CJC Chinese Journal of Chemistry
中 国 化 学 - An International Journal

Title: Fluorescent Columnar Liquid-Crystalline Polymers: Synthesis, Mesomorphic Behaviors and Tunable Emission Wavelengths

Authors: Bin Mu, Zhelin Zhang, Yu Zhao, Xiangnan Hao, and Wei Tian*

This work may now be cited as: *Chin. J. Chem.* **2021**, *39,* 10.1002/cjoc.202100051.

WILEY-VCH SIOC CCS

ISSN 1001-604X • CN 31-1547/O6
mc.manuscriptcentral.com/cjoc
www.cjc.wiley-vch.de

Cite this paper: *Chin. J. Chem.* **2021**, *39*, XXX—XXX. **DOI: 10.1002/cjoc.202100XXX**

Fluorescent Columnar Liquid-Crystalline Polymers: Synthesis, Mesomorphic Behaviors and Tunable Emission Wavelengths

Bin Mu, Zhelin Zhang, Yu Zhao, Xiangnan Hao, and Wei Tian*

Shanxi Key Laboratory of Macromolecular Science and Technology, MOE Key Laboratory of Material Physics and Chemistry under Extraordinary Conditions, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an, 710129, China.

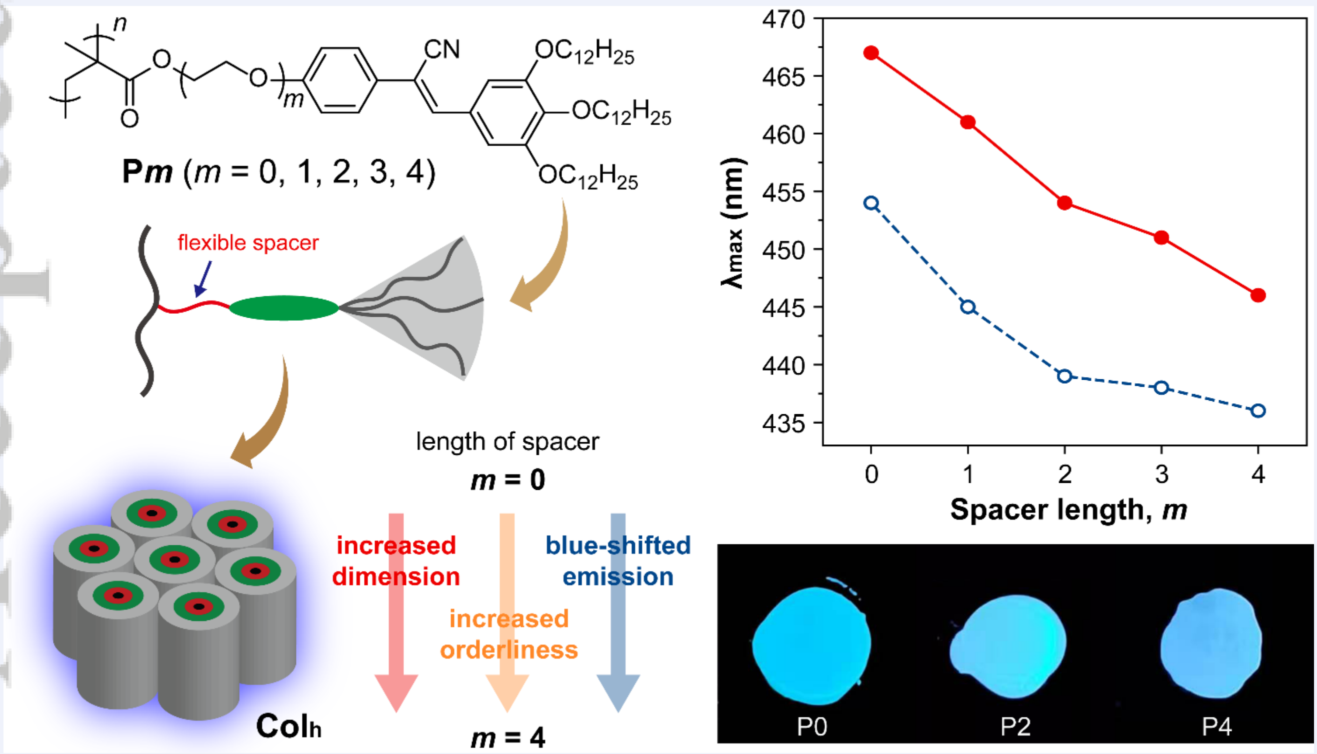
Keywords

Liquid crystals | Polymers | Columnar mesophases | Fluorescence

Main observation and conclusion

Fluorescent columnar liquid-crystalline polymers have attracted intensive attention due to their unique features that can be applied in many fields. However, the utilization of molecular engineering to achieve efficient fluorescence tuning has rarely been resolved. Herein, we report a series of liquid-crystalline polymers with α-cyanostilbene pendants attaching to polymethacrylate backbone by variant length ethylene glycol spacers, that assemble into hexagonal columnar mesophases and exhibit efficient fluorescence emission. Both the columnar ordering and the emission wavelength can be tuned just by altering the length of flexible spacers. With an elongation of the spacer, the columnar ordering and dimensions increased, and the fluorescence emission blue-shifted gradually. With good correlation of molecular design, columnar structure and fluorescence property, this study is expected to augment the understanding of spacer length influence in liquid-crystalline polymers and provide a guidance for the design and development of novel functional polymer materials.

Comprehensive Graphic Content



---

*E-mail: happytw_3000@nwpu.edu.cn

View HTML Article
Supporting Information

Background and Originality Content

Columnar morphology is of fascinating interest for the construction of various intriguing materials including in optoelectronic, biomimetic, and mechanical fields.[1-5] The self-organization of polymers into columnar mesophase can share the common properties of liquid crystals such as self-organization, self-healing, and the ability to respond to external stimuli.[6-10] Much of the effort has been devoted to discotic liquid crystal-based polymers, as the stack of discotic molecules can drive the formation of columnar phases that are capable of promising optoelectronic applications.[11-15] Besides, there are several other types of polymers that can form columnar phase, including mesogen-jacketed liquid-crystalline polymers,[16,17] dendronized polymers,[18,19] and hemiphasmid polymers,[20-25] which make it possible to incorporate much more functions and applications.

