	Value	Uncertainty	t Value (significance)	Unit
HDDA	177.4 W·m ⁻² (100%)	C = C s	χ_{Vmax}	93.10	± 0.038	2413.4	[%]
			k_{t0}	2.71·10 ⁹	± 1.26·10 ¹⁰	0.216	m ³ ·kmol ⁻¹ ·s ⁻¹
			k_{p0}	6.16·10 ⁷	± 4.96·10 ⁸	0.124	m ³ ·kmol ⁻¹ ·s ⁻¹
			ϕ	0.912	± 15.0	0.0607	
		C = C op	χ_{Vmax}	94.4	± 1.45	65.26	[%]
			k_{t0}	4.44·10 ⁹	± 9.06·10 ¹¹	0.0049	m ³ ·kmol ⁻¹ ·s ⁻¹
			k_{p0}	7.33·10 ⁷	± 2.25·10 ¹⁰	0.00325	m ³ ·kmol ⁻¹ ·s ⁻¹
			ϕ	0.721	± 579.5	0.00125	
	35.6 W·m ⁻² (20%)	C = C s	χ_{Vmax}	89.7	± 1.02	87.8	[%]
			k_{t0}	3.62·10 ⁹	± 2.81·10 ¹¹	0.0129	m ³ ·kmol ⁻¹ ·s ⁻¹
			k_{p0}	1.44·10 ⁸	± 8.80·10 ⁹	0.0164	m ³ ·kmol ⁻¹ ·s ⁻¹
			ϕ	0.639	± 15.19	0.0421	
ITO + HDDA	177.4 W·m ⁻² (100%)	C = C op	χ_{Vmax}	72.4	± 0.109	644.4	[%]
			k_{t0}	7.52·10 ⁸	± 6.63·10 ¹⁰	0.0113	m ³ ·kmol ⁻¹ ·s ⁻¹
			k_{p0}	1.63·10 ⁷	± 1.42·10 ⁹	0.0115	m ³ ·kmol ⁻¹ ·s ⁻¹
			ϕ	0.152	± 23.11	0.0066	
	35.6 W·m ⁻² (20%)	C = C s	χ_{Vmax}	72.2	± 0.137	528.83	[%]
			k_{t0}	6.92·10 ⁸	± 1.59·10 ¹⁰	0.0435	m ³ ·kmol ⁻¹ ·s ⁻¹
			k_{p0}	4.22·10 ⁷	± 5.69·10 ⁸	0.0741	m ³ ·kmol ⁻¹ ·s ⁻¹
			ϕ	0.278	± 0.978	0.284	
		C = C op	χ_{Vmax}	71.82	± 0.127	567.4	[%]
			k_{t0}	7.99·10 ⁸	± 3.12·10 ¹¹	0.00256	m ³ ·kmol ⁻¹ ·s ⁻¹
			k_{p0}	3.52·10 ⁷	± 4.34·10 ⁹	0.00812	m ³ ·kmol ⁻¹ ·s ⁻¹
			ϕ	0.178	± 47.09	0.0038	

factor ϕ in the case of the NPC film. Recent works on the polymerization kinetics of HDDA suggest numerical simulations, including diffusion mechanisms, to entirely describe the polymerization kinetics in free radical polymerization. [31, 44, 56] In this work, instead of an extensive numerical solution, a phenomenological approach based on the free volume fraction dependency of the rate constants was chosen to estimate the impact of the scaffold on network formation. Therefore, approximations from Aldea et al. [57] were combined with the work of Iedema et al. [44] to produce a fast and straightforward approach to compare the reaction rate coefficients for the different systems. The deduction of the model is explained in the appendix, leading to equation 32 to receive a degree of conversion fitting function in dependence on the reaction time: $\chi_V(\tau) = C_1(1 - C_0 \exp(-k_p \sqrt{\frac{\phi J_0 [I]_0}{\kappa k_t}} \tau)) - \frac{[I]_0}{[N_V]_0} \left(\frac{k_p}{2} \sqrt{\frac{\kappa [I]_0}{k_t \phi}} - 1 \right)^{-1} \exp\left(-\frac{2\phi J_0}{\kappa} \tau\right)$ (36).

