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PAPER

Preparation and Characterization of Side-chain Liquid Crystal Polymer/paraffin Composites as Form-stable Phase Change Materials

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A series of side-chain liquid crystal polymers (SCLCPs), named poly[ω -(4'-n-alkyl oxybiphenyl-4-oxy) hexyl methacrylatels (P6biCm, m = 1, 2, 4, 6, 8, 10, 12, 14, 16 and 18) have been synthesized. The novel SCLCPs/paraffin composite form-stable phase change materials (FSPCM) were prepared by introducing P6biCm into paraffin. The minimum gelation concentration (MGC) and gel-to-sol transition temperature

¹⁰ (T_{GS}) properties were tested by "tube-testing method". It found that P6biCm (m = 1, 2, 4, 6, 8, 10) were insoluble in paraffin, while P6biCm (m = 12, 14, 16, 18) exhibited low MGC (≤ 6 wt%) and high T_{GS} (T_{GS} of P6biC12/paraffin is 140 °C). The structure and morphology of FSPCMs were systematically investigated by FT-IR, POM, 1D WXAD and SEM. Experimental results revealed that paraffin was restricted in the three-dimensional P6biCm network, leading to FSPCM without leakage even above its

¹⁵ melting point. The thermal properties were studied by DSC and TG. The research showed that the P6biCm/paraffin exhibited excellent thermal stability and high heat storage density. The shape stability was discussed by rheological measurement, indicating that solid \leftrightarrow hard gel \leftrightarrow soft gel \leftrightarrow liquid was observed with the increase of temperature. Through researching, this work is useful in comprehending physical mechanism of shape stability, meantime, provides a novel method for FSPCMs.

20 Introduction

In recent years, with the increasing energy crisis, the rising demand of energy consumption, high cost of fossil fuels and the accompanied environmental problems, many study have focused on thermal energy storage which is an effective use of thermal ²⁵ energy as well as environment-friendly new energy-saving technique.¹⁻³ Phase change materials (PCMs) as one of most prospective techniques of storing thermal energy have gained extensive interest due to its high energy storage density and small

temperature variation during the phase change process.⁴⁻⁵

- ³⁰ According to phase change state, there are two common types of PCMs: solid-solid PCMs (SSPCMs) and solid-liquid PCMs (SLPCMs). For the SSPCMs, there is no liquid or gas generated, thus it needs no recipient to seal them in during the phase transition. However, small latent heats and the super-cooling are
- ³⁵ shortcomings limit their application.⁶⁸ For the SLPCMs, such as paraffin wax,⁹⁻¹⁰ fatty acid,¹¹⁻¹⁴ fatty alcohol¹⁵ and polyethylene glycol,¹⁶⁻¹⁷ have been studied and applied extensively in thermal energy storage for their superior properties such as proper melting temperature range, high heat storage capacity, good

- ⁴⁰ thermal stability, little or no super-cooling, low vapor pressure, no or less volume change during solid-liquid phase transition, non-toxicity, self-nucleating behavior and good thermal and chemical stability after long-term utility period and low cost made them widely produced and applied for different purposes.¹⁸⁻ ⁴⁵ ²² However, SLPCMs have to be placed in specially designed
- ⁴⁵ ²⁵ However, SLPCMs have to be placed in specially designed devices/containers during applications to prevent the leakage in their solid-liquid phase transition process, which results in extra thermal resistance and cost. To solve this problem, form-stable (or shape-stabilized) PCMs (FSPCMs) have become a research ⁵⁰ hotspot in the area of thermal energy storage in the past decade.²³⁻
- Generally, FSPCMs are composite materials which are

comprised of SLPCMs (act as thermal energy storage materials) and supporting materials (maintain the solid shape of the 55 FSPCMs). There are various methods to prepare FSPCMs: (1) Encapsulating or microencapsulating solid-liquid PCMs into a polymer matrix by blending or situ polymerization. There are many supporting polymers to be used, such as polymethyl methacrylate (PMMA),²⁶⁻²⁸ high-density polyethylene (HDPE),²⁹ ⁶⁰ low density polyethylene (LDPE),³⁰ polypropylene,³¹ SEBS,³² PVA,³³ polyurethane,³⁴ etc. (2) Absorbing solid-liquid PCMs into porous materials like expanded perlite,³⁵⁻³⁶ bentonite,³⁷ vermiculite,³⁸ diatomite³⁹ and expanded graphite.⁴⁰ (3) Grafting solid-liquid PCMs onto the skeleton of high melting temperature ⁶⁵ polymers.⁴¹⁻⁴³ (4) Encapsulating solid-liquid PCMs into gel network.⁴⁴⁻⁴⁸ However, when employing either porous materials or polymers as supporting materials to package solid-liquid

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PCMs, the encapsulation and low latent heat problems are not well resolved.

