Conjugated Ketocarbazoles as Efficient Photoinitiators: From Facile Synthesis to Efficient Two-photon Polymerization

Peng Hu¹, Junzhe Zhu¹, Ren Liu¹,², and Zhiquan Li¹,²*

¹ International Research Center for Photoresponsive Molecules and Materials,  
² Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, 214122, China  
*lzq@jiangnan.edu.cn

Exploration of straightforward synthetic strategies to construct efficient two-photon initiators (2PIs) containing a long conjugate length is essential to promote the development of two-photon photopolymerization (2PP). This paper described a series of ketocarbazoles with C=C bonds as π bridges, cyclic ketones as electron acceptors, and 9-alkyl substituted carbazoles as electron donors. The conjugated 2PIs were prepared straightforwardly via classical aldol condensation reaction and the impact of the central ring size on the photoactivity was systematically studied. The maximum absorption of the 2PIs was located at ~440 nm and good photobleaching behaviors were observed. The initiator with cyclopentanone held the largest two-photon absorption cross section of 377 GM. All the conjugated ketocarbazoles can be used as efficient 2PIs to induced 2PP and exhibited lower threshold energy compared to the widely used commercial photoinitiator TPO and the two-photon resists IP-L.

Keywords: Two-photon initiator, Two-photon polymerization, Microfabrication, Ketocarbazole, Aldol condensation reaction.

1. Introduction

Two-photon induced photopolymerization (2PP) has been intensively investigated due to its excellent spatial control by means of confinement of photopolymerization within focal volume of laser beams [1,2]. Different from the shallow surface reaction of ultraviolet polymerization [3,4], the light source used for 2PP is near-infrared femtosecond laser which hold a deeper penetrating ability, allowing a real 3D writing within the resins with high spatial resolution. Since Maruo first reported the true 3D spiral microstructure manufactured by 2PP in 1997 [5], the method has been widely used in a variety of applications, including optical devices [6,7], functional microdevices [8-11], biomaterials and tissue engineering [12-15].

An efficient 2PP process requires high sensitivity materials containing active two-photon initiators (2PIs) and monomers/oligomers to ensure high writing speeds, low polymerization thresholds, and high-quality resulting structures. As a trigger of polymerization process, 2PIs undergo two-photon absorption and generate reactive species to initiate cross-linking of monomers/oligomers. Therefore, the activity of 2PIs directly affects the fabrication efficiency and the final mechanical properties of the microstructures. Two-photon absorption (2PA) cross sections (σ²PA) is the most common parameter to evaluate the activity of 2PIs. Great efforts have been devoted to design and synthesize chromophores with large σ²PA in recent years [16,17]. To obtain high σ²PA values generally require molecules possessing planar π-system containing long conjugation length with different functional donor (D) and/or acceptor (A) groups [18,19]. To date, Sonogashira and Heck coupling reactions are commonly utilized to introduce triple and double bonds for extending the conjugation length [20-22]. The main drawbacks of such coupling reactions are high cost of palladium catalysts and difficulties associated with multistep synthesis. Therefore, exploration of straightforward and economical
synthetic routes to construct efficient 2PIs is highly desirable.

Aldol condensation reaction is a simple and practical synthetic strategy to fabricate conjugated molecules used in 2PP. Liska’s group synthesized a series of benzylidene cycloketones in one step via aldol condensation and the cycloketone derivatives were efficient 2PIs enabling fast writing speed of 80 mm/s [23]. With proper molecular modification, the benzylidene cycloketones can be used as water-soluble 2PIs [24] and exhibited excellent biocompatibility [25]. The systematic investigation of structure-activity relationships showed that the size of the central ring significantly affected two-photon initiation efficiency. Farsari et al. reported several π-expanded ketocoumarins and found that the aromatic moieties would also affect the two-photon behaviors of benzylidene cycloketones [26]. Taking advantage of the synthetic merit of aldol condensation and with a aim to explore the properties of benzylidene cycloketones with different aromatic moieties, in this paper, three novel conjugated ketocarbazoles with butterfly-shape were designed and synthesized (Fig. 1) and their photochemical behaviors under one- and two-photon excitation were investigated.

