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Effect of the structure of gelators on electro-optical properties of liquid crystal physical gels

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Abstract

Low molecular mass organic gelator (LMOG) as an important component of liquid crystal physical gel has a great influence on the electro-optical properties. In this paper, three analogues of amide gelator were synthesized and employed as LMOGs in nematic liquid crystal 5CB. Both hydrogen-bonding and π–π-stacking interactions in the gel phase were found to stabilize the self-assembled structure. It was observed that the morphology was highly dependent on the crystallinity of gelators, which was affected by the intensity of hydrogen bonding. The thicker fibril was obtained with higher crystallinity of LMOG, while the thinner fibril was obtained with lower crystallinity. Moreover, the electro-optical properties of liquid crystal physical gels were proposed to be related to the interaction between the fibrils and the liquid crystal molecules.

Keywords: Low molecular mass organic gelator; Liquid crystal physical gel; Electro-optical properties; Self-assembly

1. Introduction

Low molecular mass organic gelators (LMOGs) have attracted much attention in recent years for their potential applications in sensors, molecular electronics, drug delivery, etc. [1–4]. In these materials, common organic solvents are physically gelated by one-dimensional fibrous association of LMOGs. The fibrous association could be easily obtained by the self-assembly of LMOGs via noncovalent interactions, such as hydrogen-bonding, π–π-stacking interactions, London dispersion forces, and electrostatic attractions [3–5].

Liquid crystal physical gel could be obtained through the self-assembly of LMOGs in liquid crystal. These materials have properties of both liquid crystals and physical gels and they are able to respond to electric field in micro-phase separation states. The interesting electro-optical behavior of liquid crystal physical gel has been wildly investigated [6–14]. Kato and co-workers first reported that liquid crystal physical gel showed a significant influence on the electro-optical performance of twisted nematic (TN) cells [7–9]. The anisotropically ordered gels have shown a faster response, lower driving voltage and higher contrast ratio than those common TN cells. They also have prepared the light scattering mode liquid crystal physical gel: normal light scattering and reverse light scattering [10–12]. Such light scattering states can be electrically controlled switchable between opaque polydomain states and transparent monodomain states. As no polarizer is needed in those materials, the simple device could be directly employed in electrically controlled switchable applications. Zhao and co-workers showed that the photoluminescence intensity of gelators or quantum dots could be switched by employment of liquid crystal physical gel [13,14]. This interesting phenomenon was due to the different internal scattering of excitation light in transparent or opaque state. Those devises might open new ways of exploring the use of photoluminescence for display applications.

LMOG as an important component of liquid crystal physical gel has a great influence on the electro-optical properties. There are a few papers about the electro-optical properties of liquid crystal physical gel; however, many more works are needed before general conclusions about the relationship between the chemical structure of LMOG and the electro-optical perfor-

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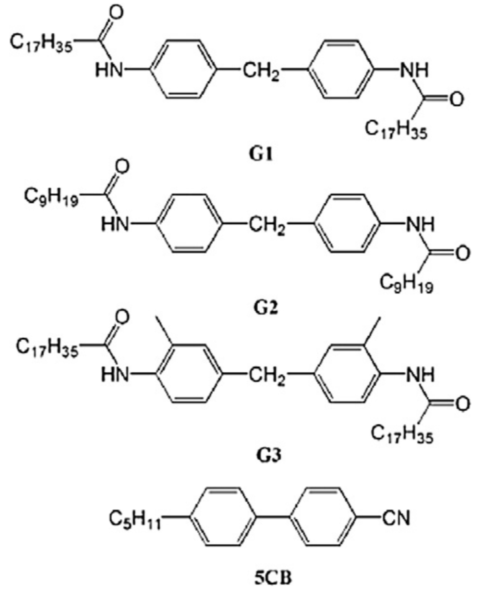

Fig. 1. Molecular structures of the amide gelators and liquid crystal.

mance of liquid crystal physical gel can be made. In this paper, three 4,4′-diaminodiphenylmethane-based gelators with amide moieties were synthesized and used as gelators for inducing light scattering liquid crystal physical gel. The light scattering behavior of the nematic gels of 5CB by gelator G1–G3 (Fig. 1) was studied. Both hydrogen-bonding and π–π-stacking interactions were found to stabilize LMOG assemblies. Moreover, it was proposed that the morphology and electro-optical performance of liquid crystal physical gel was related to the crystallization ability of the gelator.