Recently, thanks to the development of solid-state emission materials based on the concept of aggregation-induced emission,[26,27] liquid-crystalline polymers bearing aggregation-induced emission-active pendants have arisen considerable interest due to the combination of liquid crystal property and fluorescence performance that have shown great advantages on broad applications in optoelectronics.[28-37] The most common efforts have been devoted to incorporating tetraphenyl ethylene or α-cyanostilbene (CS) into polymer system for the formation of fluorescent liquid-crystalline polymers, which may assemble into various mesomorphic structures, however, in most cases lamellar mesophases were observed.[31-37] As the chemical structures of both main-chain and side-chain can be freely tailored, and subtle change may give rise to significant structural transformation and thus fluorescence color alteration, it will provide an attractive strategy for the development of smart optical materials. However, there are only a few examples concerning fluorescent columnar liquid-crystalline polymers,[28-30] especially the utilization of some key structural factors such as the alteration of spacer length and molecular weight to achieve fluorescence tuning behavior remain unresolved.

Flexible spacer usually plays a vital role in determining the assembly mechanism and supramolecular structure of liquid-crystalline polymers.[38-42] The spacer decoupling effect has been widely adopted and applied in the study of calamitic mesogen based lamellarly arranged polymers, of which longer spacer would lead to higher ordered smectic structures.[38-40] In contrast, in discotic columnar polymer system, we have proposed positive coupling between polymer backbone and discotic side groups is preferred for the formation of well-organized columnar lattices.[12,13,41,42] In view of above consideration, our intention here is to develop fluorescence columnar liquid-crystalline polymers and to regulate their supramolecular assembly mechanisms and thus fluorescence properties through tuning the length of flexible spacers.

As shown in Figure 1, we herein report a series of hemiphasmid polymers by adopting aggregation-induced emission-active α-cyanostilbene (CS)[43-47] as the calamitic mesogen with tapered dodecyl minidendrons, which is connected to a polymethacrylate main chain through variant length spacers. Hydrophilic oligo(ethylene glycol) was designed as the flexible spacer to induce the formation of columnar phase, possessing a core-shell structure as a result of the nanosegregation within the column.[48-50] All the liquid-crystalline polymers form hexagonal columnar mesophase, and notably exhibit increased columnar dimensions, increased orderliness and blue-shifted fluorescence emission with the increase of spacer length from 0 to 4 ethylene glycol subunits. With good correlation of molecular design, columnar structure and fluorescence property, this finding is expected to augment the understanding of spacer length influence in liquid-crystalline polymers and provide a guidance for the design and development of novel functional polymer materials.

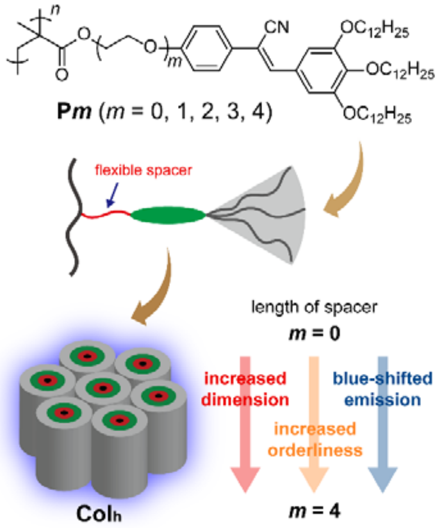


Figure 1 Molecular structure of the fluorescent liquid-crystalline polymers P*m* and their assembly into hexagonal columnar mesophase (Col_h), exhibiting increased dimension, increased orderliness and blue-shifted fluorescence emission with an elongation of the flexible spacer from *m* = 0 to 4 ethylene glycol subunits.