2. Experimental
2.1. Materials
Carbazole, 2-ethylhexyl bromide, potassium hydroxide (KOH), phosphorus oxychloride (POCl₃), N,N-dimethylformamide (DMF), cyclobutanone, cyclopentanone, and 4-methylcyclohexanone were purchased from Adams China. Trimethylolpropane triacrylate (TMPTA) and ethoxylated trimethylolpropane triacrylate (TMP3EOTA) were supplied by Jiangsu Kailinruiyang Chemical Co., Ltd., China. Other reagents and solvents used in this work were purchased from Sinopharm Chemical Reagent Co., Ltd., China and were used without further purification unless otherwise stated.

2.2. Synthesis
Synthesis of 2a: 2.0 g (11.9 mmol) of carbazole, 2.0 g (35.7 mmol) of KOH were added to 75 mL DMF and stirred for 30 minutes. Then 2.7 g (14.3 mmol) of 2-ethylhexyl bromide was added dropwise and the mixture was stirred at room temperature for 24 h. Then poured into 300 mL of water and extracted with dichloromethane (3×50 mL). The organic phase was washed with water (3×50 mL) and dried over anhydrous sodium sulfate for 30 min. After dichloromethane was evaporated under reduced pressure, the crude product was purified by column chromatography (PE: EE = 20:1) to obtain 2.86 g of oily liquid with a yield of 87%. ¹H NMR (400 MHz, chloroform-d) δ 8.35 (d, 2H), 7.73 (dd, 2H), 7.49 (d, 2H), 7.18 (d, 2H), 4.24 (dd, 2H), 1.50 – 1.21 (m, 9H), 0.95 (t, 3H), 0.88 (t, 3H).

Fig. 1. The synthetic route of the investigated 2PIs.
Synthesis of 3b: 20 mL of N,N-dimethylformamide was added into a 50 mL flask, and 3 mL of phosphorus oxychloride was added dropwise at 0 °C. The mixture was stirred for 30 minutes and then 2 g of 2a (7.1 mmol) was added and the solution was heat to 90 °C under nitrogen protection. After 4 h, the mixture was poured into 250 mL of water and extracted with dichloromethane (3×30 mL). The organic phase was dried over anhydrous sodium sulfate, and then evaporated under reduced pressure to remove the solvent. The crude product was purified by column chromatography (PE: EE = 10:1) to obtain 1.70 g of oily liquid with a yield of 78%. 1H NMR (400 MHz, chloroform-d) δ 10.12 (s, 1H), 8.63 (d, J = 1.5 Hz, 1H), 8.18 (d, J = 7.7 Hz, 1H), 8.03 (dd, J = 8.5, 1.6 Hz, 1H), 7.55 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.51-7.44 (m, 2H), 7.35 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 4.27-4.15 (m, 2H), 1.54-1.21 (m, 9H), 0.95 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H).

Synthesis of 4c: 500 mg (1.63 mmol) of 3b, 92 mg (1.63 mmol) of KOH and 228 mg (3.26 mmol) of cyclobutanone were added into 50 mL of ethanol, stirred at room temperature for 24 h, and poured into a large amount of water (200 mL). The mixture was extracted with dichloromethane (3×30 mL) and the organic phase was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, a crude product was purified by column chromatography (PE: EE = 5:1) to obtain 740 mg of yellow solid with a yield of 70%. 1H NMR (400 MHz, chloroform-d) δ 8.33 (s, 2H), 8.22 (d, J = 7.7 Hz, 2H), 7.79 (d, J = 7.3 Hz, 2H), 7.57-7.43 (m, 8H), 7.37-7.31 (m, 2H), 4.28-4.17 (m, 4H), 4.07 (s, 2H), 1.52-1.23 (m, 16H), 0.96 (t, J = 7.4 Hz, 6H), 0.90 (t, J = 7.1 Hz, 6H). 13C NMR (101 MHz, chloroform-d) δ 196.18, 141.42, 134.92, 134.84, 129.10, 127.18, 126.16, 123.32, 123.29, 122.82, 120.47, 119.53, 109.39, 109.28, 47.58, 39.45, 31.03, 28.83, 26.92, 24.42, 23.06, 14.05, 10.92. Calcd. for C49H58N2O, 690.4549, found, 690.5313.

