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Fabrication of organogels composed from carbon nanotubes through a supramolecular approach†

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A new organogelator, *N*,*N*′-bis (octadecyl)-L-(1-pyrenebutyric acid)-glutamic diamide (LPG), was designed and its interaction with pristine single-walled carbon nanotubes (SWNTs) in the gel state was investigated. It was found that LPG can form organogels with various kinds of organic solvents. Although SWNT itself is difficult to disperse into organic solvents, it can be well dispersed into LPG gel. The gelation process and the properties of the resulting nanocomposites were found to be closely related to the pyrene group in the gelator. The addition of SWNTs significantly decreased the critical gelation concentration of LPG, depressed the sol to gel transition temperature and prolonged the time required to form a gel. Rheological investigations of LPG organogels showed that the flow of nanocomposites became more resistant to the applied stress upon the incorporation of SWNTs. This happened presumably *via* effective dispersion of SWNTs into the LPG organogels through π–π interaction between the surface of SWNTs and the pyrene group of LPG. The textures of the nanocomposites were altered from layer structure to intertwined fibers upon the incorporation of SWNTs, which also supported the effective mixing of SWNTs into LPG organogels.

1. Introduction

Low molecular weight organogel (LMWG) is an important type of soft matter.[1] It has received increasing attention in recent years due to its wide applications in various fields, such as nano-materials, tissue engineering, separation technologies and catalysis.[2–4] LMWGs are usually obtained by self-assembly of low molecular weight gelators in organic solvents through non-covalent interactions such as hydrogen bonding, Van der Waals interactions, π–π stacking and so on. In organogels, the networks are composed of some self-assembled gelator fibers, strands, tapes, as well as their entanglements and immobilization of the liquid components macroscopically.[5–12] Carbon nanotube organogels in which carbon nanotubes (CNTs) are well dispersed, are now attracting more and more attention, owing to their potential applications ranging from tissue engineering, electrode materials for lithium batteries, drug-delivery systems to super-capacitors and catalyst supports for fuel cells.[13–18] However, due to the poor solubility of the carbon nanotubes, a modification is usually necessary. For example, Rao *et al.*[19] have reported an L-alanine based low molecular weight gelator cooperating with the carbon nanotubes. They found that the SWNTs functionalized with different aliphatic and aromatic chains can improve their solubility in an organogel matrix, and can further alter the thermal and mechanical properties of the gel significantly. Winey *et al.* prepared a series of organogels doped with carboxylated multi-walled carbon nanotubes.[20] They found significant improvement in the mechanical and electrical properties of the organogels by incorporating these modified carbon nanotubes. Despite the fact that chemical modification of carbon nanotubes can somehow enhance their solubility in solvents,[21–23] the graft perturbs the conjugated π systems of CNTs and results in dramatic changes in their electrical and structural properties. Thus, the supramolecular method, by which the CNT surface is modified through non-covalent interactions, is expected to improve the solubility of CNTs, as well as preserve the electronic and structural integrity of CNTs.[24] Several attempts have been made.[25,26] For example, Chen *et al.*[26] have obtained the organogels of SWNTs with ferrocene-grafted poly (*p*-phenyleneethynylene)s through non-covalent interactions. Considering pyrene is the most popular species for non-covalent attachment with CNT through π–π stacking,[27–29] in this paper, we designed a new low molecular gelator bearing a pyrene group and fabricated organogels with pristine SWNTs through mixing with LPG.

