

Article

Feasibility of Storing Latent Heat with Liquid Crystals. Proof of Concept at Lab Scale

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Abstract: In this work, the first experimental results of thermotropic liquid crystals used as phase change materials for thermal storage are presented. For that purpose, the $n = 10$ derivative from the family of 4'- n -alkoxybiphenyl-4-carboxylic acids has been prepared. Different techniques like polarized-light microscopy, differential scanning calorimetry, thermogravimetric analysis and rheological measurements have been applied for its characterization. Having a mesophase/isotropic transition temperature around 251 °C, a clearing enthalpy of 55 kJ/kg, a thermal heat capacity of around 2.4 kJ/kg and a dynamic viscosity lower than 0.6 Pas, this compound fulfills the main requirements for being considered as latent heat storage material. Although further studies on thermal stability are necessary, the results already obtained are both promising and encouraging since they demonstrate the viability of this new application of liquid crystals as thermal storage media.

Keywords: thermal storage; liquid crystals; phase change materials

1. Introduction

Thermal energy storage is a key element for thermal processes management, especially in those related to renewable technologies, where both flexibility and dispatchability are demanded. If the thermal process entails water condensation/evaporation, isothermal storage/release of energy is the most appropriate approach. This implies storing energy as latent heat with phase change materials (PCMs) that undergo state transitions at temperatures close to the steam working conditions. Up to now, the PCMs considered for the temperature range between 140 °C and 340 °C have been pure compounds or eutectic mixtures that exhibit solid to liquid transitions with enthalpies from 100 kJ/kg to 300 kJ/kg. However, despite the strong research effort made during the last years, there is still no cost-effective solution available for this temperature range. The problem is that, in most of the cases, the used PCMs have very poor thermal conductivity, and since heat transfer is driven by conduction, enhanced heat transfer mechanisms have to be implemented in the heat exchanger, with the corresponding cost increase [1,2]. Whereas in other cases, the used PCMs are organic materials, which undergo thermal degradation under service conditions [3]. The solution explored in our lab is the use of alternative PCMs that absorb/release energy when they undergo a change between two fluid phases [4]. This kind of behavior is only displayed by thermotropic liquid crystals (LCs), which are substances that do not exhibit only a single transition from solid to isotropic liquid but rather a sequence of one or more transitions involving intermediate fluid phases, called mesophases. In this respect, some bibliographic sources have very recently used the term liquid-PCMs [5] when

referring to them. The fact that LCs can change their latent energy content upon changing from one to another liquid state avoids the problem of having a poor thermal conductivity since the energy exchange takes place by convection and the influence of material conductivity is negligible. This provides a constant discharging power of the storage device, which cannot be attained with the current solid-to-liquid PCMs [6]. Apart from thermal stability at working temperature ranges, the most important requirements that should fulfill a certain LC for being used PCM are that its clearing point (*i.e.*, mesophase to isotropic liquid transition) must be close to the temperature of the process, the clearing point enthalpy must be high enough and both liquid crystal and isotropic liquid phases must display low viscosity and comparatively high fluidity [3]. Also, from the implementation point of view, issues like low environmental impact, commercial availability and low price (*i.e.*, simple synthetic route) should be of main concern.

In order to find LCs with promising values of clearing enthalpies within the temperature range of steam the working conditions mentioned above, the large review published by Acree and Chickos in 2006 was thoroughly checked [7]. Figure 1 shows a dispersion of clearing temperature-enthalpy corresponding to the selected LCs. As we can see, it is already possible to find liquid crystals with enthalpies from 70 kJ/kg to 100 kJ/kg, which in principle could be appropriate for latent heat thermal storage in the range 140 °C–340 °C [8].

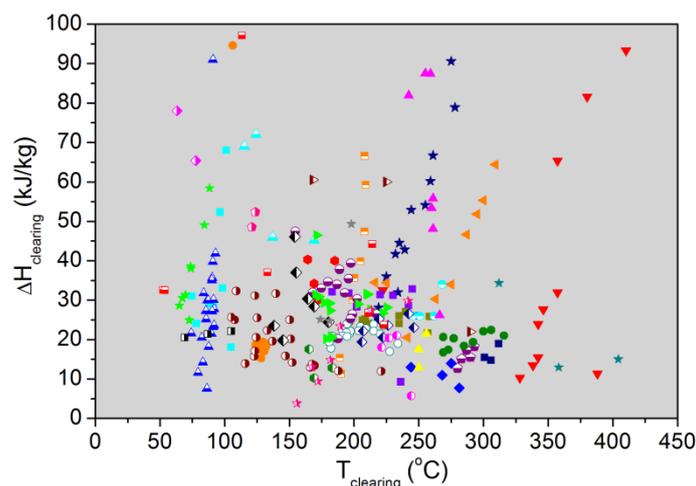


Figure 1. Clearing point enthalpy *vs.* clearing point temperature for various reported liquid crystals with properties in the desired range for latent thermal storage.