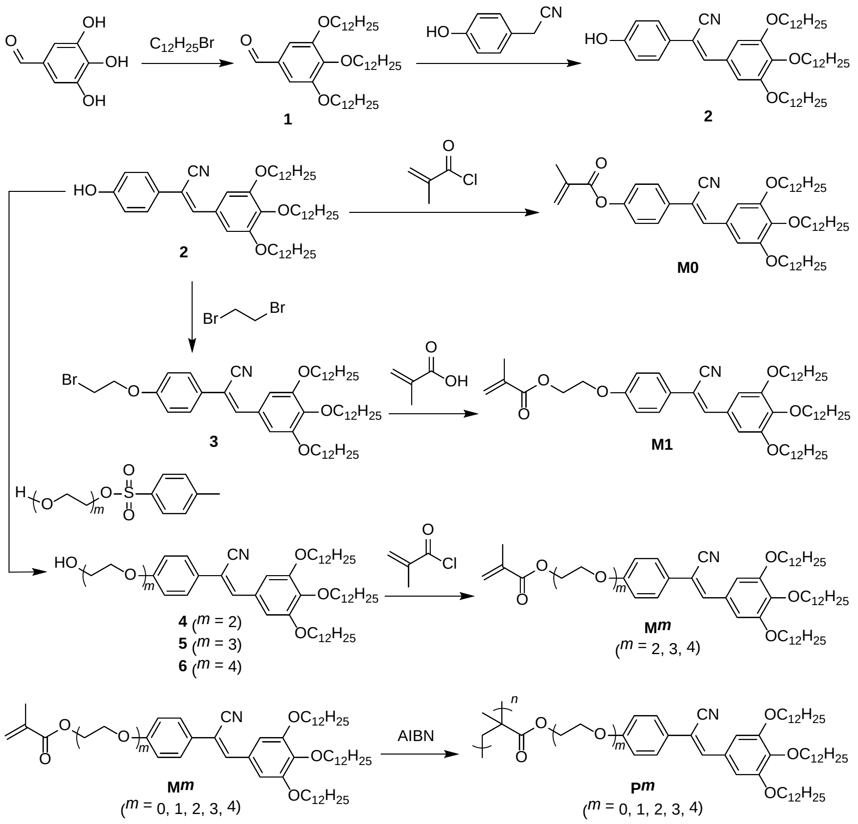
Results and Discussion

Scheme 1 outlines the synthesis of the CS-based methacrylate monomers M*m* and their corresponding polymers P*m* with different length spacers. The synthesis of monomers was performed via three synthetic routes, depending on the length of spacers, from an easily available hydroxyl CS minidendron intermediate **2**, which was obtained according to our previous publication on the synthesis of CS-based fluorescence liquid crystals.[51,52] Specifically, M0 without flexible spacer was synthesized via a simple esterification of the hydroxyl functionalized CS **2** and methacryloyl chloride under a mild condition. As for M1, an excess amount of 1,2-dibromoethane was used to undergo etherification with **2**, and the resulting **3** was subsequently treated with methacrylic acid to afford the monomer with only an ethylene glycol subunit spacer. The synthesis of M*m* (*m* = 2, 3, 4) was carried out by referring to the literature method[48] by utilizing 4-toluenesulfonate functionalized oligo(ethylene glycol) to introduce the spacers with varied number of ethylene glycol subunits. Synthetic details and molecular characterization data are available in the Supporting Information. Figure 2 displayed nuclear magnetic resonance (NMR) and mass spectroscopy (MS) analysis for representative M4 to illustrate the identified molecular structure of thus obtained monomers. All resonance shifts together with their protonic assignments and their corresponding integrations were in good agreement with the expected chemical structure of M4 (Figure 2a). Mass spectrum (Figure 2b) also provided a strong support for the identification of the monomer structure, with the appearance of molecular ionic peaks arising from $[M + H]^+$, $[M + Na]^+$ and $[M + K]^+$.

Polymerization of the methacrylate monomers M*m* was performed in tetrahydrofuran using 2,2-azobis(isobutyronitrile) (AIBN) as radical initiator (Scheme 1). Actually, attempts to synthesize the target polymers in other solvents including 1,4-dioxane, toluene, chlorobenzene and *N,N*-dimethylformamide have been carried out, but it turned out to be unsuccessful and in most cases polymer products were not obtained or only harvested in low yield. Although the occurrence of severe volatilization loss of solvent tetrahydrofuran during polymerization could not be avoided and usually a small amount of solvent remained after the completion of polymerization, a very high polymerization efficiency can be observed. The resulting polymers P*m* were obtained in about 90%

yield (Table S1) even after purification by silica-gel column chromatography (dichloromethane eluent to remove the residual monomer). After polymerization, the characteristic vinyl proton at 5.59 and 6.15 ppm of the methacrylate monomer disappeared and the whole resonance peaks became broadened and overlapped (Figure 2a), both suggesting the successful polymerization and pure polymer sample was obtained. Gel permeation chromatography (GPC) analysis (Figure 2c) of the obtained polymers showed relative number-average molecular weights around 30,000 g mol^{-1} and polydispersity indexes about 1.4 (Table S1). The successful preparation of the series carefully designed liquid-crystalline polymers with relatively high molecular weights offers an ideal platform for the systematical investigation of the spacer length dependent mesomorphic behaviors and fluorescence properties.

Scheme 1 Synthetic routes towards the methacrylate monomers (M*m*) and their polymerization into corresponding polymers P*m* with *m* = 0, 1, 2, 3, 4 denoting the ethylene glycol number of the spacer.



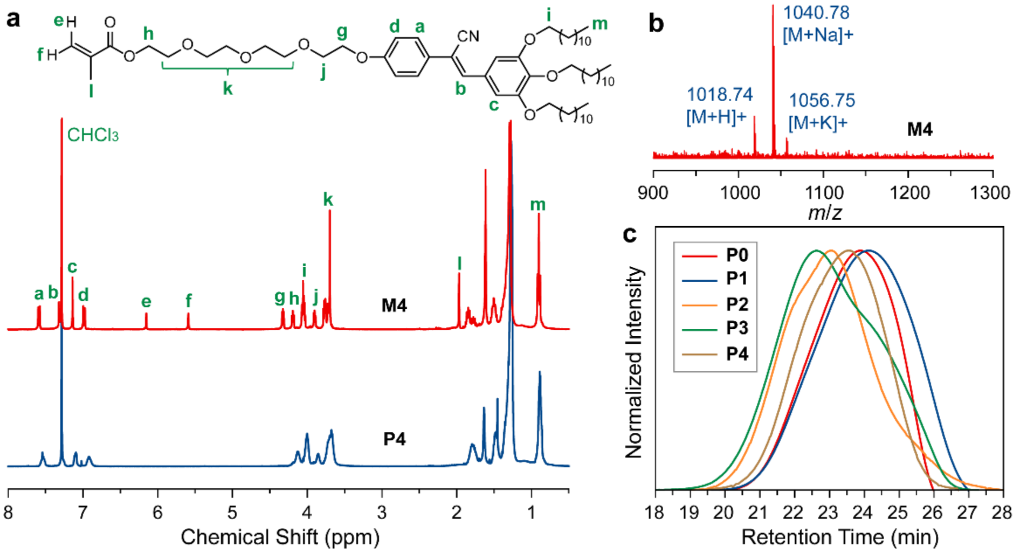


Figure 2 (a) ^{1}H NMR spectra comparison for representative monomer M4 and corresponding polymer P4 in $CDCl_3$ solution. (b) Representative mass spectrum of monomer M4 obtained via electrospray ionization mass spectrometry. (c) Normalized GPC traces of thus obtained series polymers P*m* with spacer length ranging from *m* = 0 to 4.

Table 1 Thermotropic properties, structural parameters, and fluorescence behaviors of the polymers P*m*.

