Macromolecular Research, Vol. 16, No. 7, pp 586-589 (2008)

Communications

Dendritic Physical Gel: A Liquid Crystalline Gel for Application in Light Scattering Displays

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Received June 14, 2008; Revised August 25, 2008; Accepted August 25, 2008

Introduction

Dendrimers are fascinating nano-objects which have predictable three-dimensional architecture, monodisperse molecular weight distribution,[1-4] and various remarkable properties, e.g. encapsulation,[5] catalysis,[6,7] low viscosity,[8] and unique optical properties.[9] Functionalized dendrimers, i.e. dendrimers incorporating active or reactive functionalities either in the core or at the periphery, are considered new materials with high potential for modern technology applications. The possibility of molecular design of organized supramolecular assemblies constructed from dendritic macromolecules has generated enthusiastic investigations at the frontiers of chemistry, physics, biology, and materials sciences.[10-13] Along this line, we have reported dipeptide core poly(benzyl ether) dendrimers as a new class of functional dendrimers that form a physical gel in organic solvent with a significantly high gelation ability.[14,15]

Liquid crystals (LCs) play very important roles in modern life, and various types of LC displays have been proposed and put into practical use.[16] A typical LC display has a twist nematic liquid crystal element which is composed of a pair of polarizing plates and a twisted LC layer.[17] The presence of the polarizing plates results in decreased brightness, therefore, recently, several types of display media that do not contain polarizing plates have been proposed. LC gels have great potential for use as an element in the display medium and would not require polarizing plates.[18] In this context, we report the first example of the application of dendritic physical LC gel in light scattering display materials.[19,20]

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Results and Discussion

The dipeptide core dendrimers (Figure 1) were synthesized by a previously reported procedure.[14] Typically, a distilled tetrahydrofuran (THF) solution (70 mL) of a mixture of Frechet type second generation dendritic bromide (0.192 mmol) and *tert*-Boc-(L)-Tyr-(L)-Ala-$C_{18}H_{37}$ (0.202 mmol), containing K_2CO_3 (1.92 mmol) and 18-crown-6-ether (0.0384 mmol), was stirred under N_2 at reflux for 24 h. The reaction mixture was extracted with ethyl acetate (3 × 20 mL). The combined extracts were dried over anhydrous Na_2SO_4 and chromatographed on silica gel with CH_2Cl_2 containing 1% methanol as an eluent. The product was collected and freeze-dried from benzene to give **2** (0.0979 mmol) as white solid in 52.8% yield.[21]

As reported previously, poly(benzyl ether) dendrimers with a dipeptide core can efficiently form physical gels in various organic solvent molecules, for example, nearly 20,000 acetonitrile molecules can be immobilized by one dendrimer molecule. A detailed investigation has shown that inter-dendrimer interactions serve cooperatively with hydrogen-bonding interactions at the focal core to stabilize the self-organized fibrous assembly. To investigate the gelation behavior of dendrimers against LC molecules, **5CB** was adopted as a solvent molecule. The LC gel composition was prepared from a hot isotropic solution of the dendrimer in LC, and allowed to stand at 20 °C after 1 min of ultrasonication. Typically, a suspension of 2 (10 mg) in **5CB** (500 mg) was charged in a 5 mL vial and heated to 120 °C until the gelling agent was dissolved in the LC to obtain a transparent isotropic solution. The vial containing the solution was son-

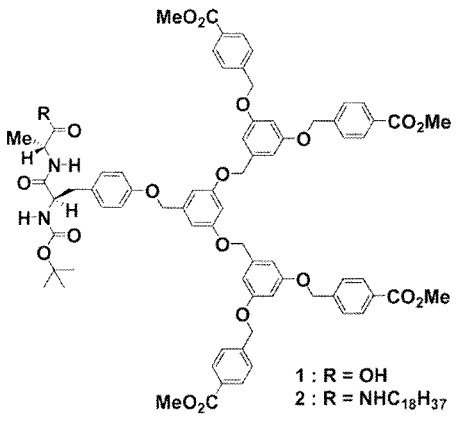

Figure 1. Schematic structures of dipeptide-core poly(benzyl ether) dendrimers.

icated for about 1 min and was then allowed to stand for about 3 h, thereby obtaining a LC gel that showed no fluidity.