We have previously reported the synthesis and characterization of an efficient gelator based on the glutamic acid, *N*,*N*′-bis (octadecyl)-L-Boc-glutamic diamide (LBG, Fig. 1a).[30] It can immobilize nearly all kinds of organic solvents, ranging from highly polar DMSO to non-polar benzene. On the basis of this compound, we introduced the pyrene group into the frame of LBG and produced a new gelator, *N*,*N*′-bis (octadecyl)-L-(1-pyrenebutyric acid)-glutamic diamide (LPG, Fig. 1b), which has a longer alkyl chain than that in ref. 31. The motivation of this study is to prepare facile, stable single-walled carbon

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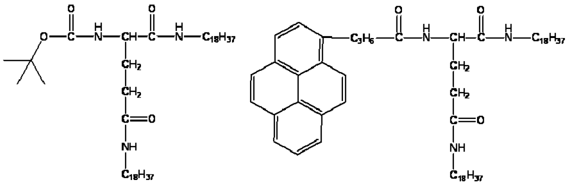

(a) LBG (b) LPG

Fig. 1 Molecular structures of LBG (a) and LPG (b).

nanotube (SWNTs) dispersion in organogels without chemical oxidization of the SWNTs' surface. The incorporation of SWNTs into an LBG or LPG organogel matrix was characterized by UV-Vis spectra, fluorescence spectra, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Rheological studies further provided information about sol–gel transition temperature, kinetic profiles of gelating and viscoelastic behaviors of these two kinds of nanocomposites.

2. Results and discussion

2.1 Gelation property of LPG

Table 1 lists the gelation properties of LPG in various solvents. The compound could gel most of the fourteen solvents investigated. We define the least amount of gelator molecules required to form an organogel as the critical gelation concentration (CGC). It has been found that CGC values varied from 1.2 mg mL^{-1} in 1,2-dichlorobenzene (DCB) to 8 mg mL^{-1} in ethyl acetate. Especially in the aromatic solvents, LPG has a very low CGC which means 1 mol of LPG could gel more aromatic solvents compared with other solvents. Furthermore, depending on the solvents, these organogels showed some different properties. In solvents such as DMF or DMSO, white gels are obtained, while in some other solvents such as aromatic solvents, transparent gels are formed. Considering the great gelation property of LPG and good dispersion of SWNTs in DCB,[20] we choose DCB as the solvent to perform our further experiments. In addition, in order to get stable organogels, 2 mg mL^{-1} LBG and 5 mg mL^{-1} LPG were used[30] in the following experiments.

Table 1 The gelation properties of LPG in various solvents

Solvents	Property[a]	CGC/mg mL^{-1}
DMF	G	2.5
DMSO	G	5
Methanol	P	
Ethanol	P	
Acetone	G	4
Ethyl acetate	G	8
Dichloromethane	G	4
Chloroform	S	
THF	G	6
Cyclohexane	TG	8
Benzene	TG	2
Toluene	TG	1.2
Chlorobenzene	TG	1.5
1,2-Dichlorobenzene	TG	1.2

[a] G = white gel; TG = transparent gel; P = precipitation; S = solution.

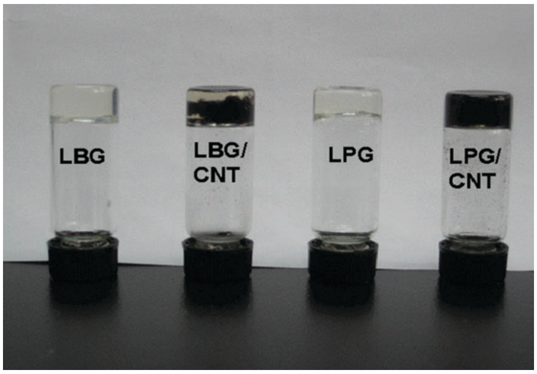

Fig. 2 Photographs of the organogels after 1 cycle of heating and cooling down. From left to the right: LBG organogel (5 mg mL^{-1}); SWNTs doped LBG organogel (concentration of LBG is 5 mg mL^{-1}, weight of SWNTs *versus* the weight of LBG in the organogel is about 4%); LPG organogel (2 mg mL^{-1}); SWNTs doped LPG organogel (concentration of LPG is 2 mg mL^{-1}, weight of SWNTs *versus* the weight of LPG in the organogel is about 4%).

