

RESEARCH ARTICLE

Carbon nitride-coated transparent glass vials as photoinitiators for radical polymerization

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Abstract

Benign polymerization routes offer new perspectives in current polymer technology. Especially for automated or continuous flow synthesis of polymers, new devices and principles have to be considered by the means of minimizing addition or separation sequences as well as the type of a polymer initiation. Near-UV and visible light-induced polymerization utilizing metal-free semiconductor polymeric carbon nitride (pCN) as heterogeneous photocatalyst was a first step into this direction. Moving from heterogeneous powder catalysis (which still requests catalyst separation) to surface photocatalysis via coating glass tubes or vials with pCN thin films is presented. Performance and effectivity of those photoactive reactors are proven by free radical photopolymerization of variety of monomers. Reusability of vials is demonstrated via reversible addition-fragmentation chain-transfer polymerization-assisted block copolymer synthesis. This strategy eliminates the necessity of adding or removing initiators, works at room temperature, and offers a platform for cheap and effective polymer synthesis at the age of automated synthesis.

KEYWORDS

carbon nitride polymer, controlled polymerization, photoactive thin film, photoactive vial, photopolymerization

1 | INTRODUCTION

On the 100th year of macromolecular science, next important steps on how to shape polymer science in the next century are being envisioned, which includes an introduction of simplicity toward high-throughput automated polymer synthesis.¹ In this regards, radical polymerization is mostly thermally initiated which results in energy losses and sluggish initiation kinetics.² This is why most

automated, high-throughput polymer syntheses are based on ionic polymerization mechanism;^{3,4} however then with the necessity to add and terminate the polymerization, which adds two steps, but also brings opportunities. Furthermore, it is also important to facilitate straightforward reaction conditions, such as polymerization with oxygen tolerance,^{5–7} which would allow more benign strategy for automated synthesis.⁸ Moving from thermal initiation to photoinitiation enables to employ the light only for the sensitive step of chain initiation, saving energy, avoiding heating and cooling delays, and in the very end puts less thermal stress on a potentially sensitive reaction system.⁹

Baris Kumru and Paolo Giusto contributed equally to this article.

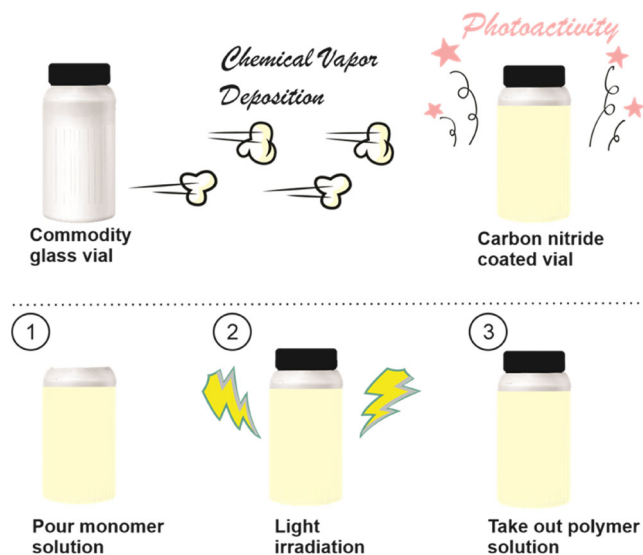
Dedicated to Professor Klaus Müllen on the occasion of his 75th birthday.

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In addition to direct radical formation by using light as a stimuli (i.e., Irgacure materials), photoredox-based initiation has been popularized recently in which Lalevee and colleagues summarized the mechanism and available molecules for photoredox-based initiation in polymer chemistry.¹⁰ The chemically more complex dissolved molecular photocatalysts^{11,12} (which are then also left as fragments in the final product) are meanwhile replaced by heterogeneous inorganic or hybrid semiconductors such as TiO₂,¹³ CdS,¹⁴ and perovskites,¹⁵ which can (and should) be removed from the system¹⁶ by an additional filtration step. Potentially questionable semiconductors based on elements such as Cd or Pb were recently replaced by polymeric graphitic carbon nitride (pCN), a metal-free polymeric semiconductor which has received much attention as it is an efficient photocatalyst operating under visible light.^{17–20} Synthesis from abundant, nitrogen-rich, and low-cost precursors (such as melamine) together with parameters as tunability of bandgap, doping level, and surface modification brought variety of applications for this material in diversified fields such as CO₂ reduction,^{21,22} photovoltaics,^{23–25} water splitting,^{26,27} iontronics,^{28,29} photoelectrochemistry,^{30,31} and very recently optics and photonics.^{32,33}