5c was synthesized via a similar procedure to 4a with a yield of 85%. 1H NMR (400 MHz, chloroform-d) δ 8.40 (s, 2H), 8.18 (d, J = 7.7 Hz, 2H), 7.90 (s, 2H), 7.78 (dd, J = 8.6, 1.6 Hz, 2H), 7.55-7.41 (m, 6H), 7.35-7.26 (m, 4H), 4.26-4.14 (m, 4H), 3.31 (s, 4H), 1.55-1.19 (m, 17H), 0.93 (dt, J = 22.4, 7.2 Hz, 12H). 13C NMR (101 MHz, Chloroform-d) δ 196.18, 141.42, 134.92, 134.84, 129.10, 127.18, 126.16, 123.32, 123.29, 122.82, 120.47, 119.53, 109.39, 109.28, 47.58, 39.45, 31.03, 28.83, 26.92, 24.42, 23.06, 14.05, 10.92. Calcd. for C48H56NO2, 682.4236, found, 662.4630.

6c was synthesized via a similar procedure to 4a with a yield of 50%. 1H NMR (400 MHz, chloroform-d) δ 8.29 (s, 2H), 8.19 (d, J = 7.7 Hz, 2H), 8.15 (d, J = 2.2 Hz, 2H), 7.69 (dd, J = 8.6, 1.6 Hz, 2H), 7.56-7.50 (m, 2H), 7.47-7.41 (m, 4H), 7.31 (dd, J = 15.4, 7.9 Hz, 2H), 4.23-4.10 (m, 4H), 1.51-1.27 (m, 10H), 1.20 (d, J = 6.5 Hz, 3H), 1.01-0.89 (m, 14H). 13C NMR (101 MHz, chloroform-d) δ 190.05, 141.39, 140.95, 138.31, 133.09, 128.93, 127.08, 126.05, 123.00, 122.95, 122.85, 120.45, 119.35, 109.32, 108.93, 47.53, 39.47, 36.94, 31.04, 29.75, 28.86, 24.44, 23.10, 21.94, 14.10, 10.95. Calcd. for C48H56N2O2, 690.4549, found, 690.5313.

2.3. Characterization

1H NMR (400 MHz) and 13C NMR (101 MHz) spectra were obtained in CDCl3 with a Bruker AVANCE III HD 400 MHz spectrometer. The high-resolution mass spectrometer measurements were performed using MALDI SYNAPT MS from Waters America. UV-vis spectra were measured with a EMC-61PC-UV spectrophotometer. Solutions of the compounds were dissolved in chloroform to a concentration of 10−5 M and placed in quartz cuvettes with an optical path of 10 mm. Fluorescence spectra were measured at the concentration of 10−6 M in chloroform using a CARY Eclipse spectrofluorometer (Varian). Solutions were placed in 10 mm quartz cuvettes. Excitation wavelengths were selected to correspond to the absorption maxima for each individual compound.

2.4. Steady-state photolysis study

The photolysis study of the novel 2PLs was carried out at the concentration of 10−5 M in chloroform. Solutions were placed in a 10 mm cuvette, and irradiated by 405 nm LED light (YW-51220, Shanghai Uvpro Co., Ltd.). The absorbance of exposed solutions was tested to obtain the UV-vis spectra for different times. The light intensity was adjusted to 20 mW/cm2 for the tests.

2.5. Two-photon cross section measurements

The σ2PA of the photoinitiators were measured by z-scan technique, and the experimental setup has been described earlier [27]. Rhodamine B was used as reference to verify the reliability of the experimental setup. Laser pulses at a wavelength of 800 nm with a pulse width of 190 fs were generated from an OPA (Orpheus) pumped by a femtosecond laser system (Pharos SP). All measurements were carried out with a photoinitiator concentration of...
10\(^{-3}\) mol/dm\(^3\) in chloroform at 300 nJ pulse energy.

