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Influence of Flexible Spacer Length on Self-organization Behaviors

and Photophysical Properties of Hemiphasmidic Liquid Crystalline

Polymers Containing Cyanostilbene

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Abstract

A series of hemiphasmidic luminescent liquid crystalline polymers, in which the hemiphasmidic mesogen containing cyanostilbene were linked to the polymethacrylate main-chains via flexible spacers with different lengths, named poly {(Z)-m-(4-(1-cyano-2-(3,4,5-tris(octyloxy)phenyl)vinyl)phenoxy)alkyl methacrylate} (donated as Pr-m, m = 2, 4, 6, 8, 10) were synthesized via free radical polymerization. The phase structures and photophysical properties of Pr-m were investigated in detail by a combination of techniques including differential scanning calorimetry (DSC), polarizing optical microscopy (POM), small-angle X-ray scattering (SAXS), UV-Vis absorption spectra (UV-Vis spectra), photoluminescence spectra (PL spectra) and particle size analyzer. The results revealed that the phase structures of Pr-m transformed from hexagonal columnar phase (m = 2, 4) to smectic A phase (m = 6, 8, 4)10) with the increasing of flexible spacer length. All of the polymers featured similar AIEE properties, however, the solid state quantum yields of Pr-m decreased with the increasing flexible spacer length, and the solid quantum yields of Pr-m decreased from 8.55 (Pr-2) to 3.71 (Pr-10) with the increasing flexible spacer length.

Key words: Hemiphasmidic luminescent liquid crystalline polymer; aggregation-induced emission enhancement characteristic; phase structure; flexible spacer.

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Introduction

Over the past few decades, liquid crystals (LCs) have been widely studied as a type of functional material [1-9]. A substantial number of LCs have been synthesized, and their physical and chemistry properties have been investigated because the LCs show excellent anisotropic physical properties that can be used in many classical fields, such as stimuli-responsive [10-12], information storage [3, 4], and photomechanical materials [13, 14] etc. Among various applications of LCs, display materials is always the most important application direction of LCs. However, the conventional liquid crystal materials are non-self-luminescent, so that a backlight needs to be added in the liquid crystal display device, which violates the development trend of energy saving and thinning of liquid crystal display device [15]. Therefore, new strategy toward more efficient liquid crystal display device is highly desirable.

Luminescent liquid crystals (LLCs), which combines optoelectronic characteristics of luminescent materials with the unique properties of anisotropic fluids, is expected to be an effective way to solve those problems mentioned above. LLCs can overcome the shortcomings of traditional liquid crystals as display materials and enjoy tremendous advantages for the construction of linear or circular polarized light emitting materials [16, 17]. In view of the traditional luminogens, researchers have tried to construct fluorescent liquid crystal materials [18-20]. However, due to the aggregation caused quenching (ACQ) effect, these fluorescent liquid crystal materials usually emit strong fluorescence only in dilute solution while hardly emit light in aggregate state, which makes the preparation of LLCs with excellent performance intractable [21-24].

In 2001, Tang firstly proposed the aggregation-induced emission (AIE) [25], which successfully solved the contradiction between fluorescence quenching in the aggregation state and the necessary order packing for liquid crystals, and provided an attractive platform for the development of LLCs. Nowadays, scientists pays a lot of attention to the combination of liquid crystal and aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE) characteristic. Based on the AIE-active or AIEE-active dye, a large number of small molecule LLCs have been

prepared and investigated in detail [26-35]. Most of those LLCs show excellent luminescence efficiency in the aggregated state. Simultaneously, abundant self-organization structures, including nematic, hexagonal columnar, and smectic phase have been observed in those LLCs system. Being unsatisfied with the achievements in the field of small molecule, researchers continue further studies on luminescent liquid crystalline polymers (LLCPs) with AIE or AIEE characteristics due to the particular advantage on processing performance and regulation of ordered structure. By click polymerization, Tang et al. synthesized a series of main-chain LLCPs (AIE-LCP), bearing tetraphenylethylene (TPE) as fluorescent group and biphenyl mesogenic units respectively [36]. All polymers in AIE-LCP series show liquid crystalline properties with high solid-state emission. Xie et al. introduced TPE into mesogen-jacketed liquid crystalline polymers system and constructed a novel series of LLCPs (Pm) by "Jacketing" effect [37]. α-Cyanostilbenic and its derivatives show AIEE characteristics, reversible photoisomerization just like azobenzene [38-40], and can be used as mesogens. Yuan first reported a series of side-chain LLCPs (PMnPVP18 and PMmPVPCN) bearing α -cyanostilbene as mesogenic units and AIEE-active chromophore [41, 42]. The liquid crystalline property, photoluminescent behaviors, and reversible photoisomerization were also studied in detail.