This model matches empirical findings toward the summation of exponential functions. [58] In this approach, the important influence of the contribution of different radical chain types, such as different macroradical species, to kinetics is not accounted for as their dynamics are averaged in this study. [59]

In order to apply the derived equation 32 to the recorded data, the free volume fraction as suggested by Marten and Hamielec [60] for the polymerization reaction must first be calculated. The free volume fraction is defined as the void space that is not filled with polymer. It should be noted that the free volume of the polymerization model must not be confused with the pore volume of the nanoparticle layer. This is done by using equation 14 to calculate the free volume as a function of the degree of conversion: $f = 0.1418 - 0.074 \bullet \exp\left(\frac{\chi_V - 0.00644}{1.97657}\right)$ (18).

Figure 9a presents the results for the free volume fraction development during the photo-polymerization reaction. The faster the degree of conversion increases, the faster the free volume fraction drops,

which slows the reaction since the diffusion of reaction partners is hindered. The free volume fraction and reactant concentrations for the polymerization are only calculated for the void space. The ITO scaffold phase is excluded from the reaction space modeling, meaning that the phase boundaries for the infiltrated HDDA are in this model considered as static system borders, whereby the reaction does not interact with either the ITO or adhered material, such as water or impurities on the surface of the nanoparticles. Thus, the concentration and free volume parameters are kept constant for both probe systems. As a consequence, the effect of confinement and a second phase will contribute to the calculated reaction rate and efficiency coefficients.

Table 1 shows the results of the refinement procedure to obtain the final degree of conversion χ_{Vmax} , the pre-exponential reaction rate factors for termination and propagation, k_{t0} and k_{p0} , respectively, and the photo-initiator efficiency ϕ for two different power settings of the UV source; all other parameters were kept constant to reduce the parameter dependency in the fitting procedures. The results of the refinement of the fit function given by equation 32 against the recorded data (Fig. 8a) are shown in Fig. 10. The two different vinyl vibration modes were analyzed independently as the background contribution to the peak intensity could not be distinctly ascertained. For HDDA, a reasonable agreement of the constants with the values from Iedema et al. could be determined. The exact values for k_t are much higher, which might be related to the particular monomer stabilizer system that was added by the

manufacturer (100 ppm monomethyl ether hydroquinone as an inhibitor). The photo-initiator efficiency ϕ decreased with lower UV light intensity for plain HDDA, whereas the propagation rate constant slightly increased. Presumably, this is a mathematical artifact due to the high entanglement of the fit parameters as they consolidate the curvature of $\chi_V(\tau)$.

For both excitation analyses and power outputs, the reaction rate constants, photo-initiator efficiency and total degree of polymerization of HDDA inside the ITO scaffold pores are much lower compared to neat HDDA. The reduced efficiency can be explained by the light absorption and scattering effects of the ITO nanoparticle scaffold; also, the effective HDDA amount is reduced to the pore volume of the layer. In the monomer bulk phase, created radicals either trigger polymerization or terminate by recombination. When a radical reacts with the surface of an ITO nanoparticle, it can be deactivated and is no longer available for the start of a polymer chain. [61] The presented findings are in contradiction to other studies of polymerization under nano-confinement, where an increase in the reaction rate was reported. [22, 62–65] These works explain the increase in the reaction rate through the well-ordered molecular assembly at the interphases in the pores, which enhances the collision of reaction partners, as well as the hindrance of radical termination reactions due to diffusion limiting.

In this study, the pore geometry is rather complex and covers a broad size range, and thus, the interphases differ depending on the specific void. The reduced rate constants of propagation and termination are a result of the nanoconfinement in the ITO as the radical movement speed is strongly reduced inside the mesopores. This contributes to a much stronger entropic dependency of the reaction rate as the phase boundary of the ITO phase hinders the free radical diffusion throughout the monomer–polymer phase. However, electron transfer processes or radical inactivation is possible through interaction with the ITO. [55, 61] From the error and significance analysis, it becomes clear that the velocity constants are over-determined as k_p and k_t always contribute to the overall reaction rate as $k_p \cdot (k_t)^{-0.5}$. In consequence, this causes high uncertainties in the pre-exponential factors as well as radical initiation efficiency.