2.2 Stability and reversibility of the organogels

Fig. 2 shows that the gels are formed by LBG or LPG in DCB, characterized by no fluid existing when the test tubes are inverted. By means of doping SWNTs into hot solutions of LBG or LPG in DCB, and then cooling the solution down to room temperature, the SWNTs/LPG organogels and SWNTs/LBG organogels can be prepared. The colorless transparent gel turned into a black gel after being doped with SWNTs. It was found that the SWNTs/LPG organogels were stable and kept uniform after at least 10 cycles in which the mixture was repeatedly heated to 60 °C and then cooled to room temperature. When the same treatment was carried out in the presence of LBG, we obtained the precipitation of SWNTs after only 1 circulation (Fig. 2). These results indicate that SWNTs can be stabilized upon incorporating into LPG organogels. Considering that both LPG and SWNT have large π-conjugate systems, it is reasonable that the strong π–π interaction between SWNTs and the pyrene moiety plays an important role in dispersing SWNTs well. The fluorescence of LPG was quenched by the addition of SWNTs (Fig. S1 in the supporting information†), which also confirms the intermolecular interaction between SWNTs and LPG.[32,33]

2.3 Effect of SWNTs on LPG critical gelation concentration

We also found that the addition of SWNTs can reduce the concentration of LPG required to form organogels (Fig. 3). The critical gelation concentration (CGC) of LPG is 1.2 mg mL^{-1} without SWNTs, while it decreases to 0.5 mg mL^{-1} when 4% (weight percent between SWNTs and LPG) SWNTs are added into the system. The critical gelation concentration of LPG upon addition of 4 wt% SWNTs (*vs.* the weight of LPG) decreases almost to 40% of that pure LPG. The decrease in CGC of LPG organogels also indicates the strong π–π interaction of SWNTs with pyrene. The large surface ratio of SWNTs can provide more functionary positions for the π–π interaction, thus decreasing the concentration of LPG required to form gels. However, the dispersion of SWNTs into LBG organogel cannot decrease its critical gelation

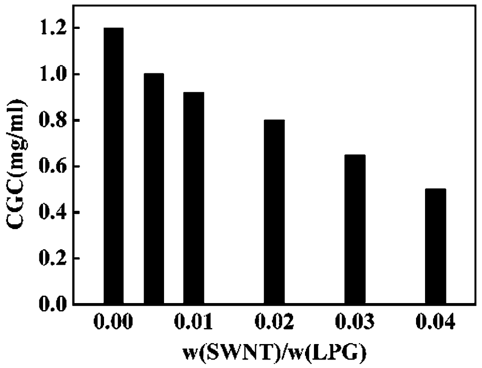

Fig. 3 Histogram of CGC for LPG in different weight proportions of SWNTs.

concentration, suggesting that there is no strong interaction between LBG and SWNTs.

2.4 SEM & AFM

In order to gain a better insight into the microstructures of the composites, the morphologies of the xerogels were undertaken by SEM and AFM. The concentrations of LPG and LBG were 2 and 5 mg mL^{-1}, respectively. The concentration of SWNTs was 4% ($W_{\mathrm{SWNTs}}/W_{\mathrm{gelator}}$). Fig. 4 shows AFM and SEM images of the xerogels prepared from LPG/SWNT$_S$ organogels. It shows that the morphology of the pure LPG xerogel is a flake-like structure with a size of about 1 μm, arranged as multilayered fabrics (Fig. 4A), which is totally different from the morphology of the LBG xerogel (Fig. 4E). This difference may be due to the strong π–π stacking between pyrene rings, as supported by the UV-Vis spectra of LPG solution and LPG organogels, in which the absorption of pyrene in organogels was broadened and slightly red shifted (Fig. S2 in supporting information†).[34] In addition, we have observed a fluorescence at a longer wavelength of 450 nm in the organogel, which also supports a strong interaction between pyrene groups (Fig. S3 in supporting information). When SWNTs were added into LPG organogels, the corresponding xerogels show an entangled fibrous superstructure of 250 nm in width, which is a sharp contrast to the morphology of the LPG xerogels. AFM images of these nanocomposites also give similar microstructures. The AFM image of LPG xerogels shows the formation of a sheet structure with a height of about 2–3 nm. With the addition of SWNTs, fibrous structures with a height of 4–6 nm and width of 130 nm appear, as shown in Fig. 4D. The probable explanation for this change is that, after being doped with SWNTs, LPG tends to interact with the surface of the carbon nanotubes by π–π interaction. That is to say, carbon nanotubes are just like the rods inserted into the original π–π stacking between LPG molecules. Thus the dispersion of the carbon nanotubes in the organogels played an effective role in determining the pattern of the organogels. However, for the LBG organogels, addition of SWNTs to the gel has no obvious effect on the structure of the gels (Fig. 4E and F).