- To solve these problems, our group has reported the preparation and properties of a novel form-stable phase change ⁵ material based on gelator.⁴⁹ The results indicated that paraffin was restricted because the gelators could self-assemble into threedimensional netted structural, leading to form the shape-stable PCMs without leakage even above its melting point. The mass percentage of paraffin can reach 97 wt% without obvious leakage ¹⁰ of paraffin above the melting point and melting and freezing enthalpies of the composites can reach 184.6 and 180.7 J g⁻¹, respectively. In order to find new efficient supporting materials
- for FSPCM, we focused on side-chain liquid crystal polymers (SCLCPs). SCLCPs as one of the most popular comb-shaped ¹⁵ polymers have attracted great attention due to their capability of self-assembling into well-ordered supramolecular structures because of the interactions of mesogenic side groups and the terminal substituent, which can be applied in many fields, such as
- optical data storage, optic, electro-optic, nonlinear optic devices, ²⁰ photomechanical etc.⁵⁰⁻⁵⁴ Through research on literatures, gel formation has been observed in nonconjugated comb-shaped polymers when their solutions in alcohols or alkanes are cooled down to lower temperature (for example, poly(hexadecyl acrylate) in n-octylalcohol at 24 °C).⁵⁵ The gel so generated is ²⁵ resulted from a formation of supermolecular networks in which crystalline intermolecular associates act as physical cross-linking sites. These phenomenons provide the possibility of SCLCPs forming supermolecular networks to immobilize paraffin into FSPCM.
- In this article, we reported the synthesis and characterization of a series of SCLCPs with different length of tail chains, named poly[ω-(4'-n-alkyloxybiphenyl-4-oxy)hexyl methacrylatels (P6biCm, m = 1, 2, 4, 6, 8, 10, 12, 14, 16 and 18). The molecular structure of polymers is shown in Chart 1. The SCLCPs/paraffin
 composites were prepared by using paraffin as latent heat material and P6biCm as supporting materials, the thermal properties and thermal stability were investigated in details. Since there was no report about form-stabilized PCMs investigated using SCLCPs, the study would bring SCLCPs to a new 40 application area as well as provide a novel creation method of preparing FSPCMs.

CH₃ $(C - CH_2)_n$ $O = C - O + CH_2)_6 O - O - O C_m H_{2m+1}$ P6biCm (m = 1, 2, 4, 6, 8, 10, 12, 14, 16, 18)

Chart 1 Chemical structures of P6biCm.

Experimental

45 Materials

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Paraffin was provided by Shanghai Huashen Recover Equipment Co., Ltd. Anhydrous tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon and used immediately.
2, 2'-azobisisobutyronitrile (AIBN) was freshly recrystallised
⁵⁰ from methanol. 4, 4'-Diphenol (98% Alfa Aesar) and bromoalkanes together with other reagents and solvents were used as received without further purification.

Synthesis of the monomers

For convenience, the ω-(4'-n-alkyl oxybiphenyl-4-oxy)hexyl
 ⁵⁵ methacrylatels monomers were named M6biCm, and the corresponding polymers were named P6biCm. The synthetic route of monomers M6biCm is shown in Scheme 1. The experimental details are described as follows:
 4-Alkyloxy-4'-hydroxybiphenyls:

4-Alkyloxy-4'-hydroxybiphenyls: 4-Alkyloxy-4-⁶⁰ hydroxybiphenyls were synthesized by standard methods from 4,

4'-biphenyldiol with bromoalkanes in the presence of K₂CO₃. The mixture was heated for 12 h in 55 °C, next the reaction mixture poured into a large amount of water to precipitate products. The products were purified by precipitation in water from THF ⁶⁵ solution three times. At last, the crude products were purified by

 $_{65}$ solution three times. At last, the crude products were purified by column chromatograph (silica gel, CH₂Cl₂). The final product of 4-octanoxybiphenol was white powder. Yield: 64%.

4-Alkyloxy-4'-(ω-bromoalkyloxy)biphenyls: 1 mol 4-Alkyloxy-4'-hydroxybiphenyls were dissolved in 150ml hot acetone and 6

- ⁷⁰ mol K_2CO_3 were added under stirring, 6 mol 1, 6-dibromohexane were added and the mixture refluxed for 20 h. The mixture was hot filtered in order to remove inorganic salts. Much of acetone was removed by rotating evaporation, then the reaction mixture was precipitated into a large amount of water, and was filtered. ⁷⁵ The precipitate washed with petroleum ether. The resulted solid
- vas dried at 40 °C under vacuum. Yield: 72%.

4-(Methacryloyloxy)alkyloxy-4-alkyloxybiphenyl: 1 mol 4-Alkyloxy-4-(ω-bromoalkyloxy)biphenyl, 5 mol methacrylic acid and 5 mol K₂CO₃ were added in 200mL DMF. After the reaction ⁸⁰ was refluxed for one night, the mixture was hot filtered in order to remove inorganic salts. The reaction mixture was precipitated into a large amount of water, and was filtered. At last, the crude products were purified by column chromatograph (silica gel, CH₂Cl₂). The detailed characterization data of M6biCm were ⁸⁵ listed in supplementary information.

Synthesis of the polymers

The polymers were obtained by conventional solution radical polymerization (see Scheme 1), typically carried out as described in the following example.