The presented results suggest a reduced reaction rate as well as a decreased final degree of conversion for the UV polymerization of HDDA in a

Figure 10 Comparison of fitting curves based on equation 32 with the data shown in Fig. 8. Numerical results are given in Table 1.

Table 2 Parameters for fitting function $\chi_v(\tau)$ of degree of conversion, which were not refined in this study. Sources of reference values are presented accordingly

Symbol	Value	Unit	Parameter name	References
$[M]_0$	4.75	$\text{kmol}\cdot\text{m}^{-3}$	monomer concentration	This work
$[N_v]_0$	9.5	$\text{kmol}\cdot\text{m}^{-3}$	double-bond concentration ($2\cdot[M]_0$)	This work
$[I]_0$	0.02568	$\text{kmol}\cdot\text{m}^{-3}$	photo-initiator concentration (1 wt.% of $[M]$)	This work
λ	384	nm	excitation wavelength of photo-initiator	Dietlin et al. [†]
ε	$8.35\cdot 10^3$	$\text{m}^3\cdot\text{kmol}^{-1}\cdot\text{m}^{-1}$	extinction coefficient ($1/2(\varepsilon_{365}^{A'} + \varepsilon_{365}^{B'})$)	Ruhland et al. ^a
κ	37.30868	$\text{Ws}\cdot\text{m}^{-2}$	quantum energy absorption factor	this work
f_0	0.038		free volume offset	Iedema et al. ^c
α_M	$4.0\cdot 10^{-4}$	K^{-1}	free volume parameter	Iedema et al. ^c
α_P	$7.5\cdot 10^{-4}$	K^{-1}	free volume parameter	Iedema et al. ^c
ρ_M	$1.01\cdot 10^3$	$\text{kg}\cdot\text{m}^{-3}$	archimedic density $[M]$	Johnson et al. ^d
ρ_P	$1.3\cdot 10^3$	$\text{kg}\cdot\text{m}^{-3}$	archimedic density $[P]$	Johnson et al. ^d
$T_{g,M}$	223	K	glass transition temperature $[M]$	Goodner and Bowman ^b
$T_{g,P}$	368	K	glass transition temperature $[P]$	Hoffmann et al. ^e
$A_{i,p}$	0.71		free volume parameter ($k_{i,p}$)	Iedema et al. ^c
$f_{c,i,p}$	0.053		critical free volume ($k_{i,p}$)	Iedema et al. ^c
$E_{Ai,p}$	$1.823\cdot 10^4$	$\text{J}\cdot\text{mol}^{-1}$	activation energy ($k_{i,p}$)	Goodner and Bowman ^b
A_t	0.69		free volume parameter (k_t)	Iedema et al. ^c
$f_{c,t}$	0.093		critical free volume (k_t)	Iedema et al. ^c
E_{At}	$2.94\cdot 10^3$	$\text{J}\cdot\text{mol}^{-1}$	activation energy (k_t)	Goodner and Bowman ^b
R_{rd}	4	$\text{m}^3\cdot\text{kmol}^{-1}$	reaction–diffusion coefficient	Goodner and Bowman ^b
M_M	0.22627	$\text{kg}\cdot\text{mol}^{-1}$	molar weight $[M]$	manufacturer
M_I	0.41846	$\text{kg}\cdot\text{mol}^{-1}$	molar weight $[I]$	manufacturer

[†][71]; ^a[43]; ^b[31]; ^c[44]; ^d[72]; ^e[11]

nanoparticle scaffold compared to pure HDDA. A higher UV irradiation intensity increases the final degree of curing in the investigated irradiance range. Torres-Knoop et al. [56] explained in this context that the glass transition temperature T_G is a function of the number of cross-links. Thus, an increase in $\chi_{V\max}$ consequently causes an indirect increase of the T_G . As the T_G for the presented system is higher in the case of the NPC (Table 2), a higher number of cross-links can be assumed. This is defined as a monomer connecting two separated monomer chains. In the composite, the predetermined scaffold structure physically separates potential reaction partners during the polymerization. As the void's phase boundaries of the nanoparticle scaffold reduce the probability of intermolecular reactions, the intramolecular chain transfer is dominating. This leads to a higher cross-linking, as also observed by Ballard in a microemulsion. [28] A higher cross-linking density increases the chemical resistance, transparency and glass transition temperature.