Polymer code	Phase behavior^a [°C(J/g)]	Lattice parameter^b [nm]	μ^c	ξ^d [nm]	$\lambda_{max,solid}$ ($w_{1/2}$)^e [nm]	Φ_{solid}^f [%]	$\lambda_{max,solution}$ ($w_{1/2}$)^e [nm]	$\Phi_{solution}^f$ [%]
P0	Cr -21(8.3) Col$_h$ 131(0.2) I	*a* = 4.74	6.23	35.3	467(100)	4.2	454(97)	0.6
P1	Cr -18(4.8) Col$_h$ 81(0.2) I	*a* = 5.16	7.02	40.1	461(99)	4.6	445(86)	0.8
P2	Cr -12(5.3) Col$_h$ 74(0.4) I	*a* = 5.37	7.24	62.0	454(97)	4.4	439(82)	0.7
P3	Cr 0(5.2) Col$_h$ 92(0.5) I	*a* = 5.52	7.31	67.8	451(92)	3.9	438(78)	0.5
P4	Cr 7(15.9) Col$_h$ 77(0.4) I	*a* = 5.75	7.58	73.5	446(89)	3.8	436(73)	0.6

^{a} Thermal data were collected from DSC heating cycles at a rate of 10 °C min^{-1}. ^{b} Lattice parameter (*a*) in the hexagonal columnar mesophase was determined by X-ray scattering analysis. ^{c} μ is the number of monomer units per column stratum. ^{d} Two-dimensional inter-columnar correlation length (ξ) was evaluated through Scherrer equation. ^{e} The emission maximum (λ_{max}) in dichloromethane solution and solid states was determined by fluorescence measurement, and $w_{1/2}$ in bracket represents the full width at half maximum of the fluorescence spectra. ^{f} The fluorescence quantum yield (Φ) was obtained from dichloromethane solution and solid states.

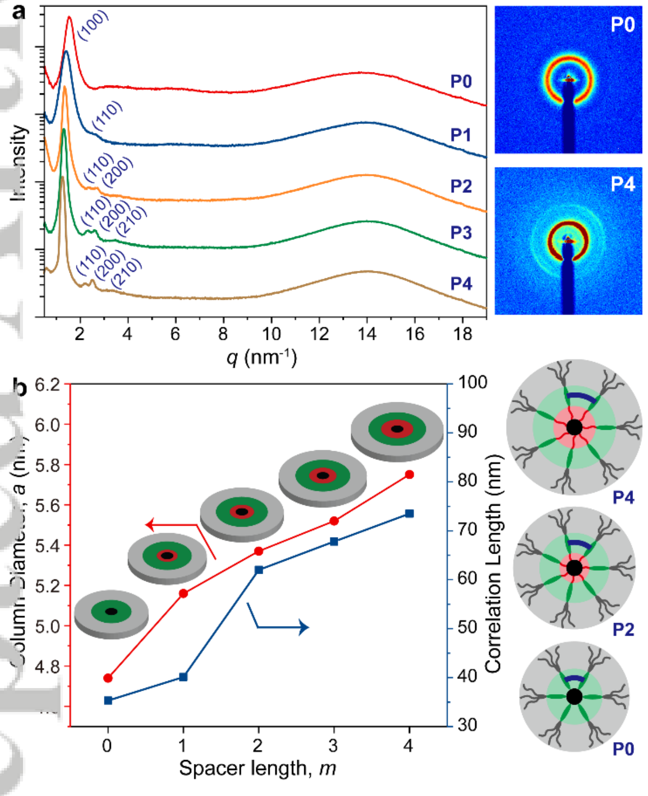


Figure 3 (a) X-ray scattering patterns indicated with proposed indexing of the series liquid-crystalline polymers with different length spacers. (b) Spacer length dependent columnar dimensions and two-dimensional inter-columnar correlation lengths, with insets showing column cross section and right side depicting representative molecular arrangement in a column stratum with different length spacers.

Thermal analysis by a combination of polarized optical microscopy (POM), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and X-ray scattering measurements demonstrated the whole polymers can transform into birefringent and shearable liquid crystal mesophases with a relatively broad temperature range that spans across the room temperature. POM observation (Figure S1) for representative P0, P2, and P4 showed obvious pseudo focal-conic fan-shaped textures, typical for columnar liquid crystal mesophases. TGA (Figure S2) demonstrated good thermal stability over 300 °C. Then DSC was utilized to examine their thermotropic properties (Figure S3), which displayed a transition peak from crystalline (Cr) to liquid-crystalline phase at low temperature and a small isotropization signal at high temperature for the whole polymers. As expected, the CS containing polymers exhibited aggregation-induced emission property (Figure S4) and thus solid-state light emission.[43-47] Fluorescence images (Figure S1) taken under 365 nm ultraviolet light illumination clearly demonstrated the polymers exhibited fluorescence emission in their orderly assembled solid state. Additionally, the emission color appeared to slightly blue-shift from cyan to blue with an increase of the spacer length. Relevant data regarding to their thermal behaviors, structural parameters, and photophysical properties in both solution and solid states are summarized in Table 1.

To confirm the presence of mesomorphic phases and further identify the detailed assembled structures for the series liquid-crystalline polymers, X-ray scattering experiments were performed with the whole scattering curves and representative scattering patterns presented in Figure 3a. A strong scattering peak at low angles and a diffuse halo in the wide-angle range can be obviously seen, both of which possibly pointed to the formation of columnar liquid crystal mesophases. Specifically, the diffuse halo was approximately 14 nm^{-1} (~0.45 nm) as a result of the liquid-like arrangement of peripheral tapered dodecyl minidendrons, while the strong peak at low angles, associated with some small scattering shoulders, if existed, were generated by the two-dimensional periodic array of the columnar arrangement. The *q*-value for all the polymers with different length spacers followed a ratio of 1:√3:√4:√7, typical for hexagonally arranged columnar liquid crystal mesophases (Col$_h$, *p6mm*).

By a preliminary comparison, it is evident to notice that the ordering of the columnar mesophases revealed increase with the longer spacer, which can be confirmed by the occurrence of higher order scattering signals and also the increased correlation length deduced by Scherrer equation (Figure 3b).[13] This is not unreasonable by taking into consideration the conventional spacer decoupling effect where longer spacer usually induced higher ordered liquid crystal structures in side-chain calamitic liquid-crystalline polymers.[38-40] Besides, the nanosegration between the hydrophilic oligo(ethylene glycol) spacer and hydrophobic aromatic and paraffinic segments may also contribute to the formation of more ordered columnar structure with a longer spacer.[48-50] The lattice parameters were calculated according to $a = 2d_{(100)}/\sqrt{3}$ based on the (100) scattering peak at small angles of the identified hexagonal columnar liquid crystal structure, which clearly indicated that the columnar dimensions underwent a significant increase with the elongation of the flexible spacers (Figure 3b). However, the number of monomer units per column stratum (μ), estimated by the literature method adopted in dendronized polymers,[18,19] appeared to be around 7 for the whole polymers with an exception of 6 for the polymer P0. This almost constant μ value irrespective of spacer length is in sharp contrast to that reported in liquid-crystalline polymers with side-chain azobenzene minidendrons where μ increased significantly as the spacer became longer.[22] Such a significant difference was probably arising from more flexible ethylene glycol spacer adopted rather than the common alkyl chain used in the literature. It is just because the constant number of monomer units per column stratum that would facilitate the interaction between adjacent

CS moieties to be controlled by the spacer length. The smaller columnar dimensions would lead to stronger interaction between adjacent CS mesogens as illustrated in the right side of Figure 3b, which accordingly would give rise to increased electronic coupling and thus red-shifted fluorescence emission as discussed later.