⁹⁰ The monomer, AIBN and chlorobenzene were added into a dried reaction tube containing a magnetic stirrer bar. The molar ratio was set with N_{monomer}: N_{AIBN} = 100 : 1, and the monomer mass concentration was 30%. After three freeze-pump-thaw cycles, the tube was sealed under vacuum. Polymerization was ⁹⁵ carried out at 70 °C over 24 h. The sample was purified by similarly re-precipitating three times from THF into methanol. The yields of polymers were listed in Table 1.



Scheme 1 Synthetic route of monomers (M6biCm) and corresponding polymers (P6biCm).

Preparation of P6biCm/paraffin composites

The mixture of P6biCm and paraffin were sealed in a test tube, s and heated to 180 °C until a transparent solution was formed. Take the preparation of 6 wt% P6biC18/paraffin as an example, the details were described as follows: 0.06 g P6biC18 was added into 0.94 g paraffin in a test tube to form a suspension. After being heated in an oil bath at about 180 °C, the mixture gradually turned into a transparent solution. Then, the tube was cooled at room temperature (25 °C) until a white gel was formed (see Fig.1). All the other composite gels were prepared via the similar method.



Fig.1 The formation of the 6 wt% P6biC18/paraffin FSPCMs.

Instruments and measurements

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¹H NMR measurements. All NMR measurements were performed on a Bruker ARX400 MHz spectrometer using with CDCl₃ as solvent, tetramethylsilane (TMS) as the internal ²⁰ standard at ambient temperature. The chemical shifts were reported on the ppm scale.

Gel permeation chromatography (GPC). The apparent number average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) were measured at 35 °C by a gel permeation 25 chromatography (GPC, WATERS 1515) equipped with three

Waters μ -Styragel columns (10³, 10⁴, and 10⁵ Å) in series, using

THF as the eluent at a flow rate of 1.0 mL min⁻¹. The GPC data were calibrated with polystyrene standards.

Minimum gelation concentration (MGC) and gel-to-sol ³⁰ transition temperature (T_{GS}) measurements. The MGC and T_{GS} properties of composites were tested by a "tube-testing method"⁵⁶: A weighted P6biCm was mixed with paraffin in a test tube (the samples were weighed in at 1.0 g in total) with a screw cap (inside diameter was 14 mm), heated until the polymer was ³⁵ dissolved. The resulting solution was cooled at 25 °C for 2 h, and then put into oil-bath whose temperature was above melting temperature of solid-liquid PCMs. When upon inversion of the test tube no fluid ran down the walls of the tube, we judged it "successful gelation". The minimum concentration of polymer necessary for gelation is MGC, the unit of MGC is wt%. The temperature that gel turn into sol is T_{GS} , and the temperature that sol turn into gel is T_{SG} .

- ⁵ Fourier transform infrared (FT-IR) analysis. Infrared spectrogram of each specimen was obtained in transmittance mode using a Nicolet Nexus 6700 FT-IR spectrophotometer with a 1 cm resolution in 32 scans collect. The samples were scanned in the range of 500 4000 cm⁻¹ using KBr pellets.
- ¹⁰ **Polarized optical microscope (POM) observation.** Polarized optical microscope observation was carried out using a Leica DMLM-P microscope equipped with a Mettler FP82 hot stage and a digital camera. Photographs were taken by a digital camera at short intervals of time.
- ¹⁵ Wide angle X-ray diffraction (WAXD) analysis. Onedimensional wide-angle X-ray diffraction (1D WAXD) experiments were performed on a BRUKER AXS D8 Advance diffractometer with a 40 kV FL tubes as the X-ray source (Cu Kα) and the LYNXEYE_XE detector. Background scattering was ²⁰ recorded and subtracted from the sample patterns.
- **Scanning election microscope (SEM) observation.** To investigate the nature of microstructures and morphologies, a SEM sample was prepared by immersing the PCMs gels in petroleum ether to extract the PCMs for 5 h followed by drying at
- ²⁵ room temperature. The surface morphology of the FSPCMs was investigated using a scanning electron microscope (JEOL JSM-6610).

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- **Differential scanning calorimetry (DSC) measurement.** DSC traces of the polymer were obtained using a TA Q10 DSC ³⁰ instrument. The temperature and heat flow were calibrated using standard materials (indium and zinc) at a cooling and heating rates of 10 °C min⁻¹. The sample with a typical mass of about 5 mg was encapsulated in sealed aluminum pans. Specific heat capacity measurements were carried out in the temperature range
- ³⁵ from -10 °C to 50 °C with a heating rate of 5 °C min⁻¹. The DSC was calibrated in the same temperature region before each experiment, using a sapphire sample as standard, with a well-known specific heat capacity. This leads to an accuracy of $\leq 2\%$ for the presented data. Heat capacity values at 30 °C are presented.
- ⁴⁰ **Thermogravimetric analysis (TGA)**. TGA was performed on a TA SDT 2960 instrument at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

Rheology measurement. A Rheometrics ARES rheometer (TA ARES rheometer) was applied to measure the viscoelastic

- ⁴⁵ properties of the samples based on oscillatory shear and temperature. The experimental temperature was controlled using forced N₂ gas convection. Dynamic temperature ramp test were performed in the region of 30 °C to 160 °C at 2 °C min⁻¹, using a 25 mm diameter parallel-plate geometry with a frequency of 1 rad
- $_{50}$ s⁻¹ and a small strain amplitude. Isothermal frequency sweeps were made using the same setup at frequencies from 0.1 to 100 rad s⁻¹.