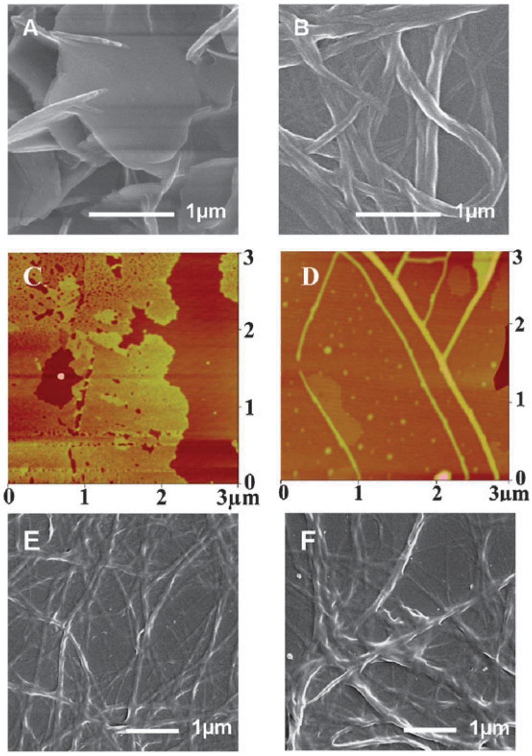

Fig. 4 SEM and AFM of the gels: (A, C) SEM and AFM of LPG xerogels; (B, D) SEM and AFM of LPG /SWNTs xerogels; (E) SEM of LBG xerogels; (F) SEM of LBG/SWNTs xerogels.

2.5 Rheological studies

To investigate other properties of SWNTs/organogel nanocomposites, we introduced rheological studies to get a further understanding. Rheological studies give an indication about the flow behavior and the rigidity of a gel. In the rheological experiments, G′ or the storage modulus represents the ability of the deformed material to restore its original geometry while G″ or the loss modulus represents the tendency of a material to flow under stress. For viscoelastic materials like gels, G′ is an order of magnitude greater than G″, demonstrating the dominant elastic behavior of the system.[35–37] The yield stress refers to the critical applied stress above which the gel starts to flow. In other words, the property of the gel changes from a dominant elastic-solid like behavior to a dominant viscous-liquid like behavior. In this experiment, we chose the concentration of carbon nanotube of 4% (weight percent *versus* LPG) as the example, because when the concentration is lower, for example, 1%, the change is not obvious for our discussion (Fig. S4–S6 in supporting information†).

In the temperature decreasing sweep experiment, for the sake of getting the critical gelation temperature (T_f), we raised the temperature to 70 °C and cooled it down slowly. The results can be seen in Fig. 5. The T_f of the LBG organogel is 14.2 °C. The addition of a carbon nanotube has no obvious effect on the T_f of the LBG organogels. For the LPG organogels, T_f is 40.2 °C while adding 4% carbon nanotube (weight percent *versus* LPG) can decrease its T_f to 35.5 °C. Fig. 6 describes the influence of SWNTs on LPG or LBG kinetics of the gelation process. First, we had to heat the gelators above their critical gelation temperature and then cool them down to a certain temperature. In our experiments, we heated them to 70 °C and cooled down to 15 °C for the LBG composite gels