Moreover, neither the infiltration nor the photopolymerization of the HDDA monomer was found to impact the pristine, mesoscopic structure of the nanoparticle scaffold. This is especially beneficial for the adjustment of the degree of infiltration, if partial imbibition of the structure is of interest, to maintain remaining porosity or facilitate filling with a second liquid.

The impact of polymerization on the nanoparticle scaffold

As the presented system is selected based on its potential application in optoelectronic systems, it was further characterized regarding its electrical conductivity. Figure 11 displays the conductivity of a nanoparticle layer during its sequential processing steps. The FSP-prepared ITO nanoparticles possess a considerably low electrical conductivity of $2.4\cdot 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ in comparison with a conventionally prepared sol–gel dispersion coating, as reported by Das et al. in the order of $\cong 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. [66] Sputtered

Figure 11 Change of nanoparticle layer conductivity during individual processing steps. Error bars correspond to repeated measurements of four individual layers. Contact resistance herein is negligible ($\approx 3 \Omega$).

ITO layers reach sheet resistances as low as $3 \text{ k}\Omega\cdot\text{sq}^{-1}$. [67] However, in the case of nanocomposites, Capozzi et al. reported a conductivity of $5.0 \cdot 10^{-8} \text{ S}\cdot\text{cm}^{-1}$ for ITO-polymer composites in PMMA, which is already exceeded in the case of loosely packed aggregates of ITO nanoparticles. [68] A slight increase in conductivity was detected after infiltration of the nanoparticle layer with the HDDA monomer. The conductivity increased to $3.3 \cdot 10^{-6} \text{ S}\cdot\text{cm}^{-1}$, i.e., by approximately one-third, during the imbibition process. The resistance for a plain *p*HDDA reference sample is out of range of the measuring equipment ($> 0.1 \text{ T}\Omega$). Classical material understanding would suggest a decrease in conductivity when the conducting nanoparticle network starts to be dispersed in an insulating phase. As this FSP nanoparticle scaffold itself withstands liquid treatment, [16] a parallel-connected coexistence of the insulator without impact on the conductivity is anticipated. However, the opposite effect was detected and also reported in another study in this field. [11] The effect is correlated with the fostering of particle–particle contact due to the strong capillary pressure during the imbibition with the monomer. Accordingly, the conductivity increases while the particle scaffold structure itself is retained and is not arbitrarily dispersed as in conventional blending techniques. [6]

When the imbibed film is subsequently polymerized, an increase by one order of magnitude is observed in the conductivity, resulting in $1.4 \cdot 10^{-5} \text{ S}\cdot\text{cm}^{-1}$, which is in the region of technically relevant

conductivity at the given transparency of the NPC film. [41]. The electrical properties of the NPC strongly depend on the polymerization process. The strong increase in conductivity of the nanoparticles cannot be solely explained by the polymerization shrinkage of the polymer, which is reported to be theoretically up to 14% in the case of HDDA as a monomer. [69] Furthermore, the polymerization process progressing under spatial hindrance must impact the effective particle percolation due to its contraction inside the void space, while the degree of cross-linking must be much smaller compared to bulk *p*HDDA, as confirmed spectroscopically. A post-polymerization for 20 h at elevated temperatures leads to a final conductivity of the $10 \mu\text{m}$ ITO-*p*HDDA-NPC film of $1.6 \cdot 10^{-5} \text{ S}\cdot\text{cm}^{-1}$, which corresponds to an increase by a factor of 6.7 caused by monomer imbibition and polymerization. The conductivity increases during the imbibition and polymerization, the nanoparticle scaffold does not segregate from the treatment (Fig. 2c, d), and the EDX spectra (Fig. 4) confirm the microscopic homogeneity of the interpenetrating co-continuous percolating network of nanoparticles and polymer. Combining these facts, it becomes clear that the initial scaffold structure is not only retained but also fostered and that polymerization takes place inside the voids of the nanoparticle scaffold, forming an interrupted polymer network.