Results and discussion

Synthesis and characterization of P6biCm

55 A series of methacrylate biphenyl SCLCPs with different lengths

of tail chain (P6biCm, m = 1, 2, 4, 6, 8, 10, 12, 14, 16 and 18) were synthesized according to the synthetic route illustrated in Scheme 1. The ¹H NMR spectra of one representative polymer P6biC18 and its monomer were shown in Fig.2. As can be seen ⁶⁰ from Fig.2a to Fig.2b, the chemical shifts and peak integrations of all the protons in M6biC18 are in excellent agreement with its expected structure, in addition the characteristic vinyl proton signals of methacryloyl group at 5.55 and 6.10 ppm disappeared

completely, and the other peaks broadened. Meantime, all ⁶⁵ polymers have the moderately high molecular weights (*Mn*) (see Table 1) to remove the influence of *Mn* on the supporting properties in the composite FSPCMs. Fig.3 shows the DSC curves of P6biCm during the first cooling scan and the second heating scan at a rate of 10 °C min⁻¹ under nitrogen atmosphere. ⁷⁰ As for the phase transition and phase structure of P6biCm, they have been discussed by our group in details. The results showed that all the polymers formed smectic phase and exhibited the high clearing temperature (T_i) (see Table 1), indicating that P6biCm could self-assemble into ordered structure with stable phase ⁷⁵ structure.



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Fig.3 DSC curves of P6biCm during the first cooling scan (a) and the second heating scan (b) at a rate of 10 °C min⁻¹ under nitrogen atmosphere.

Table 1	Molecular	Characteristics	of	Polymers

Sample	M_n (×10 ⁴) ^a	PDI ^a	Yield (%) ^b	$T_1 \left({^oC} \right){^c}$	$T_i(^{o}C)^{d}$	$T_d(^{o}C)^{e}$
P6biC1	9.85	1.88	75	114.6	139.5	323
P6biC2	8.27	1.93	86	133.7	147.6	302
P6biC4	4.35	1.87	78	124.9	165.7	329
P6biC6	4.09	1.72	80		166.5	357
P6biC8	6.45	2.21	76		170.4	358
P6biC10	5.11	2.52	82	156.1	177.8	310
P6biC12	8.36	1.81	84	163.1	179.4	375
P6biC14	5.78	2.19	82	157.6	179.2	304
P6biC16	6.92	2.01	82	158.5	178.3	370
P6biC18	9.22	1.35	86	157.7	172.6	327

^a The molecular weights (M_n) and polydispersity (PDI) were determined by GPC in THF on the basis of standard polystyrene calibration.

5 ^bThe yields of polymers by conventional solution radical polymerization.

^c Phase transitions temperature from one liquid crystalline to another one was evaluated by DSC at a rate of 10 °C min⁻¹ under the second heating.

^d The isotropic transition temperature was evaluated by DSC at a rate of 10 °C min⁻¹ under the second heating.

^e The temperature at which 5% weight loss of the sample was reached from TGA under nitrogen atmosphere.

Preparation	and	gel	properties	of	Pe	6biC	m/paraffin	25 mesogenic groups as bridge to form
10 composites								networks and subsequently become an im
								increase of tail chain the P6hiCm tend to r

The MGC and T_{GS} test results of P6biCm/paraffin were summarized in Table 2. It found that, P6biCm (m = 1, 2, 4, 6, 8, 10) were insoluble in paraffin, while paraffin can be gelated when introducing P6biCm (m = 12, 14, 16, 18) at a low mass fraction $15 (\leq 6 \text{ wt\%})$. Meantime, T_{GS} of P6biCm/paraffin at a certain mass fraction (6 wt%) decreased with the increase of tail chain of P6biCm. P6biC12/paraffin shows excellent form stability with low MGC (4 wt%) and high T_{GS} (140 °C). The selected paraffin is comprised of alkanes with 17 to 35 carbons, which is good and 20 poor solvent for the tail chain and main chain of P6biCm. The P6biCm with their test the low in (m = 1, 2, 4, 6, 8, 10) mean insclubely

P6biCm with short tail chain (m = 1, 2, 4, 6, 8, 10) were insoluble in paraffin. While P6biCm (m = 12, 14, 16, 18) with long tail chain tend to interact each other with the long chain alkanes of paraffin along with the π - π interaction between the biphenyl

 $_{25}$ mesogenic groups as bridge to form physical cross-linking networks and subsequently become an immobile gel. 57 With the increase of tail chain, the P6biCm tend to more soluble in paraffin which result in lower $T_{\rm GS}.$

The form stability characteristics of the P6biCm/paraffin ³⁰ FSPCMs were investigated according to the method presented in Ref. [58]. All samples showed good form stability without obvious leakage of paraffin when the specimen discs were heated at 70 °C for 24 h. Fig.4 shows the images of paraffin (a), P6biC18/paraffin (b), P6biC16/paraffin (c), P6biC14/paraffin (d) ³⁵ and P6biC12/paraffin (e) before and after they were heated at 70 °C for 10 min and 1 h. Fig.4 clearly shows that the paraffin was melted after 10 min and the disc totally became liquid after 1 h. On the other hand, no appreciable deformation could be found for the P6biCm/paraffin FSPCM discs. The result further approved ⁴⁰ that the prepared FSPCMs possessed good form stability.