When the concentration of dendrimer was higher than 2 wt%, **5CB** was also successfully gelled by **1**. However, the gel formed with 1 was highly brittle, and easily phase separated to a fluidic phase with aggregated particles. Therefore, to enhance the miscibility of dendrimer to LC molecules, we designed a long alkyl chain bearing dendritic dipeptide (**2**; Figure 1). Compound **2** also formed physical gels in several organic solvents, such as acetone, ethyl acetate, and acetonitrile. However, a much higher concentration of **2** was required to form physical gels in these organic solvents, and the gel formed from **2** was very turbid and brittle in comparison to that formed from **1**.

Interestingly, compound **2** showed significantly enhanced gelation ability with high stability in **5CB** molecules compared to compound **1**, where the critical gelation concentration was determined to be only 0.5 wt%. The enhanced gelation ability of **5CB** with compound **2** is possibly due to the incremental improvement in miscibility of **5CB** caused by introduction of a long alkyl chain.

To obtain morphological information, the gelled sample of **2** was observed by optical and scanning electron microscopy (SEM). Under cross-polarized microscopic observation, **2** gelled in acetonitrile showed a birefringent fibrous structure. The gelled sample of **2** in acetonitrile was dried under reduced pressure and then subjected to SEM. The SEM image of the dried gel shows bundles of submicron scale fibers with a diameter of approximately 200 nm (Figure 2).

Thermal behavior of the fibrous assembly was observed using cross-polarized microscopy equipped with a heating stage. Upon heating at a rate of 20 °C/min, the fibrous assembly of **2** melted at 148 °C. Considering that the melting point of the dried gel of **1** was observed at 112 °C, the self-assembled structure of **2** has much higher thermal stability than that of **1**. The high thermal stability of **2** is possibly due to the hydrogen bonding of C-terminal amides as well as van der Waals interactions among the long alkyl chains of C-terminal. The thermal behavior of the LC gels was studied by differential scanning calorimetry (DSC) and optical microscopy. Compound **2** showed stable gel formation in **5CB**. Upon heating at a rate of 20 °C/min from 0 °C, the LC gel with **2** (2 wt%) exhibited two endothermic peaks, where the first endothermic peak was observed at a thermal transition temperature of the LC molecules (36 °C; 2.22 J/g) from a nematic phase to an isotropic phase, while the second transition was observed at 120 °C (7.65 J/g). When the LC gel with **2** was heated up to 36 °C, a perfectly transparent gel phase was obtained, which became fluidic over 120 °C (Figure 3(a)). However, the LC gel with **1** (2 wt%) exhibited an endothermic peak only at 36 °C (1.83 J/g) (Figure 3(b)). When the LC gel with **1** was heated, it slowly became fluidic without a typical transition temperature, indicating that the self-assembled fibrous structure of **1** in LC is not stable enough to retain its intermolecular interaction in an isotropic phase.

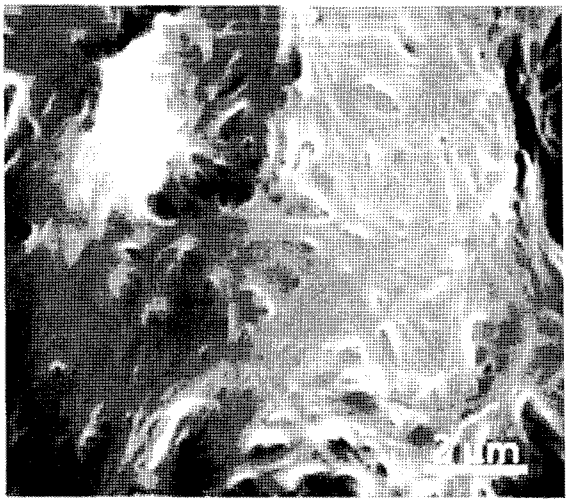

Figure 2. Scanning electron microscope (SEM) image of a dried gel of **2** (×5,000).