Conclusion

A novel inverse NPC film was reproducibly prepared and characterized in terms of its polymerization processes, changes in microstructure and material properties. For the FSP-prepared nanoparticle layer, high scaffold stability during imbibition and polymerization was proven by imaging and conductivity measurement. The preparation of the inverse NPC led to an increased conductivity compared to the neat nanoparticle layer after structural compression. Thus, imbibition and polymerization inside nano-cavities is a suitable method to foster the electrical and eventually magnetic attributes of the nanoparticles in the scaffold.

The results of this work explain the effect of in situ polymerization inside nanocavities on the polymer properties as well as the change of the reaction rate coefficients. Using DRIFT spectroscopy and the

Kubelka–Munk transformation for the polymerization of thin films, the degree of conversion was calculated as a function of the reaction time and compared regarding the effect of varying light intensity for the cases of polymerization in the plain bulk phase or, inside of mesoporous cavities. Higher irradiance intensity increased the final degree of conversion. In the case of polymerization in the mesopores, the cross-linking density was increased due to the impenetrable particle scaffold.

An explicit empirical function was presented to analyze the polymerization kinetics of a diacrylate under photo-initiation, which is in good agreement with comparable approaches to develop a kinetic model of the reaction. Based on this model and the free volume fraction theory, the rate constants for propagation and termination, the photo-initiator efficiency and the final degree of conversion were obtained. The model explains the measured data quantitatively. The final degree of conversion, the rate constants and the initiator efficiency were reduced in the case of polymerization inside a mesoporous scaffold. Hindrance of diffusion by the scaffold's phase boundary was the main reason for the lower conversion and reaction rate. The reduced efficiency was explained by the absorption and diffuse light scattering of the nanoparticle structure. The results suggest that the polymerization model inside the mesoscaled voids must also include the interplay between ITO nanoparticles and monomer–polymer system.

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Appendix

The degree of conversion as a function of time is developed to calculate the parameters from the measured Kubelka–Munk spectral traces. For the determination of the reaction velocity coefficients, a modified Goodner–Bowman model [31], based on Iedema et al.'s study [44], is employed. For this study, with a very thin semi-transparent film, the diffusion impact on the reaction velocity is neglected in the analytical approach. The species and reaction rate coefficients are labeled according to Fig. 5. k_{tp} is the termination rate coefficient for the active chain end initiator radical recombination. The real time t is converted to receive a zero offset time dimension τ . Accordingly, the ordinary differential equations for the reactants list are as follows.

$$\frac{d[I]}{d\tau} = -2k_d[I] \quad (1)$$

$$\frac{d[I\cdot]}{d\tau} = 2k_d[I] - k_i[N_V][I\cdot] - k_{tp}[\lambda_R\cdot][I\cdot] \quad (2)$$

$$\frac{d[N_V]}{d\tau} = -[N_V](k_i[I\cdot] + k_p[\lambda_R\cdot]); [N_V]_0 = 2[M]_0 \quad (3)$$

$$\frac{d[\lambda_R\cdot]}{d\tau} = k_i[I\cdot][N_V] - [\lambda_R\cdot](k_t[\lambda_R\cdot] - k_{tp}[I\cdot]) \quad (4)$$

The degree of conversion χ_V is experimentally accessed via DRIFT spectroscopy as the intensity of the vinyl stretch and out-of-plane vibration bands. The relationship between the concentration of the double bonds $[N_V]$ and the degree of conversion χ_V is defined as:

$$\chi_V = 1 - [N_V]/[N_V]_0 \quad (5)$$

The photo-initiator dissociation is calculated from the molar absorption coefficient ε , initiator efficiency ϕ , light intensity J_0 , Avogadro's constant N_A , Planck constant h , speed of light c , wave length of the absorbed light λ and penetration depth z .

$$k_d = \varepsilon \phi J_0 E^{-1} \quad (6)$$

$$E = N_A h c \lambda^{-1} \quad (7)$$

$$J(z) = J_0 \exp(-\varepsilon [I] z) \quad (8)$$

The free volume is represented by the empirical free volume fraction f according to Goodner and Bowman. [31] The reaction rate coefficient is calculated from the ratio of monomer and polymer volumes in the sample, with the activation energy E_{Aj} , the free-volume parameter A_j and the reaction-diffusion parameter R_{rd} . The free volume fraction factor f is then calculated from the free volume parameter α , critical free-volume $f_{c,j}$ and the theoretical glass transition temperature T_g .