Table 2 Tube-testing results of P6biCm/paraffin composites.							
Sample	P6biCm/paraffin (m =1, 2, 4, 6, 8, 10)	P6biC12/ paraffin	P6biC14/ paraffin	P6biC16/ paraffin	P6biC18/ paraffin		
MGC ^a	insoluble	4 wt%	6 wt%	6 wt%	5 wt%		
$T_{GS} \left({^oC} \right){^b}$		142	136	102	98		
$T_{SG}\left(^{o}C\right){}^{b}$		136	131	98	92		

^a The minimum concentration of P6biCm necessary for gelation of paraffin tested by "tube-testing method".

^bThe gel-to-sol and sol-to-gel temperatures of P6biCm/paraffin tested by "tube-testing method".



Fig.4 The photographs of PCMs paraffin (a), P6biC18/paraffin (b), P6biC16/paraffin (c), P6biC14/paraffin (d), P6biC12/paraffin (e) before and after heat treatment at 70 °C for 10 min and 60 min.

Structure characterization of the P6biCm/paraffin composite FSPCMs

- ¹⁰ The FT-IR spectra of paraffin, P6biC12 and P6biC12/paraffin FSPCMs are shown in Fig.5. In the spectrum of paraffin, the peak at 2917 cm⁻¹ signifies the symmetrical stretching vibration of its -CH₃ group, the peak at 2849 cm⁻¹ represents the symmetrical stretching vibration of its -CH₂ group. The peaks at around 1463 ¹⁵ cm⁻¹ belong to the deformation vibration of -CH₂ and -CH₃, and the peak at 719 cm⁻¹ represents the rocking vibration of -CH₂. In
- the spectrum of P6biC12, the appearance of the vibrational bands at 2840-2960, 1724 and 1470-1600 cm⁻¹ which were attributed to the vibrations of aliphatic chain (C-H), ester carbonyl (C=O) and 20 aromatic (Ar), respectively, In the spectrum of composite
- 20 aromate (AI), respectively, in the spectrum of composite P6biC12/paraffin, the same peaks as P6biC12 and paraffin still existed, and no significant new peak was observed, indicating that the composite P6biC12/paraffin was only a physical interaction between paraffin and without appreciable chemical 25 interaction between them. The same results were observed in
- other P6biCm/paraffin composites.





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Fig.6 shows the polarizing optical microscope (POM) micrographs of PCMs. As can been seen from Fig.6a to Fig.6b, no birefringence phenomenon was observed when the paraffin melted. Contrary to the neat paraffin, the P6biC12/paraffin 5 present obvious birefringence phenomenon above the melting point of paraffin (T_m), as can be seen from Fig.6c to Fig.6d, shows that the P6biC12 formed the order structure in paraffin.

The same results were obtained in P6biC14/paraffin, P6biC16/paraffin and P6biC18/paraffin. Although the paraffin component melted totally above the T_m , no obvious flow of paraffin was observed from POM micrograph, suggesting that the supporting of P6biCm network restricted the flow of melted paraffin, resulting in FSPCMs.



Fig.6 POM images of paraffin at 30 °C (a) and 70 °C (b); 6 wt% PbiC12/paraffin at 30 °C (c) and 70 °C (d). Scale bar = 50 µm.

The composite FSPCMs were further characterized by XRD to investigate the chemical compatibility between the paraffin and SCLCPs. Fig.7 shows the XRD pattern of the paraffin, P6biC12 ²⁰ and the P6biC12/paraffin composite PCM. The XRD peaks at 21.5° and 23.9° of the paraffin are due to its regular crystallization. As for P6biC12, when the temperature was below 150°C, five obvious diffraction peaks at 2θ value of 1.50°, 3.01°, 4.47°, 5.93° and 7.45° were observed (marked with arrows in Fig. 25 7). The ratio of scattering vectors was 1 : 2 : 3 : 4 : 5. A single

- diffraction peaked appeared at 2θ of 20.6° in the high-angle region, which should be contributed from the packing of biphenyl containing tail chains. Therefore, the polymers maybe form a smectic phase. The XRD pattern of the P6biC12/paraffin 30 composite PCM contains the same peaks of paraffin, whereas the
- peak intensities are relatively lower. However, peaks of P6biC12 are not found in composite FSPCM, which is ascribed to the low concentration of P6biC12. This result shows that the crystal structure of the paraffin remains unchanged during the synthesis
- ³⁵ process and is consistent with the result of FT-IR.