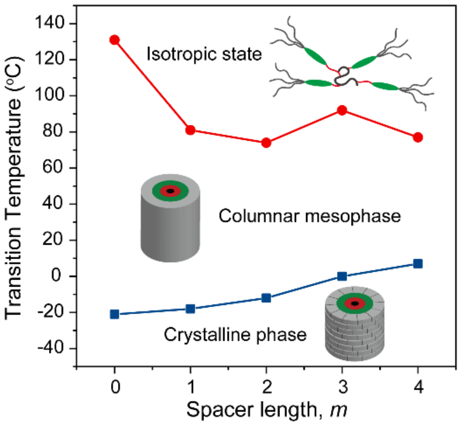


Figure 4 Dependence of phase transition temperatures versus the length of the spacer *m* of the columnar liquid-crystalline polymers P*m* determined from DSC with a heating rate of 10 °C min^{-1}.

Figure 4 shows the phase transition temperatures during heating process and their change trends as a function of the spacer length (*m*). First, it is very interesting to notice that the melting temperatures from crystalline to liquid-crystalline transition were monotonically increasing with an elongation of the spacers. This was probably arising from the decreased coupling effect with the elongation of flexible spacers that facilitated the formation of more stable crystalline phases of CS mesogens with peripheral aliphatic minidendrons, which showed great accordance to the X-ray scattering results where longer spacers induced more ordered columnar mesophases. In contrast, the isotropization temperatures exhibited a trend of decreasing with the increase of spacer length, suggesting a decrease of the columnar stability. It can be rationalized based on the core-shell columnar structures as shorter spacer would lead to stronger jacketing effect of the tapered CS minidendrons around polymethacrylate main chain, which accordingly gave rise to more stable polymer columnar morphology against temperatures. This was reminiscent of the fact found in other types of columnar polymer materials such as positive coupling between the polymer backbone and side-chain discotics,[12] and the concept of mesogen-jacketed liquid-crystalline polymers,[16,17] as they usually contributed to the formation of columnar mesophases with higher isotropization temperatures. The unexpected elevation of the isotropization temperature from P2 to P3 was supposed to be caused by the competition between the crystallinity of the CS minidendrons and the forming ability of polymer columnar phases.

To gain further insight into their spectroscopic properties, all polymers were investigated by ultraviolet visible (UV-vis) absorption and fluorescence emission experiments. The absorption maxima in both solution and solid states (Figure S5) seemed to be almost the same irrespective of the length of spacers, suggesting a simple intermolecular packing rather than the H-/J-type aggregation that was usually observed in CS-based liquid crystals.[30-32,43-47] However, the solid-state emission spectra exhibited red-shift of more than ten nanometers with respect to that in solution (Figure 5a,b), possibly suggesting the presence of electronic coupling between the CS chromophores in the excited state. Besides, the fluorescence quantum yields collected from solid-state were around 4.2%, showing several times larger than that in solution (Table 1), which further confirmed the aggregation-induced emission feature of this kind of CS-containing polymers. Notably, it is surprising to find that the emission maxima underwent a gradual red-shift and broadening with the decrease of the spacer lengths in both solution and solid states, as revealed in Figure 5c and the full width at half maximum ($w_{1/2}$) of the fluorescence spectra (Table 1), respectively. Such a red-shift with the shortening of the spacer length was supposed to be arising from the increased interaction (or electronic coupling) between adjacent CS moieties by making a comparison with the emission maximum at 436 nm of molecularly dissolved CS monomers (Figure S6), agreeing well with the result derived from the X-ray scattering analysis. This assumption could also be supported by the time-resolved fluorescence lifetime experiment (Figure S7), where the more degree of red-shift in solid state was associated with a slightly longer fluorescence lifetime (Figure 5d), while the lifetime was too short to be resolved in their solution state.

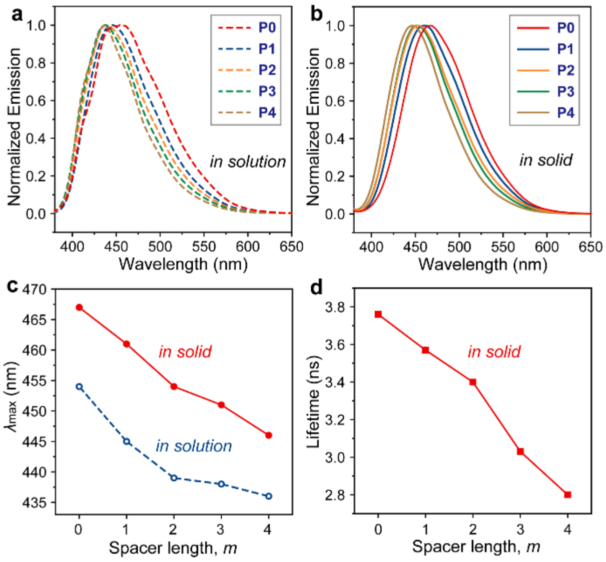


Figure 5 Fluorescence emission spectra of the series polymers (a) in dichloromethane solution and (b) in assembled solid state with the excitation wavelength at 350 nm of the maximum UV absorption. Dependence of (c) fluorescence emission maximum and (d) average lifetime versus the spacer length (*m*) of the polymers P*m* in both solution and solid states.