$$k_d = \varepsilon \phi J_0 E^{-1} \quad (9)$$

$$k_t = k_{t0} \exp(E_{AT}/Rt) \left(1 + \left(\exp\left(-A_t \left(\frac{1}{f} - \frac{1}{f_{c,t}}\right)\right) + \frac{R_{rd} k_p [N_V]}{k_{t0} \exp(E_{AT}/Rt)} \right)^{-1} \right)^{-1} \quad (10)$$

$$v_T = [M] \frac{M_W}{\rho_M} + [P] \frac{M_W}{\rho_P}; \phi_{M/P} = [M/P] \frac{M_W}{(\rho_{M/P} v_T)} \quad (11)$$

$$f = f_0 + \phi_M \alpha_M (T - T_{g,M}) + \phi_P \alpha_P (T - T_{g,P}) \quad (12)$$

As the monomer and polymer concentrations depend on the degree of double-bond conversion and the monomer consumption dominates the reaction at the beginning of the polymerization (due to the entropic control of the reaction), the decision is made to calculate $[M]$ and $[P]$ as a linear function in an approximation of the findings from Karnes et al. [70] of the double-bond concentration $[N_V]$, yielding:

$$1/2[N_V]_0 = [M]_0 = [M] + [P] \quad (13)$$

$$[P] = 1/2([N_V]_0 - [N_V]_\tau) \quad (14)$$

Substituting the concentration with $[M] = [M]_0(1 - \chi_V)$ leads to the following simplified form factor calculation, so that the form factor becomes a function of degree of conversion χ_V :

$$v_T = [M]_0 M_W \left(\frac{(1 - \chi_V)}{\rho_M} + \frac{\chi_V}{\rho_P} \right) \quad (15)$$

$$f = f_0 + \frac{\left(\frac{\alpha_M (T - T_{g,M})(1 - \chi_V)}{\rho_M} + \frac{\alpha_P (T - T_{g,P}) \chi_V}{\rho_P} \right)}{\frac{(1 - \chi_V)}{\rho_M} + \frac{\chi_V}{\rho_P}} \quad (16)$$

$$f = f_0 + \frac{(\alpha_M (T - T_{g,M}) \rho_P (1 - \chi_V) + \alpha_P (T - T_{g,P}) \rho_M \chi_V)}{\rho_P (1 - \chi_V) + \rho_M \chi_V} \quad (17)$$

By using the results of the simulation model (Supplementary Material Figure S 7b), this function can be empirically approximated as:

$$f = 0.1418 - 0.074 \bullet \exp\left(\frac{\chi_V - 0.00644}{1.97657}\right) \quad (18)$$

The form factor is then calculated with fixed parameters for the polymerization curves as a function of χ_V , which then defines the nonparameterized correction factor for the reaction rate coefficients k_j .

To calculate the degree of conversion, the differential equation for $d[N_V]/d\tau$ needs to be solved for the specific boundary conditions of this experiment. First, the concentration of the active macromolecule chain end radicals is calculated from the quasi steady-state approximation $d[\lambda_R]/d\tau := 0$ based on the model simulation:

$$[\lambda_R] = \sqrt{\frac{k_d [I]_0}{k_t}} \quad (19)$$

First, Eq. 2 needs to be rewritten as the following, after k_{tp} is set to zero and the term is omitted:

$$[I] = \frac{2k_d [I]}{k_i [N_V]} - \frac{1}{k_i [N_V]} \frac{d[I]}{d\tau} \quad (20)$$

This is applied to Eq. 3 to receive:

$$\frac{d[N_V]}{d\tau} = -[N_V] \left(k_i \left(\frac{2k_d[I]}{k_i[N_V]} - \frac{1}{k_i[N_V]} \frac{d[I]}{d\tau} \right) + k_p[\lambda_R] \right) \quad (21)$$

The differential equation can be rewritten as:

$$\frac{d[N_V]}{d\tau} = \frac{d[I]}{d\tau} - 2k_d[I] - k_p[\lambda_R][N_V] \quad (22)$$