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Fig.8 shows the photographs of the fracture surfaces of paraffin and P6biC12/paraffin investigated by SEM. From Fig.8a to 8b, the surface of paraffin is smooth and uniform. Contrary to the neat paraffin, paraffin in the composite FSPCMs dispersed well 5 in the three-dimensional net structure formed by the P6biC12. It is believed that the brighter three-dimensional network structure and smooth dark grey area on the SEM images correspond to P6biC12 matrix and paraffin, respectively.⁵⁹ This point of view was able to be confirmed by the SEM from Fig.8c to Fig.8d, the

10 three-dimensional network revealed after the paraffin in composites is etched by petroleum ether. In addition, the same microstructures of the surfaces were observed in P6biCm/paraffin (m = 14, 16, 18). According to the results, the paraffin is uniformly encapsulated and embedded inside the three-15 dimensional P6biCm network. The network traps the paraffin, so even if the environmental temperature is above its melting point, the composite FSPCMs remain in the solid state.



Fig.8 SEM images of fractured surfaces of pure paraffin: (a) before treatment, (b) after petroleum ether-etched and P6biC12/paraffin composites: (c) 20 before treatment, (d) after petroleum ether-etched. Scale bar = 5 μ m.

Thermal properties of P6biCm/paraffin composites

The heating and cooling DSC curves of the pure paraffin and P6biCm/paraffin are illustrated in Fig.9. From the DSC curves, it 25 can be seen that two peaks were detected in the pure paraffin. The first minor peak at about 39 °C should be attributed to the solidsolid phase transition of the paraffin and the second sharp peak at about 57 °C corresponding to the solid-liquid phase transition of the paraffin. As to P6biCm/paraffin, the endothermic peaks shift 30 to higher temperatures slightly and become broader. These small changes suggest that the thermal properties of P6biCm/paraffin

are mainly dominated by the paraffin in composite FSPCMs.

The thermal properties of the composite P6biCm/paraffin including melting temperature of paraffin (T_m), observed melting $_{35}$ latent heat ($\Delta H\,_{m}^{obs}$), theoretical melting latent heat ($\Delta H\,_{m}^{The}$), freezing temperature (T_f), observed freezing latent heat (ΔH_f^{obs}),

theoretical freezing latent heat (ΔH_f^{The}) were summarized in Table 3. As seen from Table 3, compared with that of the pure paraffin, there are no differences for phase transition temperatures (T_m and ⁴⁰ T_f) of the P6biC12/paraffin, showing that P6biC12 has little effect on the phase transition temperature of paraffin. Meantime, the ΔH_m^{obs} and ΔH_f^{obs} of composite FSPCMs show small impact with the introducing of P6biCm. For example, the ΔH_m^{obs} and ΔH $_{\rm m}^{\rm The}$ of 6 wt% P6biC12/paraffin was 188.1 J g $^{-1}$ and 177.9 J g $^{-1},$ 45 respectively. These results suggesting that both the paraffin and P6biC12/paraffin composites exhibit similar thermal characteristics, because there was no chemical reaction between the paraffin and P6biCm in the preparation of P6biCm/paraffin composite FSPCMs. In addition, the composite FSPCMs still 50 possess high latent heat despite of the introducing of low mass fraction of supporting materials, so that has an important potential for the application of energy storage.

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Table 3 The thermal characteristics of paraffin and P6biCm/paraffin.

	Melting				Freezing		
-	T_{m}	$\Delta H_{\rm m}^{\rm obs}$	$\Delta H_{\rm m}^{\rm The}$	$T_{\rm f}$	$\Delta H_{\rm f}^{\rm obs}$	$\Delta H_{\rm f}^{\rm The}$	Specific Heat (kJ kg ⁻¹ K ⁻¹) ^c
	(°C) ^a	$(J g^{-1})^{a}$	$(J g^{-1})^{b}$	(°C) ^a	$(J \ g^{-1})^{a}$	$(J\ g^{\text{-1}})\ ^{b}$	
paraffin	57.2	189.3	189.3	53	184.4	184.4	2.15
6 wt% P6biC18/paraffin	59.4	187.3	177.9	50.7	188.4	173.3	2.06
6 wt% P6biC16/paraffin	58.5	184.8	177.9	51.9	185.7	173.3	2.09
6 wt% P6biC14/paraffin	58.9	182.8	177.9	51.8	183.4	173.3	2.02
6 wt% P6biC12/paraffin	59.2	188.1	177.9	51.1	187.5	173.3	2.05
6 wt% P6biC12/paraffin after 200 cycles	59.3	186.3	177.9	51.5	186.5	173.3	2.05
6 wt% P6biC12/paraffin after 500 cycles	59.5	185.9	177.9	51.5	186.1	173.3	2.01

30

^a Evaluated by DSC during the second heating process at a rate of 10 °C min⁻¹ under nitrogen atmosphere.

s ^bCalculated by multiplying the weight percentage of paraffin in the composite PCM by the melting or freezing enthalpies of pure paraffin

^c Evaluated by an isothermal-ramp-isothermal with sapphire method at 30 °C.