The relation of pCN and polymer science has been blooming: after the first paper showing the utilization of mesoporous pCN as heterogeneous photoinitiator for free radical polymerization of acrylates,³⁴ many articles have explored the use of pCN in free or controlled radical photopolymerizations^{35–38} and oxidative photopolymerization^{39,40} in solution, as well as it was introduced in heterophase photopolymerizations.⁴¹ Currently we can build on an established background to decipher the mechanism upon light illumination in the presence of vinyl bonds, how to transfer radicals to monomer solution or how to keep them intact on the photocatalyst surface.⁴² However, removing pCN after polymerization might be costly and high effort as some types of pCN stable and well dispersed even after photocatalytic reaction, requiring thus a step forward to simplified synthetic procedures. A switch from bulk pCN to thin films have been recently presented by our team, which the fabrication of pCN thin films via chemical vapor deposition (CVD) was exhibited to synthesize well-defined thin films with high homogeneity and high quality using melamine as a single-source precursor.³² Very recently, we have subjected such pCN thin films as polymer photoinitiator to conduct “grafting from” conditions in order to tailor surface wettability of pCN films by grafting polymers, and to our surprise growth of very thick polymer layers (up to 600 nm) were observed, accompanied with a quasi-living type of photopolymerization.⁴³



SCHEME 1 Schematic description of the synthetic procedures. Coating glass vials with pCN via CVD method (top, inner part of vials are coated), pouring monomer solutions in so-formed photoactive transparent vessels and photopolymerization via light irradiation (thick yellow layer on vials was applied only for visual demonstration). CVD, chemical vapor deposition; pCN, polymeric graphitic carbon nitride

In the present letter, the CVD deposition approach will be combined with polymer chemistry by upgrading simple commodity glass vials as photoactive reaction vessels by coating a thin layer of pCN. The vial-coated system then acts as a readily reusable heterogeneous photocatalyst for radical initiation for polymerization (Scheme 1).

2 | RESULTS AND DISCUSSION

CVD deposition of pCN thin films allows homogeneous coating regardless the shape of the substrate, which is of great advantage compared to common thin film deposition methods that require flat surface substrates.³² In a typical preparation, six vessels (5 ml volume) are placed horizontally in the CVD reaction chamber and coated at 550°C by using 10 g of melamine as a precursor.³² After deposition took place, the coated vessels possess the typical yellowish color due to the deposited pCN film (Figure 1A). When submitted to UV illumination (366 nm) the coated vessel emits bright blue fluorescence homogeneously, whereas the bare vessel does not (Figure 1B), once more confirming that the coating method successfully leads to a homogeneous, complete coverage. The images are in good agreement with the absorbance and fluorescence spectra (Figure 1C) and previous reports on g-CN thin films.³² It should be

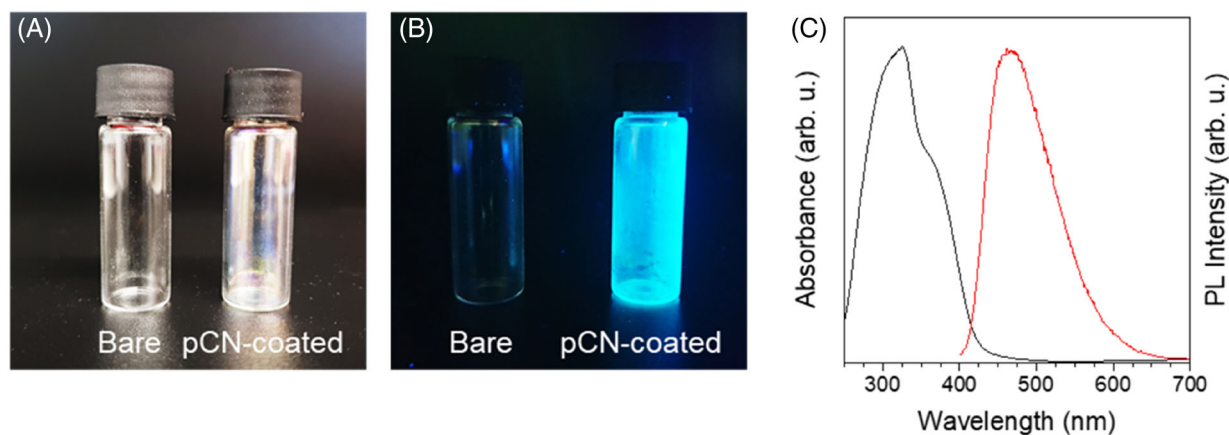


FIGURE 1 (A) Digital image of noncoated (bare) vial and pCN-coated vial, (B) same vials under UV illumination, (C) UV and PL spectra of the pCN-coated vial. pCN, polymeric graphitic carbon nitride