The reaction velocity depends on the rate of initiator radical production. However, due to the quasi steady-state approximation, $d[I]/d\tau$ does not change after the initial radical production, as simulated in Figure S7. Omitting the radical concentration change and using equations 15 and 18 yields:

$$\frac{d[N_V]}{d\tau} = -2k_d[I] - k_p \sqrt{\frac{k_d[I]_0}{k_t}} [N_V] \quad (23)$$

Solving the homogeneous differential equation 1 leads to the initiator concentration and substitutes as follows:

$$[I] = [I]_0 \exp(-2k_d\tau) \quad (24)$$

$$\frac{d[N_V]}{d\tau} = -2k_d[I]_0 \exp(-2k_d\tau) - k_p \sqrt{\frac{k_d[I]_0}{k_t}} [N_V] \quad (25)$$

As the dissociation constant k_d is a function of photo-initiator light absorption, it must be substituted with equations 2 and 3; it is clear that:

$$\frac{d[N_V]}{d\tau} = -\frac{2\varepsilon\phi J_0\lambda[I]}{N_Ahc} - k_p \sqrt{\frac{\varepsilon\phi J_0\lambda[I]_0}{N_Ahc k_t}} [N_V] \quad (26)$$

$$\frac{d[N_V]}{d\tau} = -\frac{2\varepsilon\phi J_0\lambda[I]_0 \exp(-2\varepsilon\phi J_0\lambda\tau/N_Ahc)}{N_Ahc} - k_p \sqrt{\frac{\varepsilon\phi J_0\lambda[I]_0}{N_Ahc k_t}} [N_V] \quad (27)$$

The quantum energy absorption factor describing the generation of initiating radicals is defined as absorption coefficient κ , which is constant for the experiment:

$$\kappa = \frac{N_Ahc}{\varepsilon\lambda} \quad (28)$$

Rewriting the rate equation for the double-bond concentration $[N_V]$ as degree of conversion χ_V from equation 1 yields:

$$\frac{d\chi_V}{d\tau} = \frac{2\phi J_0[I]_0 \exp(-2\phi J_0/\kappa \cdot \tau)}{\kappa[N_V]_0} + k_p \sqrt{\frac{\phi J_0[I]_0}{\kappa k_t}} (1 - \chi_V) \quad (29)$$

To access the function $\chi_V(\tau)$, the inhomogeneous linear ordinary differential equation in $[N_V]$ is solved with the first-order approximation of constant rate coefficients k_p and k_t , leading to the unique solution of the homogeneous differential equation $[N_V]_h(\tau)$; this contributes to the particular solution $[N_V]_p(\tau)$ with the undetermined coefficient function $C(\tau)$:

$$[N_V]_h(\tau) = C_0 \exp\left(-k_p \sqrt{\frac{\phi J_0[I]_0}{\kappa k_t}} \tau\right) \quad (30)$$

By the method of variation of parameters, the coefficient function and particular solution are:

$$C(\tau) = \frac{2k_p\phi J_0}{[N_V]_0\kappa} \cdot \sqrt{\frac{[I]_0^3}{k_t}} \cdot \left(\sqrt{\frac{4\phi J_0}{\kappa}} - k_p \sqrt{\frac{[I]_0}{k_t}} \right)^{-1} \exp\left(\left(k_p \sqrt{\frac{[I]_0}{k_t}} - \sqrt{\frac{4\phi J_0}{\kappa}} \right) \sqrt{\frac{\phi J_0}{\kappa}} \tau \right) + C_1 \quad (31)$$

$$[N_V]_p(\tau) = \frac{2k_p\phi J_0}{\kappa} \cdot \sqrt{\frac{[I]_0^3}{k_t}} \cdot \left(\sqrt{\frac{4\phi J_0}{\kappa}} - k_p \sqrt{\frac{[I]_0}{k_t}} \right)^{-1} \exp\left(\left(k_p \sqrt{\frac{[I]_0}{k_t}} - \sqrt{\frac{4\phi J_0}{\kappa}} \right) \sqrt{\frac{\phi J_0}{\kappa}} \tau \right) + C_1 \quad (32)$$