Very recently, our group constructed a novel series LLCPs through introducing the cyanostilbene, as the rod-like segments, into hemiphasmidic side chain LCPs [43]. By adjusting the number and the length of terminal alkoxy chains, we successfully regulated the self-organization structures and fluorescence properties of such LLCPs. Actually, flexible spacer is also crucial to the hemiphasmidic side chain LCPs. As a result of positive coupling effect and decoupling effects imposed by spacer, the self-organization behavior of hemiphasmidic side chain LCPs would be closely related to the flexible spacer length [44, 45]. Sheng Chen reported a new series of hemiphasmidic side-chain liquid crystalline polymethacrylates containing biphenyl mesogens with different spacer lengths [44]. With increasing spacer length, the liquid crystalline phase structures of polymers turned from columnar phase to smetic phase. Er-Qiang Chen reported A series of new azobenzene containing hemiphasmidic side-chain liquid crystalline polymers (P-n, n = 2, 6, 10, 14) [45]. P-2 and P-6 exhibited a hexagonal columnar (Φ_H) phase. As longer spacers are introduced, P-10 and P-14 can form a centered rectangular columnar (Φ_R) phase at low temperatures, and turned into the Φ_H phase upon heating. Furthermore, according to the previous studies, we can recognize that the influence of flexible spacer on emission efficiency are distinct in different LLCPs systems [37, 41, 42, 46, 47]. Hence, an interesting point arises concerning how the flexible spacer affects the self-organization behaviors and fluorescence properties of hemiphasmidic LLCPs containing cyanostilbene.

With this in mind, in this paper, we rationally designed and synthesized a novel series of hemiphasmidic LLCPs (the structures of the polymers are shown in **Scheme 1**, donated as Pr-m, m is the carbon number of flexible spacer, m = 2, 4, 6, 8, 10), in which the hemiphasmidic mesogen containing cyanostilbene are linked to the polymethacrylate main chains via flexible spacers with different lengths. With changing the length of flexible spacer for Pr-m, a phase transition from smectic A (m = 2, 4) to hexagonal columnar phase (m = 6, 8, 10) can be observed. In despite of all the polymers shows similar AIEE characteristics, the solid-state quantum yields of Pr-m decreases with the increasing spacer length. This research enables us to have a deeper understanding of the relationship between structures and properties of hemiphasmidic LLCPs, and provides a powerful route to fabricate promising LLCPs materials with abundant self-assembly structures and AIEE characteristic.



Pr-m, m = 2, 4, 6, 8, 10

Scheme 1. The chemical structures of Pr-m.

Experimental Section

The synthetic route for monomers (Mr-m) and corresponding polymers (Pr-m) issummarizedinScheme2.

(Z)-2-(4-hydroxyphenyl)-3-(3,4,5-tris(octyloxy)phenyl)acrylonitrile was used as initial material, and (Z)-2-(4-hydroxyphenyl)-3-(3,4,5-tris(octyloxy)phenyl) acrylonitrile were prepared according to previous literature [43, 48]. Taking Mr-2 as an example, specific synthesis procedures for monomers and corresponding polymers are given in supporting information.



Scheme 2. Synthetic route for the monomers and the corresponding polymers.

Results and Discussion

Characterization of monomers and polymers

Combining ¹H NMR and mass spectrometry, we characterized and confirmed the structures of Mr-m and Pr-m. **Fig. 1(a)** exemplifies the ¹H NMR spectrum of Mr-2. All the protons in the structure of Mr-2 could be assigned to peaks corresponding to the chemical shift in ¹H NMR spectrum and the chemical shift of each proton agreed well with the expected structures, which suggested we successfully obtained the desired monomer. The result of mass spectrometry (see **Fig. 1(b)**) also helped us confirm the accuracy of Mr-2. **Fig. 1(c)** shows the ¹H NMR spectrum of Pr-2. After the polymerization, the signals at 6.16 ppm and 5.61 ppm attributed to the representative resonances of the vinyl group in Mr-2 completely disappeared, and the other peaks of the polymer were broader than that of the monomer due to the slow motion of the protons. All other monomers and polymers were also characterized in a similar way and the results conformed to the desired structures. Except Mr-8 was amorphous viscous liquid, all the other monomers were crystalline at room temperature.