TABLE 1 Polymerization conditions and results on polymer products

Monomer	Cocatalyst	Light source	Conversion (%) ^a	M_n (g mol ⁻¹) ^b	\bar{D}^b
MMA	Triethylamine	Visible light	27	11,500	2.2
Styrene	Triethylamine	Visible light	13	12,000	2.4
DMA	Triethylamine	Visible light	20	7600	2.7
PEGMEMA	Triethylamine	Visible light	9	2050	2.8
1-vinyl imidazole	Triethylamine	Visible light	19	6400	2.4
MMA	–	Visible light	–	–	–
MMA	Triethylamine	UV light	40	41,200	2.3
MMA	Triethylamine	No light	–	–	–
MMA ^c	Triethylamine	Visible light	–	–	–

Note: Reactions were conducted for 2 h for each entry.

Abbreviations: DMA, dimethyl acrylamide; MMA, methyl methacrylate; PEGMEMA, polyethyleneglycol methyl ether methacrylate.

^aMeasured gravimetrically.

^bData obtained via size exclusion chromatography (SEC).

^cReaction conducted in a non-coated glass vial.

mentioned that the extinction coefficient of pCN as a solid-state semiconductor is so high that a 100 nm layer can practically instrumentalize the complete light illumination. And actually, AFM data exhibits 127 (\pm) 20 nm thick pCN layer coated in a vial (Figure S1) thus a photoactivity is expected in so-formed vials.

pCN-coated photoactive vessels were contacted with variety of monomer solutions and illuminated under vigorous stirring (SI for details, Table 1). The monomers were purified in a column prior to use, however monomer solutions were not degassed as previous reports fortified the idea of the presence of oxygen can help the formation of radicals by photoredox initiation.³⁶ Variety of monomers, such as methyl methacrylate (MMA), styrene, *N,N* dimethyl acrylamide (DMA), polyethyleneglycol methyl ether methacrylate 300 (PEGMEMA) and 1-vinyl imidazole (vI), were photopolymerized (1:2 weight ratios of

monomer: solvent) The polymers were then purged out with solvent into a petri dish and dried in vacuum at room temperature (SI for details). An important point to underline is that the triethylamine is needed as a mediator for polymerization to take place, the photoredox cycle forms the radical cation on tertiary amine which then initiates solution polymerization as delineated before.³⁴ In a control experiment, in the absence of trimethylamine, no PMMA was found in solution (Table 1). Similarly, reaction under dark conditions does not occur, which confirms the necessity of light for polymerization initiation. Likewise, the ideal condition does not produce a polymer when reaction is carried out in a non-coated glass vial.

Conversion in 4 h differs in monomers, highest conversion (37%) was obtained for PMMA whereas aqueous radical photopolymerization of PEGMEMA was not so successful (9%). DMA was polymerized with 20% conversion in 4 h,

similar to 1-vinyl imidazole (19%) and conversion of styrene was 13%. Relatively high polydispersities (2.2–2.8) were attained for all samples as polymerization was conducted in non-controlled fashion. Fourier transform infrared (FTIR) spectra of dried polymers are presented in Figure S2–7. As g-CN thin films have more absorption on the UV range, polymerization of MMA was performed under UV light illumination as well, which showed higher conversion (40%) compared to the visible light-induced analog, which leads to a well-known conclusion that light absorption is the key aspect to form initiating species in photo-induced polymerization. Prolonged polymerization under UV light (16 h) using MMA without solvent yielded complete gel formation (Figure S8). Suggested procedure grants the ease of product