Combining the homogeneous and particular solution to $[N_V]_{ih}(\tau) = [N_V]_h(\tau) + [N_V]_p(\tau)$ and equation 1 leads to the time-dependent degree of conversion function, integrated and solved under the approximation of constant reaction rate coefficients:

$$\chi_{Vih}(\tau) = 1 - C_0 \exp\left(-k_p \sqrt{\frac{\phi J_0[I]_0}{\kappa k_t}} \tau\right) - \frac{[I]_0}{[N_V]_0} \left(\frac{k_p}{2} \sqrt{\frac{\kappa[I]_0}{k_t\phi J_0}} - 1 \right)^{-1} \exp\left(-\frac{2\phi J_0}{\kappa} \tau\right) \quad (33)$$

This equation 29 fulfills the differential Equation 25. Herein, the parameters are fixed except for C_0 , ϕ , k_p and k_t , which are calculated using Equations 5 and 6. The fixed parameters used to calculate the free volume contribution and initiating rate are given in Table 2. As the reaction rate constants are only considered constant in the approximated

solution of the conversion function, the free volume terms to correct for the rate coefficients are calculated as a function of χ_V with equations 5, 6 and 13. As equation 29 converges against full conversion $\chi_V = 1$, it must be corrected for the experimental final degree of conversion, approximated as:

$$\lim_{\tau \rightarrow \infty} \chi_{V\max}(\tau) = 1 - \exp\left(-k_p \sqrt{\frac{2\phi[I]_0}{J_0 \kappa k_t}}\right) = C_1 \quad (34)$$

From the boundary conditions, the parameter constraints are derived as follows:

$$\lim_{\tau \rightarrow 0} \chi_{V\max}(\tau) := 0 \Rightarrow C_0 = 1 - \frac{[I]_0}{[N_V]_0} \left(\frac{k_p}{2} \sqrt{\frac{\kappa[I]_0}{k_t \phi J_0}} - 1 \right)^{-1} \quad (35)$$

Hence, the regression in $\chi_V(\tau)$ is performed under the refinement of C_1 , ϕ , k_{p0} and k_{t0} . As the effective reaction rate coefficients k_p and k_t depend on the free volume parameter, the correction term is calculated for the corresponding degree of conversion so that the refinement of the implicit function can be done for the pre-exponential rate constants k_{p0} and k_{t0} . The concentration of double bonds $[N_V(\tau)]$ and free volume fraction $f(\tau)$ as reaction coordinate-dependent parameters are calculated from the measured $\chi_V(\tau)$. However, due to flaws of the model, an exponential expansion is added for τ .

$$\chi_V(\tau) = C_1 \left(1 - C_0 \exp\left(-k_p \sqrt{\frac{\phi J_0 [I]_0}{\kappa k_t}} \tau^u\right) - \frac{[I]_0}{[N_V]_0} \left(\frac{k_p}{2} \sqrt{\frac{\kappa [I]_0}{k_t \phi J_0}} - 1 \right)^{-1} \exp\left(-\frac{2\phi J_0}{\kappa} \tau^u\right) \right) \quad (36)$$

To calculate the fitting parameters, the degree of double-bond conversion is determined as follows based on the Kubelka–Munk intensities $KM(\tilde{\nu}, t)$:

$$\chi_V(\tau) = 1 - \frac{\frac{\tilde{\nu}_2^{(C=C)}}{\tilde{\nu}_2^{(C=O)}} \int_{\tilde{\nu}_1^{(C=O)}}^{\tilde{\nu}_2^{(C=C)}} KM(\tilde{\nu}, \tau=t) d\tilde{\nu}}{\frac{\tilde{\nu}_1^{(C=C)}}{\tilde{\nu}_2^{(C=O)}} \int_{\tilde{\nu}_1^{(C=O)}}^{\tilde{\nu}_2^{(C=C)}} KM(\tilde{\nu}, \tau=t_0) d\tilde{\nu}} \quad (37)$$

The specifications of the integration areas for the individual IR bands are given in the FT-IR section of the Supplementary Material. From the modeling function, a fit function is defined, from which the numerical results and the unfixed pre-exponential reaction rate coefficients are then calculated.

See Table 2

Supplementary Information: The online version contains supplementary material available at <http://doi.org/10.1007/s10853-021-06634-2>.

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