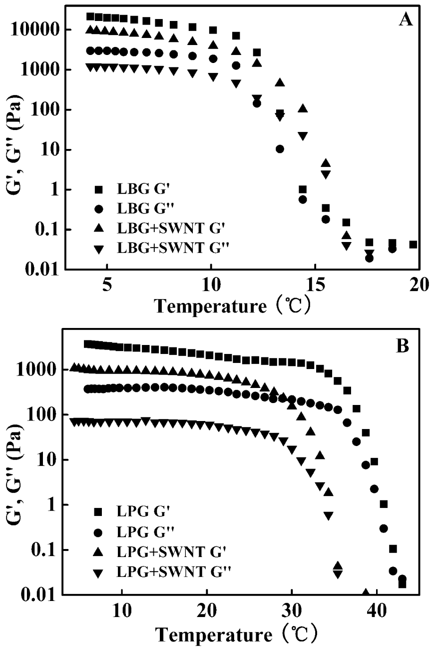

Fig. 5 Temperature decreasing sweep experiments: (A): G′ and G″ for LBG organogels and LBG organogels doped with SWNTs; (B): G′ and G″ for LPG organogels and LPG orgnanogels doped with SWNTs.

and 40 °C for the LPG composite gels respectively. The difference comes from the fact that the T_f of LPG is above 30 °C. If we directly cooled them down to 15 °C, the gelation process would be too fast for us to observe the kinetic changes. As time goes by, we cannot see much change for the LBG organogels and SWNTs/LBG organogel composites. But for the LPG organogels, along with the addition of the SWNTs, the gelation time increases (from 130 s to 220 s when the weight percent of SWNTs is up to 4%wt). The depression in the sol-to-gel phase transition temperature and the prolonged gelation time for LPG organogels after being doped with SWNTs suggested an interaction between LPG and SWNTs. This interaction is attributed to the efficient mixing of SWNTs in the textures of LPG organogels.[19]

Fig. 7 focuses on the rheological responses of LPG organogels. A stress ramp of 1 Pa s^{-1} (frequency 1Hz) was applied on the gels and G′ and G″ were plotted as a function of the applied stress. The width of the linear viscoelastic regime (LVE) of the gels indicates the ability of the gels resistant to the stress. We observed that the pure LPG gel made in DCB succumbed to the applied stress and began to flow at about 10 Pa (Fig. 7). Incorporation of 4% SWNTs considerably prolonged LVE to more than 30 Pa. This suggests that the well dispersed SWNTs in the LPG organogel made the organization of the composite flow harder than the one-component LPG organogel. Similar results have also been reported by some other groups.[19,20] They attributed the prolonged LVE to the effect of good dispersion of CNTs in the gel matrix. But the yield stress of LBG gel does not show any change while being doped with the same amount of SWNTs. Coupled with the result from Fig. 2, LBG does not have a strong interaction with SWNTs, thus it is hard for SWNTs to be well dispersed into the LBG organogel. So the non-covalent interactions become crucial in the dispersion of SWNTs and further control the resistant ability of the LPG/SWNTs composite to succumb to the applied stress. Their microcosmic structure obtained from AFM and SEM can demonstrate this phenomenon well. In other words, the fibrous network of SWNT

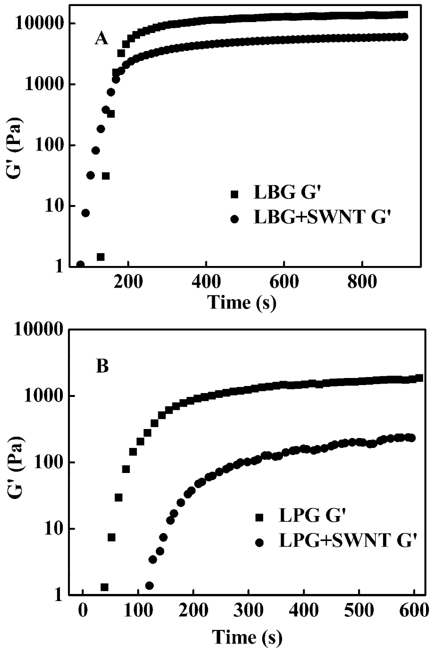

Fig. 6 Gelation kinetic sweep experiments: (A): G′ for LBG organogels and LBG organogels doped with SWNTs; (B): G′ for LPG organogels and LPG organogels doped with SWNTs.