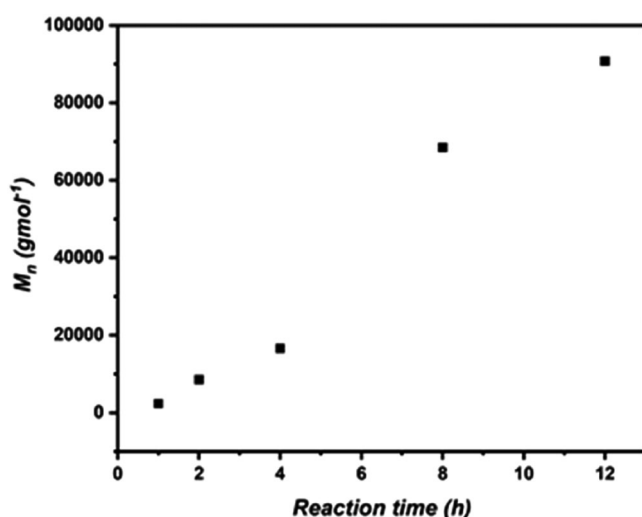


FIGURE 2 Evolution of M_n values for PS via visible light-induced polymerization in pCN-coated vial. pCN, polymeric graphitic carbon nitride; PS, polystyrene

separation as there is no need to remove the photocatalyst from solution, thus forming clean and colorless polymers (Figure S9). $^1\text{H-NMR}$ spectra of the precipitated and dried polystyrene (PS) sample can be found in Figure S10 as an exemplary sample, indicating a clean polymerization process. Furthermore, washing the vial with CDCl_3 after polymerization and investigating its $^1\text{H-NMR}$ spectra revealed an empty spectra (data not shown) thus concluding that there is no adsorption of styrene or PS on pCN surface. A trace amount of monomer is observed in the spectra, however all the samples obtained in this manuscript were subjected to only one precipitation step for a purification.

At this point, we investigated the conversion of styrene during polymerization conditions (Figure 2). The initiation was quite slow and the linear increase in M_n values was observed after 4 h, which is different than a traditional free radical polymerization. This might be due to the photoredox-based nature of radical formation that requires multiple steps to form an active initiating radical. Increase in M_n values was climbed up to 90,000 g mol^{-1} in 12 h, which leads to a conclusion that pCN-coated glass vials can efficiently initiate polymerization if proper conditions are satisfied.

Reusability of catalysts is an important factor that determines the economy of the process and the plausibility of the design of the overall system, from lab scale to industrial scale. Controlled radical polymerization based on reversible addition-fragmentation chain-transfer polymerization (RAFT) method offers a control on polydispersity and introduces a living character to a so-formed polymer thus block copolymerization through chain end fidelity is enabled.⁴⁴ Herein, reusability of pCN-coated glass vials was demonstrated via block copolymer synthesis utilizing a RAFT agent. As explained in more detail in

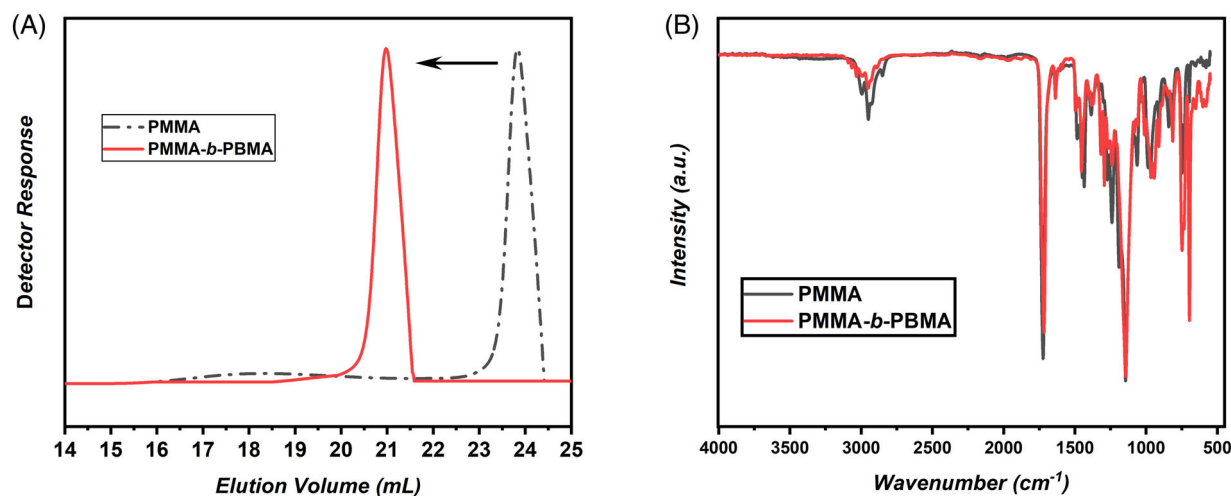


FIGURE 3 (A) SEC elugrams of PMMA and PMMA-*b*-PBMA, (B) FTIR of PMMA and PMMA-*b*-PBMA. FTIR, Fourier transform infrared; SEC, size exclusion chromatography