The multi-cycle DSC scans were performed to investigate the working reliability of P6biCm/paraffin composites during a long-term phase change process. P6biC12/paraffin was tested as an ¹⁰ example. The DSC curves are shown in Fig.10 and the thermal characteristics before and after 200 cycles, 500 cycles are summarized in Table 3. The phase change temperature, latent heat and specific heat varied slightly, for example, the melting

- latent heat of 6 wt% P6biC12/paraffin only decreased 1.17% after 15 500 cycles. The results suggest that the P6biCm/paraffin composite FSPCMs could always maintain the stable phase change temperatures, enthalpies and specific heat over the multicycle phase transitions. Therefore, the prepared FSPCMs have a
- high working reliability to perform the energy storage-release ²⁰ repetitiously at an almost stable temperature. Moreover, the comparison of latent heat of P6biC12/paraffin prepared in present study with that of the different composite PCMs in literature was also given in Table 4. Based on the data in this table, it can remarkably be noted that P6biC12/paraffin composite PCMs
- 25 exhibit higher latent heat than that of other composite PCMs. The results further suggest that P6biCm/paraffin composite FSPCMs

have an important potential for the application of energy storage.





FSPCM	Mass ratio	$T_m (^{o}C)^a$	$T_{\rm f}(^{\rm o}C)^{\rm b}$	$\Delta H_m \left(J \ g^{\text{-1}}\right)^c$	Reference
SEBS/paraffin	10/90	54.5	49.1	158.5	Q. Zhang et al. ³²
EPDM/paraffin	50/50	56.4	48.8	85.0	G. Song et al. ⁶¹
HDPE/paraffin	23/77	55.7	45.2	162.2	A. Sarı et al. ⁶²
calcined diatomite/paraffin	39/61	33.04		89.54	Z. Sun et al. ⁶³
PMMA/paraffin	34/66	55.8	50.1	112.3	Y. Wang et al. ⁶⁴
P6biC12/paraffin	6/94	59.2	51.1	188.1	Present study
P6biC18/paraffin	6/94	59.4	50.7	187.3	Present study

Table 4 Comparison of thermal properties of the composite prepared with that of some FSPCMs in literatures.

^a Melting temperature of paraffin.

^bFreezing temperature of paraffin.

^c Melting latent heat of FSPCMs.

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⁵ The TGA and DTG curves of paraffin, P6biCm and P6biCm/paraffin composite FSPCMs were shown in Fig.11a and 11b. The degradation datas are summarized in Table 5. The results show that pure paraffin has a single degradation process and decreased at lower temperature at about 206.4 °C, because it ¹⁰ is composed of alkane molecules with lower decompose temperature. The SCLCPs show excellent thermal stability and decreased at higher temperature (as seen in Table 1). For the FSPCMs, both the T_d and T_{peak} are about 30 °C higher than the paraffin (see Table 5). There are two-step weight loss processes ¹⁵ during thermal degradation: The first step weight loss processes of composite FSPCMs occur roughly at around 230 °C is attributed to evaporation of the paraffin so that the weight loss rates reach almost 93%. The second step weight loss processes almost take place at about 370 °C mainly caused by the ²⁰ decomposition of P6biCm, which can be evidenced by the TG curve of P6biCm shown in the figure. Contrary to the pure paraffin, the weight loss time of paraffin in the FSPCMs has been prolonged, P6biCm/paraffin composites have obviously higher thermal stability than pure paraffin. The results indicate that ²⁵ P6biCm restrain the evaporation of paraffin and can prevent the paraffin from degrading quickly.



Table 5	Thermal	degradation	properties	of 1	paraffin and	P6biCm/	paraffin com	posite FSP	CMs
		acguation	properties	· · ·	paratin and	1 0010114	paratin com	poone i oi	C1110

Sample	$T_d (^{o}C)^{a}$	T_{peak} (°C) ^b
paraffin	206.4	298.9
P6biC12/paraffin	235.8	336.2
P6biC14/paraffin	234.2	331.3
P6biC16/paraffin	243.9	338.3
P6biC18/paraffin	231.2	328.8

³⁰ ^a The temperature at which 5% weight loss of the sample was reached from TGA under nitrogen atmosphere.

^b The temperature of maximum weight loss rate.

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Rheology measurement

The shape stability is a vital property for FSPCM, the rheological measurement was used as a general technique to investigate the viscoelastic hehaviors of polymer or gel materials. To examine ⁵ the phase transition behavior and shape stability, the

- ⁵ the phase transition behavior and shape stability, the P6biCm/paraffin FSPCMs were characterized by rheological measurements. The storage modulus (G') is an important parameter which characterizes the strength of the gels and can estimate the degree of resistance that PCMs gels against ¹⁰ mechanical disturbance. On the other hand, the loss modulus (G')
- measures the tendency of a material to flow under stress.