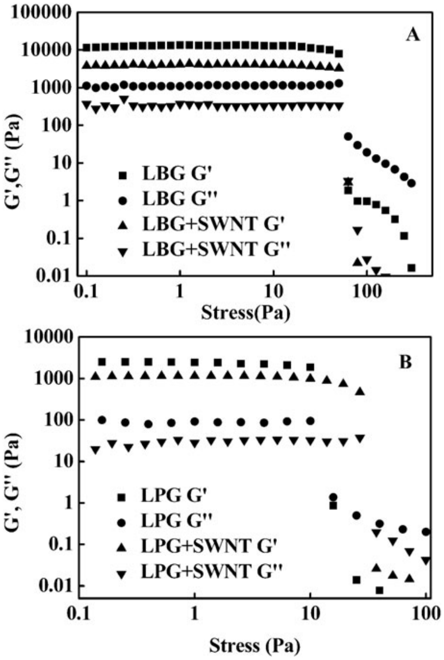

Fig. 7 Yield shear stress sweep experiments: (A): G′ and G″ for LBG organogels and LBG organogels doped with 4% weight percent SWNTs; (B): G′ and G″ for LPG organogels and LPG organogels doped with 4% weight percent SWNTs.

doped LPG gel plays a great role in extending the linear viscoelastic systems.

3. Conclusions

We have fabricated pristine carbon nanotubes into a soft composite using a new low molecular weight gelator, *N*,*N*′-bis(octadecyl)-L-(1-pyrenebutyric acid)-glutamic diamide. Its amide linkage, pyrene ring and two long hydrophobic chains all contribute to its great gelation ability. The great conjugated system of the pyrene ring also determined its ability to disperse the single-walled carbon nanotube well and resulted in the formation of stable nanocomposites with SWNTs doped into the LPG organogel. Incorporation of SWNTs decreased the critical gelation concentration of LPG in DCB and altered the thermal and mechanical properties of LPG organogels. The linear viscoelastic system of the LPG organogels, an indicator of the ability of resistance to the stress of the gel, extended with the incorporation of 4 wt% of the pristine SWNTs. However, there was no obvious change in the critical gelation concentration, thermal and mechanical properties of LBG organogels upon addition of same amount of SWNTs. Thus, the dispersion of SWNTs into organogels through π–π interaction with the pyrene group of LPG resulted in enhancement of the resistance to applied stress of organogel/SWNT nanocomposites as compared to the naked organogels. The morphology of the gel changed from layered structures to intertwined fibers, which also supported the dispersion of SWNTs, and then led to the improvement in mechanical properties.