SI, MMA was photopolymerized in pCN-coated glass vials in the presence of RAFT agent (benzyl benzodithioate), to introduce a living and controlled character to a final polymer product.⁴⁵ After the product separation and drying (~14% conversion), polymer and benzyl methacrylate (BMA) monomer were introduced to the same pCN-coated glass vial where the photo-induced chain extension takes place. It is a good indication for the stability of the coated pCN that they do not disintegrate from the surface via swelling.

SEC elugram clearly indicates a change in molecular weight after chain extension (Figure 3A), M_n value increased from 6000 to 14,300 gmol^{-1} , and polydispersity has only slightly increased from 1.45 (for PMMA) to 1.65 (PMMA-*b*-PBMA). A slight change in FTIR was observed after chain extension, intensity of $-\text{CH}_3$ and $\text{C}=\text{O}$ peaks has slightly decreased whereas slight increase in benzylic peaks was observed (Figure 3B). Overall, pCN-coated glass vials could be used for the controlled radical polymerization and chain extension, whereas the reusability of photoactive pCN-coated vials grants improved economy and processing. Eventually, this new approach will allow a clean polymer synthesis in forthcoming new lab design, using automated systems for large synthesis batches.⁴⁶

3 | CONCLUSION

We have demonstrated the upgrading of commodity glass vials by introducing photoactivity. Coating metal-free semiconductor pCN on the walls of glass vials via CVD produces photoactive vessels, which can be utilized for polymer photoinitiation under UV and visible light. The robustness of the technique was stressed out by performing free radical and controlled radical photopolymerizations without deoxygenation procedures, while the vials can be reused. We believe this approach offers a technological platform that is susceptible to be applied in an automated robotic synthesis conditions, and photopolymerizations as such can be conducted in a simple, reproducible, and scalable way.

4 | EXPERIMENTAL SECTION/ METHODS

4.1 | Materials

All materials were used as received, and monomers were purified through passing basic alumina column. 1-vinyl imidazole (vI, 99%, Alfa Aesar), aluminum oxide (basic, Sigma Aldrich), benzyl benzodithioate (99%, Sigma Aldrich), BMA (96%, Sigma Aldrich), melamine (99%,

Sigma Aldrich), MMA (99%, Sigma Aldrich), DMA (99%, TCI), poly(ethylene glycol) methyl ether methacrylate (PEGMEMA, M_n 300, Sigma Aldrich), styrene (99%, Sigma Aldrich), tetrahydrofuran (THF, 99%, Sigma Aldrich), triethylamine (99.5, Sigma Aldrich), toluene (99.5%, TCI). 50 W LED chips (Foxpic High Power 50 W LED Chip Bulb Light DIY White 3800LM 6500 K) and 30 W UV chip (Fdit, 395–400 nm UV LED chip) were connected to a self-made circuit and cooling system. CVD was performed using a planarGROW-3S-OS CVD System for Organic Semiconductor, provided by planarTECH, with a 3 in. quartz tube.

4.2 | Synthetic procedures

4.2.1 | Coating glass vials with pCN

The preparation of pCN thin films was conducted in a two-zone CVD reactor, as previously reported by our group.⁴⁷ In a typical recipe, 10 g of melamine was placed in a glass boat and heated at 300°C (10°/min) at 10 Torr pressure. The target vials were placed in the second zone and heated up at 550°C for 90 min. The samples were allowed to cool down naturally at room temperature before collecting them.

4.2.2 | Polymerization of MMA

Two-grams of MMA, 0.02 g triethylamine, and 4 g toluene were placed in a pCN-coated vial and irradiated via visible light for 4 h (placed between 2 LED sources). Afterwards, sample is diluted with THF and precipitated in cold methanol (50 ml). Alternatively, diluted solution can be poured in petri dish and dried in vacuum overnight.

4.2.3 | Polymerization of MMA via UV light

Two-grams of MMA, 0.02 g triethylamine, and 4 g toluene were placed in a pCN-coated vial and irradiated via UV light for 4 h (placed between two LED sources). Afterwards, sample is diluted with THF and precipitated in cold methanol (50 ml). Alternatively, diluted solution can be poured in petri dish and dried in vacuum overnight.