Fig. 1. ¹H NMR spectra of Mr-2 (a) and Pr-2 (c) in CDCl₃; (b) Mass spectrum of Mr-2.

Gel permeation chromatography (GPC) was applied to characterize the number average molecular weights (M_n) and the dispersity of Pr-m. As shown in **Table 1**, the number average molecular weights (M_n) of Pr-m ranged from 6.20×10^4 to 9.12×10^4 g/mol, with the dispersity from 1.73 to 2.42. All polymers possess moderately high molecular weights to remove the effect of molecular weight on the properties of polymers.

Samples	$M_n{}^a(\times 10^4)$	Dispersity ^a	$T_g(^{o}C)^{b}$	$T_i(^{o}C)^{b}$	$T_i(^{o}C)^{c}$	$T_d (^{o}C)^d$	
Pr-2	7.27	2.32	43.6	130.3	130.1	377.2	
Pr-4	6.20	1.95	10.2	104.6	107.7	345.4	
Pr-6	7.68	2.12	-1.4	71.2	72.6	350.6	
Pr-8	9.12	2.42	-13.0	59.1	61.9	359.3	
Pr-10	7.25	1.73	-14.4	34.3	38.5	374.2	

Table 1 Molecular characteristics and properties of the series of Pr-m.

^a The apparent number-average molecular weight (M_n) and dispersity were measured by GPC using PS standards.

^b The glass transition temperatures and transition temperature from the liquid crystalline phase to isotropic were measured by DSC at a heating rate of 10 °C/min under a nitrogen atmosphere during the second heating process.

 $^{\circ}$ The transition temperature from the liquid crystalline phase to isotropic phase measured by POM at a heating rate of 10 $^{\circ}$ C/min.

^d The temperatures of 5% weight loss under nitrogen were measured by TGA heating experiments at a rate of 20 °C/min.

Phase transition and phase structure of the polymers

The thermal properties and phase transition of Pr-m were first investigated in detail by a combination TGA, DSC and POM. As shown in **Fig. S1** and **Table 1**, the temperatures at 5% weight loss for Pr-m were higher than 340 °C in nitrogen atmosphere, indicating all the polymers showed excellent thermal stabilities. Subsequently, we studied the phase transitions behavior of Pr-m by DSC experiment. **Fig. 2(a)** shows the DSC traces of the Pr-m recorded during the second heating process at a rate of 10 °C/min. Two distinct phase transitions could be observed in the DSC curves for all polymers: Firstly, there was an endothermic platform between -15° C and 45° C, corresponding to the glass transition temperature (T_g) of the polymers; Then, another phase transition peak could be observed between 30°C and 130°C. Combined with POM results (discussed below), we considered that the corresponding temperature was the temperature at which the Pr-m transformed from order to disorder, i.e. the clearing point (T_i). In addition, no any other phase transition processes had been observed, indicating when the temperature was lower than the clearing point, the

Pr-m were always showed the same supramolecular ordered structure. As shown in **Fig. 2(b)**, the T_g of the Pr-m decreased with the increase of the flexible spacer length because the introduction of the flexible spacer can effectively eliminate the limitation of the side group to the main chain movement, thereby making the main chain easier to move. On the other hand, the T_i of Pr-m also decreased as the flexible spacer length increased, implying the flexible spacer is not conducive to the stable existence of the liquid crystalline phase for Pr-m.



Fig. 2. (a) Differential scanning calorimetry thermograms of Pr-m with a heating rate of 10 °C /min during the second heating process. (b) The transition temperatures of Pr-m.