2.6. Two-photon polymerization tests

A fiber femtosecond laser (LF7808, Shanghai Langyan Optoelectronics Technology Co., Ltd.) was used and its wavelength, pulse width, and repetition rate are 780 nm, 100 fs, and 80 MHz respectively. Detailed information of the equipment can be found elsewhere [28]. Laser focus can be scanned point by point in the material (the distance between two points at x-y-z axis was 150 nm, each scanning point stays for 200 μs). During fabrication, a glass substrate with 170 μm thickness (Menzel-Glaser) was used as the substrate. The acrylate-based resin (TMPTA/TMP3EOTA, 1:1 equiv. of functional groups) containing the 2PI (1.3 × 10\(^{-6}\) mol PI/g resin) was placed on the glass substrate and microstructures were written in resins by controlling the position of the laser focal spot. The microstructure was then rinsed with ethyl alcohol and uncured resin was washed away, leaving only the microstructure bonded to the glass substrate.

3. Results and discussion

3.1. Synthesis

All 2PIs were synthesized by aldol condensation reactions between commercially available cyclic ketones and 3-aldehyde carbazole derivatives. Aldol condensation reaction is effective for the formation of carbon-carbon double bond between various carbonyl compounds. The reactions were carried out using sodium hydroxide as catalyst for ease of preparation and reduced costs. High yields of 70% and 80% were obtained for 4c and 5c, respectively. When increasing the size of the central ring from cyclopentanone to cyclohexanone as in 6c, the yields decreased to 50%. Reduced yield may be attributed to a steric hindrance effect of cyclohexanone, which is obstructive for the nucleophilic addition reaction between the aldehyde and the enols formed via deprotonation at the α-position of the ketones. The branched alkyl chains were introduced to increase the solubility of the conjugated molecules in resins.

![Fig. 2. (a) UV-vis absorption spectra and (b) fluorescence emission spectra of the photoinitiators measured in chloroform with concentrations of 10\(^{-5}\) M and 10\(^{-6}\) M, respectively.](image)

Table 1. Photophysical properties data of the photoinitiators.

| PIs | \(\lambda_{\text{max}}(>400\text{ nm})\) | \(\lambda_{\text{em}}\) | Stokes shift | \(\varepsilon_{\text{max}}\) | \(\sigma_{2PA}\) |
|-----|---------------------------------|-----------------|-------------|----------------|-------------|
|     | (nm)                            | (nm)            | (cm\(^{-1}\)) | (10\(^4\) M\(^{-1}\) cm\(^{-1}\)) | (GM)       |
| 4c  | 442                             | 533             | 3862        | 5.08           | 357         |
| 5c  | 438                             | 515             | 3413        | 5.16           | 377         |
| 6c  | 418                             | 560             | 6066        | 5.20           | 340         |
3.2. Photophysics

Figure 2a shows UV-vis absorption spectra of the photoinitiators in chloroform at room temperature. Similar absorption bands’ shape and intensity were observed for 4c and 5c with a maximum absorption peak located at ~440 nm. Notably, the absorption of cyclohexanone-based compound 6c covered a broad range from 200 nm-500 nm with higher molar extinction coefficients in the ultraviolet region. The size of the central rings impacted not only the absorption behavior but also the fluorescence emission. As shown in Fig. 2b and Table 1, the $\lambda_{em}$ of 6c redshifted to 560 nm compared to that of 5c (515 nm). The largest Stokes shift of 6066 cm$^{-1}$ was observed for 6c, suggesting a more significant change in geometry between the ground state and the first excited singlet state [29].