4.2.4 | Polymerization of MMA in the absence of triethylamine

Two-grams of MMA and 4 g toluene were placed in a pCN-coated vial and irradiated via visible light for 4 h

(placed between two LED sources). Afterwards, sample is diluted with THF and poured in cold methanol (50 ml). Yet, no polymer product was observed.

4.2.5 | Polymerization of MMA in the absence of light

Two-grams of MMA, 0.02 g triethylamine, and 4 g toluene were placed in a pCN-coated vial and mixed in the absence of light source. Afterwards, sample is diluted with THF and poured in cold methanol (50 ml). Yet, no polymer product was observed.

4.2.6 | Polymerization of MMA in a noncoated glass vial

Two-grams of MMA, 0.02 g triethylamine, and 4 g toluene were placed in a noncoated vial and irradiated via visible light for 4 h (placed between two LED sources). Afterwards, sample is diluted with THF and poured in cold methanol (50 ml). Yet, no polymer product was observed.

4.2.7 | Polymerization of styrene

Two-grams of styrene, 0.02 g triethylamine, and 4 g toluene were placed in a pCN-coated vial and irradiated via visible light for 4 h (placed between two LED sources). Afterwards, sample is diluted with THF and precipitated in cold methanol (50 ml). Alternatively, diluted solution can be poured in petri dish and dried in vacuum overnight.

4.2.8 | Polymerization of DMA

Two-grams of DMA, 0.02 g triethylamine, and 4 g water were placed in a pCN-coated vial and irradiated via visible light for 4 h (placed between 2 LED sources). Afterwards, sample is diluted with water, dialyzed, and freeze-dried overnight.

4.2.9 | Polymerization of PEGMEMA

Two-grams of PEGMEMA, 0.02 g triethylamine, and 4 g water were placed in a pCN-coated vial and irradiated via visible light for 4 h (placed between two LED sources). Afterwards, sample is diluted with water, dialyzed, and freeze-dried overnight.

4.2.10 | Polymerization of vI

Two-grams of vI, 0.02 g triethylamine, and 4 g toluene were placed in a pCN-coated vial and irradiated via visible light for 4 h (placed between two LED sources). Afterwards, sample is diluted with THF and precipitated in cold methanol. Alternatively, diluted solution can be poured in petri dish and dried in vacuum overnight.

4.2.11 | Polymerization kinetics of St

Two-grams of styrene, 0.02 g triethylamine, and 8 g toluene were placed in a pCN-coated vial and irradiated via visible light for 6 h (placed between two LED sources), and 0.5 ml samples were taken in some certain intervals to determine conversion and Mn. Afterwards, samples were precipitated in cold methanol, poured in petri dish, and dried overnight.

4.2.12 | Controlled polymerization of MMA

Two-grams of MMA, 0.01 g triethylamine, 0.1 g RAFT agent, and 4 g toluene were placed in a pCN-coated vial and irradiated via visible light for 4 h (placed between two LED sources). Afterwards, sample is diluted with THF, precipitated in cold methanol (50 ml), and dried in vacuum overnight.

4.2.13 | Block copolymerization with BMA

One-gram of controlled PMMA, 5 mg triethylamine, 0.2 g BMA, and 4 g toluene were placed in the same pCN-coated vial and irradiated via visible light for 4 h (placed between two LED sources). Afterwards, sample is diluted with THF, precipitated in cold methanol (50 ml), and dried in vacuum overnight.

4.3 | Characterization

FTIR spectra of polymer samples were collected using Nicolet iS 5 FTIR spectrometer. SEC of PMMA sample series and PvI were collected in THF using PSS 1260-Iso as a pump, a column system of PSS SDV column with a PSS SDV precolumn, PSS-SECcurity-VWD, and PSS-SECcurity-RID as detectors and a calibration with PMMA standards from PSS. Similar setup was used for PS samples; however, using PS as internal standard. SEC results of PDMA and PEGMEMA were collected using water as eluent in SEC. UV-vis spectra were collected with

Shimadzu UV-2600 in the range 800–300 nm equipped with an integrating sphere. Photoluminescence spectra were recorded by Horiba FluoroMax-4 equipped with a thin film sample holder set at 60° with respect to the excitation beam. Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded on Agilent 400 MHz and chemical shifts were reported in ppm downfield from TMS as an internal standard. Atomic force microscopy analysis has been conducted on NanoScope-Multimode AFM (Digital Instruments) atomic force microscope.

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