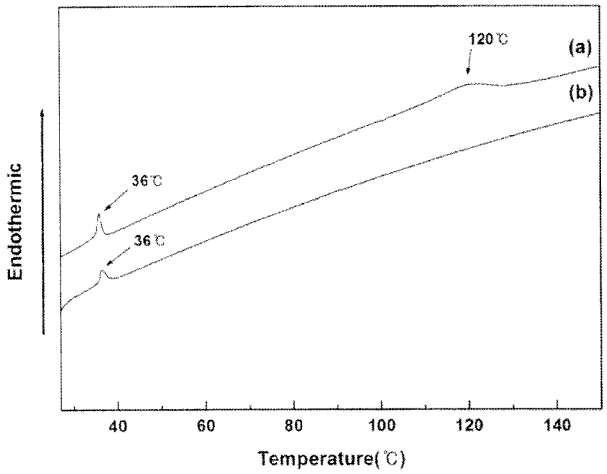

Figure 3. Differential Scanning Calorimetry (DSC) profiles of **5CB** gels containing 2.0 wt% of **1** (a) and **2** (b).

Hot solutions of **1** or **2** in 5CB formed stable physical gels in the glass substance at room temperature.

The gel with **2** showed significantly high turbidity, and may therefore be used in light scattering devices. The high turbidity of the LC gel is due to the formation of micro-domains (Figure 4(a)), which are stabilized by the formation of a strong fibrous assembly of compound **2**.

To examine the light scattering behavior of the LC gels, the gels were charged into a 10 μm thick ITO glass cell where the concentration of gelling agents was adjusted to 2 wt% **5CB**. Two transparent glass substrates with a conductive ITO coating served as electrodes and were oriented opposed to one another with an inner distance of about 10 μm between the electrodes, the distance being main-

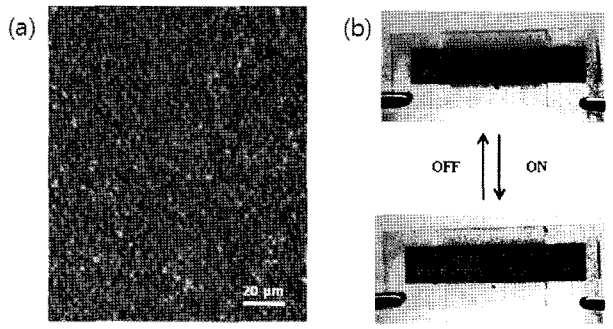

Figure 4. Photographs of a cell containing **5CB** gel with **2** (2.0 wt%). (a) Polarized optical microscopy image at 20 °C. (b) Electro-optical response upon applied voltage of 30 V.

tained by a resin spacer. The hot isotropic solution of dendrimers in **5CB** was introduced into a cell, preheated to 120 °C in a drying oven, and the cell was cooled to room temperature. To determine the electro-optic activity of the cell, a He-Ne laser (632 nm) was used as an incident light source and the cell was placed between the laser and a polarizing plate. AC electric fields (1 kHz) were applied to the cell and the transmitted light intensity was measured with a photodiode. The light transmission of the display medium as measured with no applied photo voltage (T_{100}) was defined as 100%, and the light transmission of the display medium as measured when the change in light transmission stopped (T_0) was defined as 0%. Then, the contrast ratio T_{100}/T_0 was calculated. An applied voltage, V_{90}, necessary to obtain a light transmission of 90% and an applied voltage, V_{10}, necessary to obtain a light transmission of 10% were also measured. The results are summarized in Table I. While increasing the applied electric field, the light transmittance of the ITO glass cells at each voltage was measured. Voltage and light transmittance data are shown in Figure 5, and the electro-optical properties of the gels are summarized in Table I. Gels containing **1** and **2** showed increases in transmittance when the electronic field was applied, and the observed threshold voltages were about 4 and 7 V, respectively. The light transmittances of incident light for gels containing **1** and **2** were about 3% and 25%, respectively, in the electric field off-states. Although the LC gel based on **1** showed a low threshold voltage and increases in transmittance, it is not suitable for light scattering display devices because of the low light scattering in the off-state.