3.3. Steady-state photolysis

Steady-state photolysis tests were conducted at room temperature with a 450 nm wavelength LED source (20 mW/cm$^2$) to investigate the behaviors of the photoinitiators after absorbing light. Photoinduced reactions would change the shape and intensity of the absorption peaks. As shown in Fig. 3, with prolonged irradiation time, the main absorption peaks in visible light region (above 400 nm) of the photoinitiators decreased significantly, indicating the photoinitiators possess a photobleaching property (Figs. 3a-c). Benzylidene cyclopentanone dyes have been widely used as highly efficient triplet photosensitizers in the UV-vis photopolymerization industry [30]. The observed photobleaching is essential for deep curing and improved homogeneity properties of the cured materials because the photolysis products do not absorb visible light, allowing incident visible light penetrating farther into the resin [29]. The completely bleached performance of 6c was observed in solvent (Fig. 3d).

Fig. 3. Steady-state photolysis of photoinitiators (a) 4c; (b) 5c; (c) 6c in chloroform (10$^{-5}$ M) upon irradiation of 405 nm LED (20 mW/cm$^2$); (d) photobleaching of 6c after 3 min irradiation.

Fig. 4. SEM picture of "doughnut" shaped microstructure arrays using 4c as 2PI with a concentration of 1.3 $\times$ 10$^{-6}$ mol/g resin.
3.4. Two-photon absorption cross section (\(\sigma_{2\text{PA}}\))

To investigate the 2PA properties of the new 2PIs, an open aperture z-scan analysis was performed to determine the \(\sigma_{2\text{PA}}\) at 800 nm and all calculated \(\sigma_{2\text{PA}}\) values are given in Table 1. The \(\sigma_{2\text{PA}}\) of the reference compound Rhodamine B (154 GM) is in good agreement with the literature, verifying the reliability of the experimental setup. Since intramolecular charge transfer is the “driving force” for 2PA, the presence of strong electron-donor and electron-acceptor groups are needed. Additionally, long \(\pi\)-conjugated bridges and good coplanarity, beneficial for extended charge separation, are critical in enhancing the efficiency of intramolecular charge transfer [31]. The investigated conjugated ketocarbazoles comprise typical D-\(\pi\)-A-\(\pi\)-D core structures, where alkylated carbazoles groups act as donors, vinyl as \(\pi\)-conjugated bridges, and cycloketones as acceptors. The cyclobutanone-based compound 4c exhibits a \(\sigma_{2\text{PA}}\) of 357 GM, while the \(\sigma_{2\text{PA}}\) value of cyclopentanone-based compound 5c increased to 377 GM. When increasing the size of the central ketone from cyclopentanone to cyclohexanone as in 6c, the \(\sigma_{2\text{PA}}\) value dropped to 340 GM. The reduced \(\sigma_{2\text{PA}}\) might be attributed to the nonplanarity of the six-membered ring, which decreases the degree of conjugation [23]. Since z-scan measurement can only provide information of the absorption behavior of the initiators, 2PP structuring tests were performed to further characterize the initiation efficiency of the new 2PIs under two-photon excitation.

3.5. Two-photon polymerization (2PP) tests

Two-photon initiation activity of the synthesized 2PIs in the acrylate resin system was investigated via a femtosecond laser processing platform with 2PI concentrations of \(1.3 \times 10^{-6}\) mol/g resin. For reference, commercially available initiator TPO and commercial two-photon resist IP-L were also studied. Figure 4 shows a series of "doughnut" shaped microstructure arrays (inner diameter 8 \(\mu\)m, outer diameter 12 \(\mu\)m, layer height 3 \(\mu\)m) fabricated using 4c as 2PI. From left to right, the laser writing speed is constant (\(~750\) \(\mu\)m/s), and the laser power gradually increased (left to right). The corresponding microstructures from partly written (polymerization threshold) to well-defined and then to burned (burning threshold) were classified to evaluate the initiation efficiency of the 2PIs (Fig. 4). The processing window defined as the power range between the polymerization threshold and burning threshold was exhibited in Fig. 5. The beginning of yellow region represents the polymerization threshold, while that of red region refers to the burning threshold, and the green region between yellow and red represents the good structuring range (Fig. 5). Good microstructures can be prepared using the laser power within this interval.

Fig. 5. 2PP processing window of all investigated 2PIs and references under irradiation of a 780 nm pulsed laser (PIs concentration: \(1.3 \times 10^{-6}\) mol PI/g resin).