4. Experimental

4.1 Materials

In previous reports, we have described the synthesis of an organogelator containing a Boc group: *N*,*N*′-bisoctadecyl-L-Boc-glutamic-diamide (LBG).[30] In this paper, we changed the Boc group to a 1-pyrenebutyric acid. The Boc group of LBG was changed to free amino by mixing with trifluoroacetic acid in dichloromethane. 1.50 g LBG were dispersed in dichloromethane in an ice bath. Then 5 mL trifluoroacetic acid were added to the above mixture and stirred at 0 °C for 3 h. After that, the solvent was removed by rotary evaporation and oily product was obtained. The oily compound was dissolved in 10 mL THF and poured into 300 mL saturated aqueous solution of $NaHCO_3$. After filtration, the product was purified by reprecipitation in THF to give a white solid (1.28 g, 98%). Then we dispersed a certain amount of the white solid (0.65 g, 1 mmol) mentioned above in dichloromethane (60 mL) and stirred for 30 min. Then, 1-pyrenebutyric acid (0.29 g, 1 mmol) was added into the above mixture and stirred at 0 °C for 30 min. After that, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl) (0.23 g, 1.2 mmol) and 1-hydroxybenzotrizole (HOBt, 0.16 g, 1.2 mmol) were added to the mixture. The obtained mixture was stirred for 5 days at room temperature. After that, the solvent was removed by rotary evaporation and orange solid was obtained. The crude product was dissolved in 10 mL THF, and poured into 300 mL saturated aqueous solution of $NaHCO_3$. After filtration, the product was purified by reprecipitation in methanol to give a light yellow solid (0.8 g, 87% yield). ^{1}H-NMR (CDCl3), δ (ppm): 8.28 (d, J = 9.0 Hz, 1H); 8.15 (d, J = 7.5 Hz, 2H); 8.10 (d, J = 8.3 Hz, 2H); 7.96–8.02 (m, 3H); 7.85 (d, J = 7.7 Hz, 1H); 4.36 (br s, 1H); 3.37–3.39 (m, 2H); 3.21 (br s, 4H); 1.96–2.41 (m, 10H); 1.47 (br s, 5H); 1.20–1.25 (m, 68H); 0.86–0.89 (m, 7H). MALDI-TOF MS calculated for $C_{61}H_{97}N_3O_3$ 920.0; found 943.0 $(M+Na)^+$, 959.0 $(M+K)^+$. Anal. Calcd for $C_{61}H_{97}N_3O_3$ C: 79.60, H: 10.62, N: 4.57; found C: 78.85, H: 10.60, N: 4.59.

1,2-Dichlorobenzene (DCB) was obtained from Jinke Chemical Engineering Corporation, Tianjin with a purity of 99.0%. Single-walled carbon nanotubes with purity over 95% were received from Thomas Swan & Co. Ltd. without further purification. The average diameter of the nanotubes was 2 nm and average length was less than 1 μm.

4.2 Gel formation

Gels were formed by dissolving the gelators in hot DCB (60 °C) to make a clear solution. Then the solution was cooled down to room temperature, and the transparent organogel formed. Gelation was determined by the absence of flow of the solvent when the tube was inverted. To measure the critical gelation concentration, we increased the solvent by 100 μL every time to 5 mg mL^{-1} LPG organogel with DCB as the solvent until the concentration was insufficient to form a stable gel. To prepare the organogel/SWNT composite, SWNTs were dispersed in DCB with the aid of ultra-sonication for 12 h and then the nanotube suspension was added to hot LPG or LBG solutions. The mixture in DCB was sonicated for 5 min at 60 °C and then quenched to room temperature.

4.3 Procedures

A piece of clean hydrophobic silicon slide and a piece of freshly cleaved mica was dipped into the hot solution and cooled to room temperature to form a gel, then the slide was pulled out and dried under vacuum for SEM and AFM measurements. All AFM pictures were measured with a Digital Instrument Nanoscope III Multimode system (Santa Barbara, CA) with a silicon cantilever using the tapping mode. SEM measurements were carried out on Hitachi S-4300 at 15 kV and 10 mA. UV spectra were recorded by a JASCO UV-550 spectrophotometer. Fluorescence emission spectra were recorded on a Hitachi F-4500 spectrometer. Rheological characterization was performed by using a TAAR2000ex stress-controlled rheometer with 40 mm parallel plate geometry. A hot solution of the compound was transferred onto the plate kept at 25 °C and allowed to form a uniform layer. The evolution of moduli (G' and G'') *versus* time was tested at 15 °C and 40 °C for LBG and LPG respectively, with a frequency of 1 Hz and a strain of 0.2%. The temperature ramp was measured at 1 Hz frequency and a strain of 0.2%, with a fixed heating or cooling rate of 5 °C min^{-1}.

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