Table I. Electro-Optical Properties of 5CB Gel on Light Scattering Mode

Gelator	Transmittance (%)		V_{10}/(V)	V_{90}/(V)	Contrast Ratio
	Off-State	On-State			
1	25.4	77.25	4.09	16.9	3.04
2	3.4	37.01	7.33	30.70	10.88

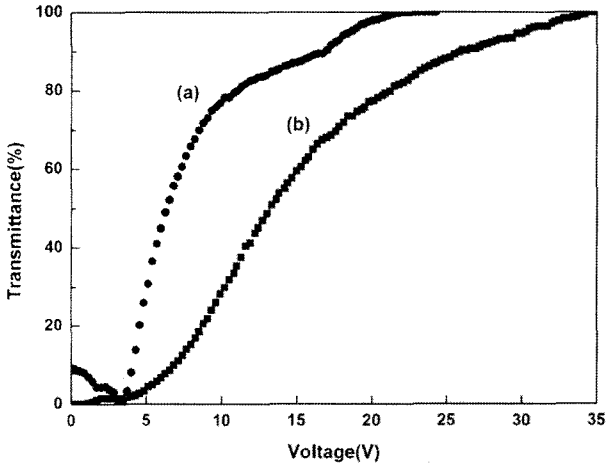

Figure 5. Relationship between transmittance and applied voltage for LC gels containing 2.0 wt% of **1** (a) and **2** (b).

The gel containing **2** showed sufficiently high light scattering in the off-state, and has a high contrast ratio relative to the gel containing **1**. In addition to the successful response to an applied electric field (Figure 4(b)), the LC gels exhibited a stable orientation change of LC molecules in both step-up and step-down voltage scans. Considering the high contrast ratio and successful response to an electric field, the LC gel component containing **2** is a promising candidate for the development of light scattering display devices. Because the dendritic molecules can be used to introduce large numbers of functionalities into the dendrimer periphery, there is great potential to develop multi-functional devices.

In this study, we have shown the physical gelation of LC molecules by dendritic dipeptides. By introducing a long alkyl chain to the C-terminal of the dipeptide core, the dendritic dipeptide formed a stable physical LC gel with a very low critical gelation concentration. The LC gel substances showed successful responses to an electric field with a high contrast ratio, and have great potential for application in light scattering electro-optical devices. Further optimization of the gel composition to improve its electro-optical properties is on-going.

Acknowledgments. This research was supported by KOSEF (Center for Bioactive Molecular Hybrids at Yonsei University and R & E Program).

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(21) Characterization of **2**; MALDI-TOF-MS for $C_{92}H_{111}N_3O_{19}$ *m/z*: calcd: 1585.86 $[M+Na]^+$; found: 1585.9. ^1H NMR ($CDCl_3$): 0.872 (t, 3H; $-CH_3$ in alkyl chain), 1.27 (m, 32H; $C-(CH_2)_{16}-$), 1.41 (m, 9H; ^{tert}-Boc), 2.99 (m, 2H; $N-CH_2-$), 3.13 (m, 2H; $C-CH_2-Ar$), 3.91 (s, 12H; CO_2CH_3), 4.25 (m, 1H; C-H in Tyr), 4.39 (m, 1H; C-H in Ala), 4.96 (d, 6H; mid and inner $ArO-CH_2-Ar$), 5.09 (s, 8H; outer $ArO-CH_2-Ar$), 6.53 and 6.66 (d, 9H; *o*, *p* in C_6H_3), 6.90 and 7.09 (d, 4H; C_6H_4 in Tyr), 7.47 and 8.04 (d, 16H; C_6H_4 in dendritic wedge).