2. Experiment

2.1. Materials

Nematic liquid crystal 5CB ($T_{N\text{-I}} = 35\,^\circ\mathrm{C}$, $n_0 = 1.52$, $\Delta n = 0.180$) was purchased from Yantai XianHua Chem-Tech. Co., Ltd. G1–G3 were prepared by stearoyl chloride or dodecanoyl chloride with corresponding 4,4′-diaminodiphenylmethane (see supporting information). The liquid crystal physical gels were obtained by mixing the liquid crystal and the gelators, heating to isotropic states, followed by cooling to room temperature.

2.2. Characterizations

^{1}H NMR was characterized at a Unity INVOA-400 MHz NMR spectrometer in d_6-DMSO. Infrared (IR) spectra were investigated with Nicolet 560 Fourier transform infrared spectra from 4000 to 400 cm^{-1}. X-ray diffraction measurements were performed with Ni-filtered Cu$K\alpha$ X-rays ($\lambda = 1.54056$ Å) on a Rigake D/MAX-Ra diffractometer consisting of a rotating anode X-ray generator operated at 40 kV × 80 mA at room temperature. The morphologies of the gels were characterized with a JSM-5900LV scanning electron microscopy (SEM). A SEM sample was prepared by immersing the cells in hexane to extract the liquid crystal for 48 h followed by drying at room temperature. Molecular calculations of the lowest energy conformations and molecular dimensions were performed with the semiempirical Parametric Method 3 (PM3) of the HYPERCHEM package [4,5]. The electro-optical properties of samples were measured with the UV 1810 PC spectrometer as reported [15]. The wavelength of incident light was 550 nm and these measurements were corrected by atmosphere directly. The detailed parameters are shown in supporting Fig. S1.

3. Results and discussion

3.1. 4,4′-Diaminodiphenylmethane-based gelators

G1–3 containing 4,4′-diaminodiphenylmethane moieties have been prepared in this study as shown in Fig. 1. They were designed to form hydrogen-bonding and π–π-stacking interacted fibrous aggregates. Temperature-dependent ^{1}H NMR spectra of G1 were carried out in d_6-DMSO at different temperatures between 100 °C ($>T_{\text{sol-gel}}$) and 22 °C ($<T_{\text{sol-gel}}$) shown in Fig. 2. The chemical shifts of the proton signals of amide group signals shifted downfield from 9.53 to 9.72 ppm and there signals narrowed with a decrease of temperature. On the other hand, the signals of aromatic proton signals in phenyl at high field became weaker, and those signals at low field got stronger. Similar results have been observed in other two gelators. These results afforded noticeable evidence for the self-assembled structure stabilized by hydrogen-bonding and π–π-stacking interactions in the gel phase [16,17].

3.2. IR spectral studies

IR spectrum is a useful method for characterizing the intermolecular hydrogen bonding. It was observed that IR peaks of H–N and C=O moieties appeared at ∼3293 and 1659 cm^{-1}, respectively. Furthermore, the similar spectral positions in neat powders of the amide and their liquid crystal physical gels were also observed as shown in Fig. 3. It could be inferred that hydrogen bonding is similar in the two phases. However, the H–N stretching vibration band in the gel state was broader than that of neat state for the disorder in the gel fibrils. Moreover, it was also noted that the H–N stretching vibration peaking of G1–G3 appeared at 3295.53, 3292.75, and 3293.90 cm^{-1}, respectively. The difference of H–N stretching vibration was possibly corresponding to the intensity of intermolecular hydrogen bonding [17]. The results suggested that G2 and G3 should offer more efficient intermolecular hydrogen-bonding interactions than G1.

3.3. Fibrous aggregates of LMOGs in liquid crystal

The X-ray diffraction (high angle) of the neat powder of LMOGs (G1–G3) and characteristic gel (G2 in 5CB) are shown in Fig. 4. By comparison of the diffraction patterns, there are two typical characters: (1) the diffraction peaks from the neat powders coincided with those from the gels despite the