Fig.12a shows the effect of temperature on G' and G'' of 6 wt% P6biC12/paraffin composites at a heating rate of 2 °C min⁻¹. It can be seen that two peaks of G' and G'' at around 39 °C and 59

- ¹⁵ °C are ascribe to a solid-solid phase transition and solid-liquid transition of the paraffin component, which is consistent with the DSC curves. However, with temperature increasing gradually above 59 °C, G' increased after the valley and then remained larger than G" and the value kept nearly invariant up to about 120
- ²⁰ °C, implies that paraffin can be packaged in the network of P6biC12 even above its melting point and the composite PCMs remains shape stable. We denominate this solid-like gel with higher modulus as hard gel. With the increase of temperature, both G' and G'' began to decrease steadily, but still G' > G'', in ²⁵ the temperature range from 120 to 144 °C, suggesting the trend of loging colid like characters for P6biC12/composite
- losing solid-like characters for P6biC12/paraffin composite PCMs. We denominate this solid-like gel with lower modulus as soft gel. A crossover point of G' and G'' traces was found at around 144 °C, which was the symbol of gel-sol transition for

³⁰ rheological measurement, after that G" would be larger than G', indicating that composites change to fluid completely.⁶⁵⁻⁶⁷ The transition temperature is well fit the results from "tube-testing method".

To further validate the analysis above, dynamic frequency 35 sweeps of P6biC12/paraffin were conducted at indicated temperatures, namely 70 °C, 120 °C, 140 °C and 150 °C. As can be seen in Fig.12b, at a relatively low temperature of 70 °C, which is slightly higher than melting point of paraffin, G' is much higher than G" throughout the investigated frequencies, ⁴⁰ meanwhile, both G' and G" are almost independent of frequency. The results manifest that the sample presents a typical solid-like behavior even after paraffin melts. When the temperature went up to 120 °C, G' was still larger than G", it is notable that G' shows a power-law relationship with ω in the low frequency range, while 45 G" decreases slightly with ω throughout the entire investigated frequency.³² The slight frequency dependence of G' indicates the gel is not strong enough to maintain its structural integrity completely and starts to lose its solid-like characters and partially lose shape stability. At this temperature, the composite undergoes 50 a transition of hard gel to soft gel. With the temperature further rise to 140 °C, G' remains higher than G", while both G' and G" tend to level off with decreasing ω and exhibit a plateau at low frequencies indicating the formation of perfect P6biC12 networks. Finally at 150 °C, the composite completely loses its 55 solid-like characters and behaved as a gel (G'' > G'). The transition temperature is between 140 °C and 150 °C which is well consistent with the result of dynamic temperature sweep.



Fig.12 (a) Temperature dependence of storage modulus (G') and loss modulus (G'') for 6 wt% P6biC12/paraffin composite at 30 °C to 160 °C. Condition: 0.05% strain, 1 rad s⁻¹ frequency and 2 °C min⁻¹ heating rate. (b) Frequency dependence of G' and G'' for 6 wt% P6biC12/paraffin composite at indicated temperature. Condition: 0.05% strain.

With the reference to Fig.13, the P6biCm/paraffin composites were in a solid-like gel state (G' > G'') after the paraffin melted (70 °C), while G' and G'' decreased as well as the difference value 65 between G' and G'' narrowed with the increase of alkyl tail of P6biCm. The result implies that P6biCm/paraffin (m = 12, 14, 16, 18) exhibited solid-like behaviour above the melting temperature of paraffin and the shape stability of P6biCm/paraffin decreased with the tail chain of P6biCm which accords with the "tube-70 testing" results.



Fig.13 Frequency dependence of G' and G" for P6biCm/paraffin composite FSPCMs. Condition: 0.05% strain, 70 °C.

Conclusions

- ⁵ In this work, a series of SCLCPs (P6biCm, m = 1, 2, 4, 6, 8, 10, 12, 14, 16 and 18) have been synthesized. Meanwhile, a series of novel P6biCm/paraffin composite FSPCMs were successfully prepared by introducing P6biCm (m = 12, 14, 16, 18) into paraffin. FT-IR, POM, WAXD and SEM
 ¹⁰ measurement suggested that the paraffin acted as latent heat storage material and P6biCm served as supporting material, and the paraffin was restricted by three-dimensional netted structural of P6biCm to keep the shape stable even above their melting point. The P6biCm/paraffin composites
 ¹⁵ exhibited high heat storage density and excellent thermal stability from the DSC and TG. The mass percentage of paraffin can reach 94 wt% without obvious leakage of paraffin above the melting point and the composites can keep their shapes in a long range of temperature due to the
- ²⁰ excellent supporting ability of three-dimensional network of P6biCm. The high latent heat, excellent thermal stability and high working reliability over the multi-cycle phase transitions make the P6biCm/paraffin composite an effective and promising material to store or release thermal energy in
- ²⁵ practical application. The rheological measurement revealed the solid ↔ hard gel ↔ soft gel ↔ liquid phase transition mechanism in the composite FSPCMs along with the increase of temperature. The research using SCLCPs as supporting materials may provide a novel creation method of
- ³⁰ preparing FSPCMs as well as broad the practical application of SCLCPs. At present, our group is preparing other SCLCPs for supporting material of FSPCMs, and the work will be presented in the near future.

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Table of contents entry:



Highlight

SCLCPs/paraffin composite as a novel FSPCM supported by SCLCPs three-dimensional network with high heat storage density and excellent thermal stability.

1