The commercially available photoinitiator TPO was unable to provide any acceptable microfabrication results at 780 nm. The commercial two-photon resists IP-L, can be used to build fine microstructures at a laser intensity of about 14 mW (Fig. 5). Since the specific composition is unknown for such premixed commercial resins, the degree of freedom to adjust the formulation is limited. All the formulations containing conjugated ketocarbazoles as 2PIs showed lower polymerization thresholds than IP-L. Low polymerization threshold are beneficial for high throughput in mass production because it allows a splitting of the initial laser beam for parallel processing with multiple laser heads at high feed rates. The cyclopentanone-based 2PI 5c exhibited the lowest polymerization threshold (10 mW) and the widest processing window due to its large \(\delta_{2\text{PA}}\) value of 377 GM.

Additionally, 3D Chinese characters of Jiangnan University and 3D Great Wall microstructure were fabricated using 5c as 2PI (Fig. 6). A complete 3D microstructure can be printed out at a laser power of 15 mW. Slight deformation occurred due to the large aspect ratio of the Great Wall model and the shrinkage during the curing process of the acrylate resins.
Fig. 6. SEM micrographs of microstructures of (a) Chinese characters of Jiangnan University and (b) the Great Wall fabricated using 5c as 2PI.

4. Conclusion

A series of conjugated ketocarbazoles comprise typical D-π-A-π-D core structures, where alkylated carbazoles groups act as donors, vinyl as π-conjugated bridges, and cycloketones as acceptors, were facilely prepared via classical aldol condensation reactions. The size of the central rings impacted not only the absorption behavior but also the fluorescence emission. The photobleachable property of the conjugated ketocarbazoles shows potential for the application of deep photopolymerization. In 2PP fabrication tests, the formulation containing novel 2PIs exhibited lower threshold energy compared to the widely used commercial photoinitiator TPO and the two-photon resists IP-L.

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References

1. Y. Lin and J. Xu, Adv. Opt. Mater., 6 (2018) 11.
2. K. Sugioka and Y. Cheng, Appl. Phys., Rev., 1 (2014) 35.
3. Z. Q. Li, H. Chen, C. Wang, L. Chen, J. C. Liu, and R. Liu, J. Polym. Sci. A: Polym. Chem., 56 (2018) 994.
4. R. Liu, H. Chen, Z. Q. Li, F. Shi, and X. Y. Liu, Polym. Chem., 7 (2016) 2457.
5. S. Maruo, O. Nakamura, and S. Kawata, Opt. Lett., 22 (1997) 132.
6. Y. Peng, S. Jrdi, X. Y. Yang, M. Dupont, F. Hamie, X. Q. Dinh, X. W. Sun, T. Xu, and R. Bachelot, Adv. Mater. Technol., 4 (2019) 10.
7. R. Woods, S. Feldbacher, D. Zidar, G. Langer, V. Satzinger, V. Schmidt, N. Pucher, R. Liska, and W. Kern, Opt. Mater. Express, 4 (2014) 486.
8. D. D. Han, Y. L. Zhang, J. N. Ma, Y. Q. Liu, B. Han, and H. B. Sun, Adv. Mater., 28 (2016) 8328.
9. T. Y. Huang, M. S. Sakar, A. Mao, A. J. Petruska, F. M. Qiu, X. B. Chen, S. Kennedy, D. Mooney, and B. J. Nelson, Adv. Mater., 27 (2015) 6644.
10. R. Kawano, T. Osaki, H. Sasaki, and S. Takeuchi, Small, 6 (2010) 2100.
11. S. Kim, S. Lee, J. Lee, B. J. Nelson, L. Zhang, and H. Choi, Sci. Rep., 6 (2016) 9.
12. M. Lunzer, L. Y. Shi, O. G. Andriotis, P. Gruber, M. Markovic, P. J. Thurner, D. Ossipov, R. Liska, and A. Ovsianikov, Angew. Chem. Int. Ed., 57 (2018) 15122.
13. A. Marino, C. Filippeschi, V. Mattoli, B. Mazzolai, and G. Ciofani, Nanoscale, 7 (2015) 2841.
14. J. F. Xing, M. L. Zheng, and X. M. Duan, Chem. Soc. Rev., 44 (2015) 5031.
15. W. Zhu, X. Y. Ma, M. L. Gou, D. Q. Mei, K. Zhang, and S. C. Chen, Curr. Opin. Biotechnol., 40 (2016) 103.
16. B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I. Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X. L. Wu, S. R. Marder, and J. W. Perry, Nature, 398 (1999) 51.
17. X. M. Wang, F. Jin, Z. G. Chen, S. Q. Liu, X. H. Wang, X. M. Duan, X. T. Tao, and M. H. Jiang, J. Phys. Chem. C, 115 (2011) 776.
18. Z. Li, A. Rosspeintner, P. Hu, G. Zhu, Y. Hu, X. Xiong, R. Peng, M. Wang, X. Liu, and R. Liu, Polym. Chem., 8 (2017) 6644.
19. R. Nazir, F. Bourquard, E. Balciunas, S. Smolen, D. Gray, N. V. Tkachenko, M. Farsari, and D. T. Gryko, ChemPhysChem, 16 (2015) 682.
20. R. Nazir, E. Balciunas, D. Buczyńska, F. Bourquard, D. Kowalska, D. Gray, S. Mackowsk, M. Farsari, and D. T. Gryko,
21. Y. P. Tian, L. Li, J. Z. Zhang, J. X. Yang, H. P. Zhou, J. Y. Wu, P. P. Sun, L. M. Tao, Y. H. Guo, C. K. Wang, H. Xing, W. H. Huang, X. T. Tao, and M. H. Jiang, *J. Mater. Chem.*, 17 (2007) 3646.