Therefore, a good correlation can be obtained between the molecular design especially the spacer lengths, assembled liquid crystal structures, and fluorescence emission properties. Although fluorescent liquid-crystalline polymers have been reported in some cases,[28-37] the utilization of molecular engineering strategy to achieve efficient tuning of their emission remain a challenge, especially lacking systematical and well-regulated investigations. Thus the finding herein allowing a precise control on the emission wavelength via tuning the spacer length of this kind of fluorescent columnar liquid-crystalline polymers, will provide a guidance for the design and development of novel functional polymers that will have potential applications in optoelectronic devices. Besides, the spacer length influence, a key question in liquid-crystalline polymers,[38-41] can be better understood by quantitatively comparing the sensitive change of fluorescence in response to the subtle difference of molecular arrangement.

Conclusions

In conclusion, we have reported here a series of fluorescent liquid-crystalline polymers by attaching aggregation-induced emission-active CS minidendrons to polymethacrylate main chains with variant length ethylene glycol spacers, which assembled into hexagonal columnar mesophases. Although the columnar dimensions underwent a significant increase with the elongation of the flexible spacers, the number of monomer units per column stratum (μ) appeared to be around 7 for the whole polymers. Such an almost constant μ value irrespective of the spacer length facilitated the interaction (or electronic coupling) between adjacent CS moieties to be controlled by the spacer length. The fluorescence emission displayed a gradual blue-shift from cyan to blue with an increase of the spacer length from 0 to 4 ethylene glycol subunits. The study provides an efficient strategy to get better understanding towards the influence of spacer lengths in liquid-crystalline polymers, and contributes to the design and development of novel functional polymer materials.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2021xxxxx.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (21805228, 22022107 and 22071197), China Postdoctoral Science Foundation (2018M633563) and Natural Science Basic Research Plan in Shaanxi Province of China (2020JC-20). We would also like to thank the Analytical & Testing Center of Northwestern Polytechnical University for DSC measurement.

References

[1] Woehrle, T.; Wurzbach, I.; Kirres, J.; Kostidou, A.; Kapernaum, N.; Litterscheidt, J.; Haenle, J. C.; Staffeld, P.; Baro, A.; Giesselmann, F.; Laschat, S. Discotic Liquid Crystals. *Chem. Rev.* **2016**, *116*, 1139-1241.

[2] Sergeyev, S.; Pisula, W.; Geerts, Y. H. Discotic Liquid Crystals: A New Generation of Organic Semiconductors. *Chem. Soc. Rev.* **2007**, *36*, 1902-1929.

[3] Wu, J.; Pisula, W.; Müllen, K. Graphenes as Potential Material for Electronics. *Chem. Rev.* **2007**, *107*, 718-747.

[4] Kato, T.; Yoshio, M.; Ichikawa, T.; Soberats, B.; Ohno, H.; Funahashi, M. Transport of ions and electrons in nanostructured liquid crystals. *Nature Rev. Mater.* **2017**, *2*, 17001.

[5] Zhao, R.; Zhao, T.; Jiang, X.; Liu, X.; Shi, D.; Liu, C.; Yang, S.; Chen, E.-Q. Thermoplastic High Strain Multishape Memory Polymer: Side-Chain Polynorbornene with Columnar Liquid Crystalline Phase. *Adv. Mater.* **2017**, *29*, 1605908.

[6] Fleischmann, E.-K.; Zentel, R. Liquid-Crystalline Ordering as a Concept in Materials Science: From Semiconductors to Stimuli-Responsive Devices. *Angew. Chem. Int. Ed.* **2013**, *52*, 8810-8827.

[7] Tschierske, C. Development of Structural Complexity by Liquid-Crystal Self-assembly. *Angew. Chem. Int. Ed.* **2013**, *52*, 8828-8878.

[8] Kato, T.; Uchida, J.; Ichikawa, T.; Sakamoto, T. Functional Liquid Crystals towards the Next Generation of Materials. *Angew. Chem. Int. Ed.* **2018**, *57*, 4355-4371.

[9] Bisoyi, H. K.; Li, Q. Stimuli Directed Alignment of Self-Organized One-Dimensional Semiconducting Columnar Liquid Crystal Nanostructures for Organic Electronics. *Prog. Mater. Sci.* **2019**, *104*, 1-52.

[10] Kumar, S. *Chemistry of Discotic Liquid Crystals: From Monomers to Polymers*; CRC: Boca Raton, FL, 2010.

[11] Mu, B.; Wu, B.; Pan, S.; Fang, J.; Chen, D. Hierarchical Self-Organization and Uniaxial Alignment of Well Synthesized Side-Chain Discotic Liquid Crystalline Polymers. *Macromolecules* **2015**, *48*, 2388-2398.

[12] Mu, B.; Pan, S.; Bian, H.; Wu, B.; Fang, J.; Chen, D. Well-Organized Columnar Superlattices via Positive Coupling between Polymer Backbone and Discotic Side Groups. *Macromolecules* **2015**, *48*, 6768-6780.

[13] Mu, B.; Hao, X.; Chen, J.; Li, Q.; Zhang, C.; Chen, D. Discotic columnar liquid-crystalline polymer semiconducting materials with high charge-carrier mobility via rational macromolecular engineering. *Polym. Chem.* **2017**, *8*, 3286-3293.

[14] Zhu, Y.-F.; Guan, X.-L.; Shen, Z.; Fan, X.-H.; Zhou, Q.-F. Competition and Promotion between Two Different Liquid-Crystalline Building Blocks: Mesogen-Jacketed Liquid-Crystalline Polymers and Triphenylene Discotic Liquid Crystals. *Macromolecules* **2012**, *45*, 3346-3355.

[15] Yu, Z.-Q.; Lam, J. W. Y.; Zhao, K.; Zhu, C.-Z.; Yang, S.; Lin, J.-S.; Li, B. S.; Liu, J.-H.; Chen, E.-Q.; Tang, B. Z. Mesogen jacketed liquid crystalline polyacetylene containing triphenylene discogen: synthesis and phase structure. *Polym. Chem.* **2013**, *4*, 996-1005.

[16] Zhou, Q. F.; Li, H. M.; Feng, X. D. Synthesis of liquid-crystalline polyacrylates with laterally substituted mesogens. *Macromolecules* **1987**, *20*, 233-234.