We performed POM experiment to observe the birefringence of polymers. The sample films cast from THF solutions and slowly dried at ambient temperature. Initially, all the polymers exhibited obvious birefringence at room temperature, indicating that Pr-m were liquid crystalline. However, during the process of cooling from the T_i , the development situation of birefringence for Pr-m was quite different. When the spacer length was short (m = 2, 4), if the sample was annealed at a temperature above the T_g for a certain time (around 0.5 h for Pr-2 and 2 h for Pr-4, respectively), the polymer could develop visible birefringence (see Fig. 3(a) and Fig. 3(b)). Moreover, Pr-2 could even develop needle-like texture of columnar phase. For

Pr-m with long flexible spacers (m = 6, 8, 10), the birefringence could not spontaneously develop even after 24 h isothermal annealing above the T_g . Nevertheless, if applied a shear force, the birefringence phenomena of these samples immediately appeared and could be maintained as long as the temperature was below the T_i (see **Fig 3(c)**, **Fig 3(d)** and **Fig 3(e)**). This phenomenon is not uncommon in many MJLCPs [37] and hemiphasmidic side-chain LCPs system [43, 44, 49]. Most probably because these polymers had a poor self-assembly ability and could only form LC phase with small domains, which could not be observed directly by POM. The external stimuli, such as precipitation and shear force, would induce LC phase with bigger domains formation leading to obvious birefringence could be discovered for these polymers. The different development situation of birefringence of Pr-m also indicated the self-assembly ability of Pr-m decreased with the increasing of flexible spacer length.



Fig. 3. Representative POM images of the texture of Pr-2 maintained at 80°C (a), Pr-4 maintained at 40°C(b), Pr-6 maintained at 55°C (c), Pr-8 maintained at 45°C (d) and Pr-10 maintained at 25°C (e) (magnification: \times 200).

The phase transition behavior of the Pr-m were further confirmed by recording the change curve of birefringent light intensity during the second heating process. As can be observed in **Fig. 4**, during the heating process, all the polymers showed only a process of sharply decreasing the light intensity, and the temperature when the light intensity decreased to 20% of the initial intensity was well accordance with the T_i obtained by DSC experiment, further indicating that Pr-m have only one phase transition from order to disorder.



Fig.4. The influence temperature exerts on reflection light intensity for polymers at a heating rate 10 °C/min in POM.

In order to clarify further the self-assembled structure structures of Pr-m, SAXS experiment was conducted. Before the experiment, about 30 mg of the Pr-m were annealed at temperature below the T_i but above the T_g for 3 h. According to the results of SAXS, the supramolecular ordered structures of polymers could be divided into two types. The first category consists of two samples namely Pr-2 and Pr-4. As observed in Fig. 5(a), in wide-angle region, only an amorphous halo shows at q =14.45 nm⁻¹ (d \approx 0.44 nm) for Pr-2 and Pr-4, corresponding to the characteristic dimensions of amorphous packing of the alkyl chains. In low-angle region, three diffraction peaks could be observed on the SAXS curve of Pr-2. The q values were 1.55 nm⁻¹, 2.73 nm⁻¹ and 3.12 nm⁻¹, respectively. The q-ratio of 1: $3^{1/2}$: 2, which corresponded to the (100), (010) and (200) characteristic diffractions in the hexagonal columnar phase, suggesting Pr-2 formed a long-range ordered hexagonal lattice and the diameter of the column was 4.68 nm. Similarly, for Pr-4, the q-ratio of 1: $3^{1/2}$: 2: 7^{1/2} clearly suggested Pr-4 could self-assembly into a hexagonal column phase. However, with the increase of spacer length, the diameter of column in the self-assembly structure of Pr-4 increased to 5.18 nm. According to the "multi-chain column" model [49-51] the column in hexagonal lattice of hemiphasmidic LCPs should not be constructed by a single polymer chain. The number of repeating units

 (Z_{rep}) could be estimated as : $Z_{rep} = (N_A/M) (d_{100}^2 csin60^\circ)\rho$, where the N_A is the Avogadro's number, ρ is experimental density, M is the molar mass of repeating unit and c is considered to be the average layer thickness of the side chain. Based on the SAXS results, c approximately equaled to 0.44 nm. According to the data in Table 2, the calculated values of Z_{rep} were 5.10 and 6.16 for Pr-2 and Pr-4, respectively, indicating that approximately 5~6 repeating units were arranged in a stratum as thin as ~0.44 nm of each column. Considering that the dimension of ~0.44 nm is roughly the projection length of backbone with two repeating units on the column axis, the number of chains involved in each column were around 3 for Pr-2 and Pr-4. The second category included Pr-6, Pr-8 and Pr-10. As observed in Fig. 5b, three diffraction peaks were observed on the SAXS spectra of those three polymers. The scattering vector ratio of the diffractions were 1 : 2 : 3 which could be assigned to (100), (200) and (300) diffractions of smectic phase. Therefore, we considered Pr-n with longer spacer length (n = 6, 8, 10) formed a layered smectic phase. Compared to the theoretical length obtained from Materials Studio (see Table 2), the scale of d-spacing of Pr-m is larger than the theoretical value, but less than twice the theoretical value, suggesting Pr-m (m = 6, 8, 10) formed a smectic A taking a double layer arrangement.