22. J. F. Xing, W. Q. Chen, J. Gu, X. Z. Dong, N. Takeyasu, T. Tanaka, X. M. Duan, and S. Kawata, *J. Mater. Chem.*, 17 (2007) 1433.

23. Z. Li, N. Pucher, K. Cicha, J. Torgersen, S. C. Ligon, A. Ajami, W. Husinsky, A. Rosspeintner, E. Vauthey, S. Naumov, T. Scherzer, J. Stampfl, and R. Liska, *Macromolecules*, 46 (2013) 352.

24. Z. Li, J. Torgersen, A. Ajami, S. Mühleder, X. Qin, W. Husinsky, W. Holnthoner, A. Ovsianikov, J. Stampfl, and R. Liska, *RSC Adv.*, 3 (2013) 15939.

25. M. Tromayer, P. Gruber, M. Markovic, A. Rosspeintner, E. Vauthey, H. Redl, A. Ovsianikov, and R. Liska, *Polym. Chem.*, 8 (2017) 451.

26. R. Nazir, P. Danilevicius, A. I. Ciuciu, M. Chatzinikolaidou, D. Gray, L. Flamigni, M. Farsari, and D. T. Gryko, *Chem. Mater.*, 26 (2014) 3175.

27. Z. Q. Li, P. Hu, J. Z. Zhu, Y. J. Gao, X. Xiong, and R. Liu, *J. Polym. Sci. A: Polym. Chem.*, 56 (2018) 2692.

28. Z. N. Tian, Q. D. Chen, Z. Y. Hu, Y. K. Sun, Y. H. Yu, H. Xia, and H. B. Sun, *Opt. Lett.*, 43 (2018) 3116.

29. Z. Q. Li, X. C. Zou, G. G. Zhu, X. Y. Liu, and R. Liu, *ACS Appl. Mater. Interfaces*, 10 (2018) 16113.

30. B. Monroe, W. Smothers, D. Keys, R. Krebs, D. Mickish, A. Harrington, S. Schicker, M. Armstrong, D. Chan, and C. Weathers, *J. Imag. Sci.*, 35 (1991) 19.

31. G. S. He, L. S. Tan, Q. Zheng, and P. Prasad, *Chem. Rev.*, 108 (2008) 1245.