[17] Chen, X.-F.; Shen, Z.; Wan, X.-H.; Fan, X.-H.; Chen, E.-Q.; Ma, Y.; Zhou, Q.-F. Mesogen-jacketed liquid crystalline polymers. *Chem. Soc. Rev.* **2010**, *39*, 3072-3101.

[18] Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. Dendron-Mediated Self-Assembly, Disassembly, and Self-Organization of Complex Systems. *Chem. Rev.* **2009**, *109*, 6275-6540.

[19] Sun, H.-J.; Zhang, S.; Percec, V. From structure to function via complex supramolecular dendrimer systems. *Chem. Soc. Rev.* **2015**, *44*, 3900-3923.

[20] Zheng, J.-F.; Liu, X.; Chen, X.-F.; Ren, X.-K.; Yang, S.; Chen, E.-Q. Hemiphasmidic Side-Chain Liquid Crystalline Polymer: From Smectic C Phase to Columnar Phase with a Bundle of Chains as Its Building Block. *ACS Macro Lett.* **2012**, *1*, 641-645.

[21] Liu, X.-Q.; Wang, J.; Yang, S.; Chen, E.-Q. Self-Organized Columnar Phase of Side-Chain Liquid Crystalline Polymers: To Precisely Control the Number of Chains Bundled in a Supramolecular Column. *ACS Macro Lett.* **2014**, *3*, 834-838.

[22] Xu, Y.-S.; Shi, D.; Gu, J.; Lei, Z.; Xie, H.-L.; Zhao, T.-P.; Yang, S.; Chen, E.-Q. Synthesis and self-organization of azobenzene containing hemiphasmidic side-chain liquid-crystalline polymers with different spacer lengths. *Polym. Chem.* **2016**, *7*, 462-473.

[23] Lin, C.; Ringsdorf, H.; Ebert, M.; Kleppinger, R.; Wendorff, J. H. Structural variations of liquid crystalline polymers with phasmidic-type mesogens. *Liq. Cryst.* **1989**, *5*, 1841-1847.

[24] Percec, V.; Heck, J.; Ungar, G. Liquid-crystalline polymers containing mesogenic units based on half-disk and rodlike moieties. 5. Side-chain liquid-crystalline poly(methylsiloxanes) containing hemiphasmidic mesogens based on 4-[[3,4,5,-tris(alkan-1-yloxy)benzoyl]oxy]-4'-[[p-(propan-1-yloxy)benzoyl]oxy]biphenyl groups. *Macromolecules* **1991**, *24*, 4957-4962.

[25] Percec, V.; Heck, J. Liquid crystalline polymers containing mesogenic units based on half-disc and rod-like moieties. I. Synthesis and characterization of 4-(11-undecan-1-yloxy)-4′-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]biphenyl side groups. *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 591-597.

[26] Mei, J.; Leung, N. L. C.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015**, *115*, 11718-11940.

[27] Zhao, Z.; Zhang, H.; Lam, J. W. Y.; Tang, B. Z. Aggregation-Induced Emission: New Vistas at the Aggregate Level. *Angew. Chem. Int. Ed.* **2020**, *50*, 9888-9907.

[28] Zhu, Y.; Zheng, M.; Tu, Y.; Chen, X.-F. Supramolecular Fluorescent Polymers Containing α-Cyanostilbene-Based Stereoisomers: Z/E-Isomerization Induced Multiple Reversible Switching. *Macromolecules* **2018**, *51*, 3487-3496.

[29] Wu, Y.; Zhang, S.; Pei, J.; Chen, X.-F. Photochromic fluorescence switching in liquid crystalline polynorbornenes with α-cyanostilbene side-chains. *J. Mater. Chem. C* **2020**, *8*, 6461-6469.

[30] Yang, M.; Liu, Z.; Li, X.; Yuan, Y.; Zhang, H. Influence of flexible spacer length on self-organization behaviors and photophysical properties of hemiphasmidic liquid crystalline polymers containing cyanostilbene. *Euro. Polym. J.* **2020**, *123*, 109459.

[31] Yuan, Y.; Li, J.; He, L.; Liu, Y.; Zhang, H. Preparation and properties of

side chain liquid crystalline polymers with aggregation-induced emission enhancement characteristics. *J. Mater. Chem. C* **2018**, *6*, 7119-7127.

[32] Chen, Y.; Lu, P.; Yuan, Y.; Zhang, H. Preparation and property manipulation of high efficiency circularly polarized luminescent liquid crystal polypeptides. *J. Mater. Chem. C* **2020**, *8*, 13632-13641.

[33] Guo, Y.; Shi, D.; Luo, Z.-W.; Xu, J.-R.; Li, M.-L.; Yang, L.-H.; Yu, Z.-Q.; Chen, E.-Q.; Xie, H.-L. High Efficiency Luminescent Liquid Crystalline Polymers Based on Aggregation-Induced Emission and "Jacketing" Effect: Design, Synthesis, Photophysical Property, and Phase Structure. *Macromolecules* **2017**, *50*, 9607-9616.

[34] Luo, Z.-W.; Tao, L.; Zhong, C.-L.; Li, Z.-X.; Lan, K.; Feng, Y.; Wang, P.; Xie, H.-L. High-Efficiency Circularly Polarized Luminescence from Chiral Luminescent Liquid Crystalline Polymers with Aggregation-Induced Emission Properties. *Macromolecules* **2020**, *53*, 9758-9768.

[35] Li, Q.; Li, X.; Wu, Z.; Sun, Y.; Fang, J.; Chen, D. Highly efficient luminescent side-chain polymers with short-spacer attached tetraphenylethylene AIEgens via RAFT polymerization capable of naked eye explosive detection. *Polym. Chem.* **2018**, *9*, 4150-4160.

[36] Yuan, W. Z.; Yu, Z. Q.; Tang, Y.; Lam, J. W. Y.; Xie, N.; Lu, P.; Chen, E. Q.; Tang, B. Z. High Solid-State Efficiency Fluorescent Main Chain Liquid Crystalline Polytriazoles with Aggregation-Induced Emission Characteristics. *Macromolecules* **2011**, *44*, 9618-9628.