Fig. 5. Small-angle X-ray scattering of (a) Pr-2 and Pr-4; (b) Pr-6, Pr-8 and Pr-10 at 25 °C.

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Samples	LC phase	d(Sm, nm) ^a	$a(\Phi_{\rm h},{\rm nm})^{\rm a}$	$l_{\rm sc}(\rm nm)^b$	$\rho_{exp}(g/cm^3)^c$	Zrep ^d
Pr-2	${oldsymbol{\varPhi}}_{ m h}$		4.68	2.83	1.01	5.10
Pr-4	$oldsymbol{\Phi}_{\mathrm{h}}$		5.18	3.13	1.03	6.16
Pr-6	SmA	4.87	-	3.39	-	-
Pr-8	SmA	5.41	-	3.65	-	2
Pr-10	SmA	5.51	-	3.89	- ()	-

Table 2 SAXS results, estimated l_{sc} (excluding the methacrylatebackbone), ρ_{exp} and Z_{rep} in acolumn of polymers.

lsc: Side-chain lengths; ρ_{exp} : experimental density; Z_{rep}: repeat unit.

^a Layer spacing of SmA phase or the diameter of Φ_h phase obtained from SAXS.

^b Assuming the m-alkyl tails in the side chains have an all-trans conformation.

^c Experimental density of Pr-2 and Pr-4 obtained by suspension method.

^d Number of repeat units in a column stratum with a thickness of 0.44 nm.

Combining the results of POM, DSC and SAXS, it can be realized that flexible spacer makes significant influence on the self-assembled structures and behaviors of Pr-m. On the one hand, with the length of the flexible spacer increases, the supramolecular ordered structures of the polymers translate from hexagonal columnar phase (m = 2, 4) to smectic A phase (m = 6, 8, 10) taking a double layer arrangement (As shown in **Fig. 6**). On the other hand, the introduction of flexible spacers is not conducive to the development of birefringent texture for Pr-m. Special self-assembly properties of hemiphasmidic mesogen should be responsible for this phenomenon. When the flexible spacer was short (m = 2, 4), "spatial volume effect" of side group plays a dominant role in the self-assembly process of Pr-m. The bulky side groups forces the main chain to adopt a straight conformation, so that the main chain and the side groups together forms a hexagonal columnar phase. However, the flexible spacer is unfavorable for the interaction between the side group and the backbone. Hence, the self-assembly ability of Pr-2 is stronger than that of Pr-4. When the flexible spacers length further increases (m = 6, 8, 10), although Pr-m can rely on the alignment of the rod-like elements to form smectic phase, "half-disc pendant" of

hemiphasmidic mesogen would hinder the overlapping arrangement between the side groups. Therefore, the self-assembly ability of Pr-m with long flexible spacers (m = 6, 8, 10) are weaker than that of Pr-2 and Pr-4.



Fig. 6. The schematic drawing of the phase structures of Pr-m.

Photoluminescent properties of polymers

The photophysical properties of the Pr-m were investigated in detailed by UV-Vis absorption spectroscopy and fluorescence emission spectroscopy. We first characterized the UV-Vis absorption of Pr-m in pure THF (as shown in **Fig. 7(a)**). All polymers show three typical absorption peaks occurred at 210 nm, 247 nm and 355 nm, respectively, assigning to the π - π * transition absorption of E1, E2 and B bands. **Fig. 7(b)** shows the UV-Vis absorption of Pr-m in solid film state. All polymers also show the similar UV-Vis absorption. Subsequently, the UV-Vis absorption of polymers in THF and water mixed solvents were studied. **Fig. 7(c)** shows the change of UV-Vis absorption of Pr-6 in a mixed solvent of THF/water with different water contents. As observed from **Fig. 7(c)**, the maximum absorption wavelength of the Pr-6 gradually shifted to the long wavelength with the increase of the water content. Finally, the maximum UV absorption wavelength of Pr-6 shifted from 355 nm in THF to 363 nm in THF/water mixed solvents (95% water content). The planarization degree of cyanostilbene increased with the increasing of water content was probably responsible for this phenomenon.