[37] Meng, Z.; Fu, K.; Zhao, Y.; Zhang, Y.; Wei, Z.; Liu, Y.; Ren, X. K.; Yu, Z. Q. Aggregation-induced red-shifted emission and fluorescent patterning of poly(aryleneethynylene) with a lateral AIEgen substituent. *J. Mater. Chem. C* **2020**, *8*, 1010-1016.

[38] Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H. W.; Vill, V. *Handbook of Liquid Crystals: High Molecular Weight Liquid Crystals*, Volume 3; Wiley-VCH: Weinheim, Germany, 1998.

[39] Wang, X.-J.; Zhou, Q.-F. *Liquid Crystalline Polymers*; World Scientific Publishing: Singapore, 2004.

[40] Yu, Z. Q.; Li, T. T.; Zhang, Z.; Liu, J. H.; Yuan, W. Z.; Lam, J. W. Y.; Yang, S.; Chen, E. Q.; Tang, B. Z. Phase Behaviors of Side-Chain Liquid Crystalline Polyacetylenes with Different Length of Spacer: Where Will the Decoupling Effect Appear? *Macromolecules* **2015**, *48*, 2886-2893.

[41] Mu, B.; Wu, B.; Chen, D. Macromolecular Engineering on Triphenylene Based Discotic Side-chain Liquid Crystalline Polymers. *Acta Polym. Sin.* **2017**, 1574-1590.

[42] Guo, Y.; Shi, D.; Luo, Z. W.; Xu, J. R.; Li, M. L.; Yang, L. H.; Yu, Z. Q.; Chen, E. Q.; Xie, H. L. *Macromolecules* **2017**, *50*, 9607-9616.

[43] Martínez-Abadía, M.; Giménez, R.; Ros, M. B. Self-Assembled α-Cyanostilbenes for Advanced Functional Materials. *Adv. Mater.* **2018**, *30*, 1704161.

[44] Zhu, L.; Zhao, Y. Cyanostilbene-based intelligent organic optoelectronic materials. *J. Mater. Chem. C* **2013**, *1*, 1059-1065.

[45] An, B.-K.; Gierschner, J.; Park, S. Y. π-Conjugated Cyanostilbene Derivatives: A Unique Self-Assembly Motif for Molecular Nanostructures with Enhanced Emission and Transport. *Acc. Chem. Res.* **2012**, *45*, 544-554.

[46] Lin, S.; Gutierrez-Cuevas, K. G.; Zhang, X.; Guo, J.; Li, Q. Fluorescent Photochromic α-Cyanodiarylethene Molecular Switches: An Emerging and Promising Class of Functional Diarylethene. *Adv. Funct. Mater.* **2021**, *31*, 2007957.

[47] Zhao, J.; Chi, Z.; Zhang, Y.; Mao, Z.; Yang, Z.; Ubba, E.; Chi, Z. Recent progress in the mechanofluorochromism of cyanoethylene derivatives with aggregation-induced emission. *J. Mater. Chem. C* **2018**, *6*, 6327-6353.

[48] Percec, V.; Tomazos, D.; Heck, J.; Blackwell, H.; Ungar, G. Self-assembly of taper-shaped monoesters of oligo(ethylene oxide) with 3,4,5-tris(n-dodecan-1-yloxy)benzoic acid and of their polymethacrylates into tubular supramolecular architectures displaying a columnar hexagonal mesophase. *J. Chem. Soc. Perkin Trans. 2* **1994**, 31-44.

[49] Percec, V.; Schlueter, D.; Kwon, Y. K.; Blackwell, J.; Moeller, M.; Slangen, P. J. Dramatic Stabilization of a Hexagonal Columnar Mesophase Generated from Supramolecular and Macromolecular Columns by the Semifluorination of the Alkyl Groups of Their Tapered Building Blocks. *Macromolecules* **1995**, *28*, 8807-8818.

[50] Percec, V.; Schlueter, D.; Ungar, G.; Cheng, S. Z. D.; Zhang, A. Hierarchical Control of Internal Superstructure, Diameter, and Stability of Supramolecular and Macromolecular Columns Generated from Tapered Monodendritic Building Blocks. *Macromolecules* **1998**, *31*, 1745-1762.

[51] Mu, B.; Li, X.; Zhao, Y.; Quan, X.; Tian, W. Processing-Dependent Lamellar Polymorphism of Hyperbranched Liquid-Crystalline Polymer with Variable Light Emission. *Macromolecules* **2020**, *53*, 5720-5727.

[52] Mu, B.; Zhao, Y.; Li, X.; Quan, X.; Tian, W. Enhanced Conductivity and Thermochromic Luminescence in Hydrogen Bond-Stabilized Columnar Liquid Crystals. *ACS Appl. Mater. Interfaces* **2020**, *12*, 9637-9645.

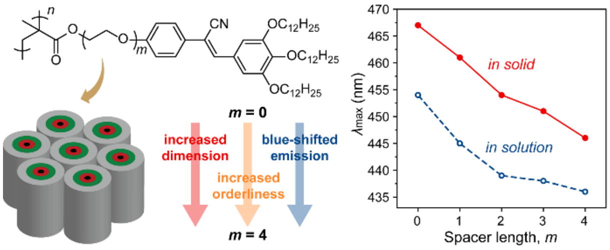
(The following will be filled in by the editorial staff)
Manuscript received: XXXX, 2021
Manuscript revised: XXXX, 2021
Manuscript accepted: XXXX, 2021
Accepted manuscript online: XXXX, 2021
Version of record online: XXXX, 2021

Entry for the Table of Contents

Fluorescent Columnar Liquid-Crystalline Polymers: Synthesis, Mesomorphic Behaviors and Tunable Emission Wavelengths

Bin Mu, Zhelin Zhang, Yu Zhao, Xiangnan Hao, Wei Tian*

Chin. J. Chem. **2021**, *39*, XXX—XXX. **DOI: 10.1002/cjoc.202100XXX**



A series of fluorescent polymers in hexagonal columnar liquid crystals were prepared, and their mesomorphic behaviors and emission wavelengths were tuned by the lengths of flexible spacers.