300 325 350 375 400 425 450 475 500 Wavelength (nm)

Fig. 7. UV-Vis spectra of (a) Pr-m in THF solution and in solid film state (b); (c) UV-Vis spectra of Pr-6 in THF/water mixtures with varied water content (Concentration: 5×10^{-5} mol/mL).

In the Pr-m system, cyanostilbene acted both as a rigid rod-like core and as a typical AIE/AIEE-active molecule, thus, Pr-m were expected to be fluorescent materials with AIE/AIEE properties. In order to confirm this speculation, we explored the fluorescence behavior of Pr-m in THF/water mixed solvents. As representative of different self-assembled structures, the PL emission spectra of Pr-2 and Pr-6 in THF/water mixtures with different volume fraction of water are shown in **Fig. 8(a)** and **Fig. 8(c)**, respectively. As observed, both Pr-2 and Pr-6 featured similar AIEE properties. In THF solution, they emitted weak luminescence in THF, however, with the addition of water, the luminescence emission intensity enhanced gradually. This is because the polymers could be well dissolved in the THF solution resulting in a very weak interaction between the molecules. The cyanostilbene mainly existed in a spatially curved configuration, and the excited state energy was dissipated in a

non-radiative manner in THF solution. However, with the addition of water, the solubility of polymers in the mixed solvent became worse, leading to mutual aggregation between cyanostilbene units. Enhancement of the interaction between the cyanostilbene molecules caused by aggregation would force the planarization of cyanostilbene, resulting in the fluorescence enhancement. As shown in **Fig. 8(b)** and



Fig. 8. (a) PL emission spectra of Pr-2 (a), Pr-6 (c) in THF/water with varied water content (Concentration = 8 x 10^{-5} mol/mL; $\lambda_{ex} = 370$ nm); plots of I/I₀ values and the λ_{max} depended on water content for Pr-2 (b), Pr-6 (d); fluorescence images of Pr-2 in THF/water with varied water content (e) (under 365 UV light).

Fig. 8(d), when the water content was 95%, the fluorescence intensity of the Pr-2 and Pr-6 reached the maximum, which were around 5-fold than that in the THF solution. In addition, the planarization of cyanostilbene during aggregation process would also caused a red-shift in the fluorescence emission wavelength, hence, the maximum emission wavelength of fluorescence of Pr-2 and Pr-6 had a red shift of around 27 nm when the water content was 95%. Fig. 8(e) shows the fluorescence images of Pr-2 in THF/water with varied water content. In accordance with the result of PL emission spectra, in pure THF solution, Pr-2 showed almost no fluorescence emission while the fluorescence intensity of Pr-2 increased obviously with the addition of water. Simultaneously, a red-shift trend with the increasing of water content for the fluorescent color of Pr-2 could be observed. The PL emission spectra of other polymers in THF/water mixed solvents were shown in Fig. S2 and similar results were obtained from other polymers, indicating that all polymers showed AIEE properties. The fluorescence spectra of polymers Pr-m in solid film state were also measured. As observed from Fig. 9, Pr-m showed the similar fluorescence spectra as they had the similar chemical structure.



Fig. 9. Fluorescence spectra of Pr-m in solid film state ($\lambda_{ex} = 370$ nm).

Zetasizer nano ZS90 particle size analyzer was applied to investigate the aggregation process of the polymers. As observed from **Fig. 10**, the average diameter of Pr-6 in THF solutions was only about 26 nm. With the addition of water, the diameter increased greatly. When the volume fraction of water achieved 10%, the

average diameter of Pr-6 was about 536 nm. The diameter of Pr-6 increased with further increasing addition of water and the average diameter of Pr-6 achieved 1033 nm when the volume fraction of water reached 90%. This test results indicated that the addition of water leaded the gradual aggregation of polymers, and the aggregation induced the planarization of cyanostilbene, resulting in the enhanced emission intensity of polymers.



Fig. 10 Distributions of sizes of Pr-6 in in THF/water with varied water content; Concentration = 8 x 10^{-5} mol/mL.

In spite of Pr-m showed similar fluorescence spectra and AIEE properties, Pr-m with different flexible spacer length had different solid quantum yields $\Phi_{\text{E}s}$ ($\Phi_{\text{E}s} = N_{\text{em}}(\lambda_{\text{ex}})/N_{\text{abs}}(\lambda_{\text{ex}})$, $N_{\text{abs}}(\lambda_{\text{ex}})$ and $N_{\text{em}}(\lambda_{\text{ex}})$ represent the absorbed photons and the number of emitted photons at the excitation wavelength λ_{ex} respectively, $\lambda_{\text{ex}} = 370$ nm). The solid quantum yields of Pr-m were measured by fluorescence spectroscopy equipped with integrating sphere and the results were shown in **Fig. 11**. As observed, the solid quantum yields of Pr-m decreased from 8.55 (Pr-2) to 3.71 (Pr-10) with the length of flexible spacer increasing. As a well-known AIE/AIEE molecule, the solid quantum yield is closely related to the degree of molecular planarization in the aggregation state. In previous research on conventional side-chain LCPs containing cyanostilbene as rod-like liquid crystal mesogen [41, 42], due to the decoupling effect of flexible spacers, the self-assembly ability of polymers to form ordered structures increased with the increasing of spacer length, which was beneficial to the planarization of cyanostilbene. Therefore, the solid quantum yields with the

increasing of flexible spacer length. However, in our cases, the T_g of Pr-m decreased sharply with the increase of flexible spacer, meaning the increase of spacer length could effectively make the polymer to be soft. Accordingly, polymers were more likely to dissipate energy through non-radiation transition process, resulting in the low fluorescence emission intensity of polymers. Therefore, the solid quantum yields of Pr-m decreased with the increasing of flexible spacer length.



Fig. 11. Solid quantum yield of Pr-m in solid state.

Conclusion

In summary, a series of hemiphasmidic side-chain LCPs bearing cyanostilbene as rigid-core with different flexible spacer length (Pr-m, m = 2, 4, 6, 8, 10) were synthesized by free radical polymerization. The influence of flexible spacer length on the self-assembly behaviors and fluorescence properties of Pr-m have been studied in detail in this paper. All the polymers featured similar AIEE properties, however, with the increasing of flexible spacer length, the solid quantum yield of Pr-m gradually decreased. Meanwhile, the supramolecular ordered structures of the polymers translated from hexagonal columnar phase (m = 2, 4) to smectic A phase (m = 6, 8, 10) with the length of the flexible spacer increased. It is remarkable that unlike the conventional side-chain LCPs containing rod-like liquid crystal mesogen, the self-assembly ability of Pr-m to form ordered structure were reduced as the increasing of flexible spacer length due to the "half-disc pendant" in hemiphasmidic mesogen.

For these hemiphasmidic side-chain LCPs, the short spacer length helps to obtain better liquid crystal property and higher solid quantum yield. This research deepens our understanding about the effect of molecular structure on self-assembly behavior and fluorescence properties of hemiphasmidic side-chain LLCPs, and provides theoretical basis and practical experience for the preparation of promising LLCPs materials.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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Influence of Flexible Spacer Length on Self-organization Behaviors

and Photophysical Properties of Hemiphasmidic Liquid Crystalline

Polymers Containing Cyanostilbene

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



- 1. A series of hemiphasmidic luminescent liquid crystalline polymers were successfully designed and synthesized.
- 2. The relationship among flexible spacer length, phase structure and luminescent property of hemiphasmidic luminescent liquid crystalline polymers was established.
- 3. A theoretical basis and practical experience were provided to prepare high efficiency luminescent liquid crystal polymers.

Author Statement

Hailiang Zhang, Yongjie Yuan and Ming Yang designed experiments. Ming Yang,Zui Liu, Xitian Li and Yongjie Yuan carried out experiments. Hailiang Zhang,Yongjie Yuan and Ming Yang analyzed experimental results. Hailiang Zhang,Yongjie Yuan and Ming Yang wrote the manuscript. All authors reviewed andapproved the manuscript.