Despite these good perspectives, applications related to the ability of liquid crystals to store thermal energy under fluid phases have been mentioned only once in a patent about drilling fluid refrigerants [9]. Therefore, no special attention has been paid to investigate LCs with adequate features for thermal storage. On the other hand, the review published by Acree and Chickos [7] only includes compounds for which enthalpy data are reported in the literature. However, there should exist other LCs that are also expected to present high clearing enthalpy values but that are not included in that review. In this respect, compounds leading to stable mesophases due to the presence of intermolecular hydrogen bonds are expected to display both high clearing temperatures and enthalpies. Liquid crystals based on aromatic carboxylic acids are a significant and well investigated group that can form intermolecular hydrogen bonds [10–12]. These compounds, either alone or as mixtures, lead to supramolecular liquid crystals through the formation of two hydrogen bonds between the carboxylic groups of two different molecules, as shown in Figure 2.

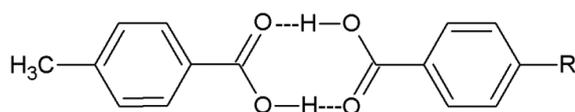


Figure 2. Intermolecular hydrogen bonds between two aromatic carboxylic acid molecules.

In the family of liquid crystals containing the carboxylic acid group we can find the para-*n*-alkoxybenzoic acids (*n*-PhCOOH) [13], the 4'-*n*-alkoxybiphenyl-4-carboxylic acids (*n*-BPhCOOH) [14], the trans-para-*n*-alkoxycinnamic acids (*n*-CinnCOOH) [15] and the 6-*n*-alkoxy-2-naphtic acids (*n*-NaphCOOH) [16]. The molecular structures of these compounds are shown in Figure 3.

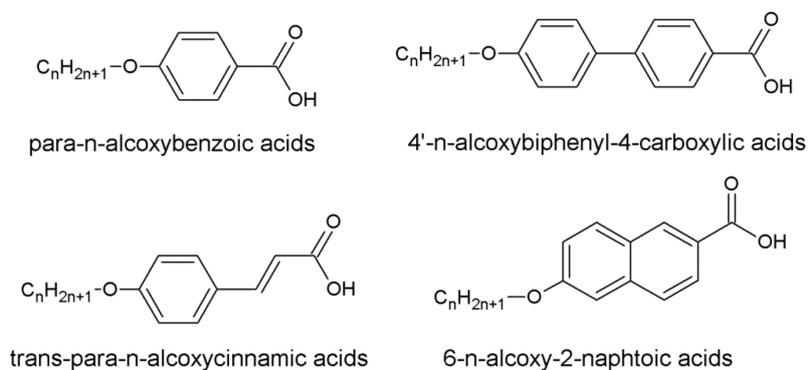


Figure 3. Molecular structures of different liquid crystal families with carboxylic acid as functional group.

The preparation of all these compounds is already reported in the literature [13–16], together with their phase transition temperatures and the kind of mesophase observed by polarized-light microscopy. The mesogenic behavior of each LC family included in Figure 3, in terms of transition temperatures variation with the alkyl chain length (*n*), is graphically displayed in Figure 4.

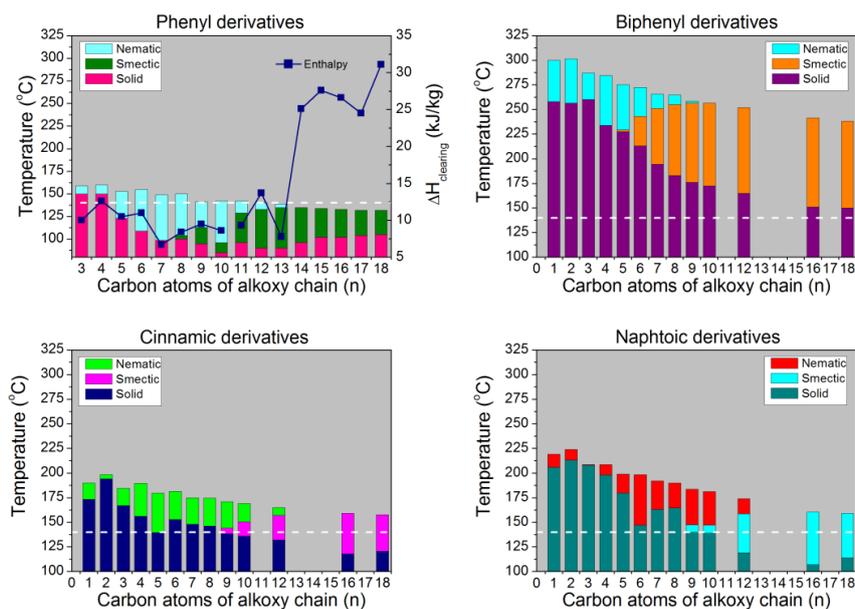


Figure 4. Variation of phase transition temperatures with the alkoxy chain length for the four families of liquid crystals displayed in Figure 3.

As we can see, almost all compounds of these families have clearing temperatures above 140 °C. The biphenyl derivatives present the highest clearing temperatures, which vary from nearly 300 °C to 240 °C as alkoxy chain increases from $n = 1$ to $n = 18$. In contrast the phenyl derivatives show the lowest clearing temperatures so that only derivatives with $n < 10$ attain values higher than 140 °C. As for the energy associated to each transition, data are not available for all these LC families since they were prepared in the 50's and the measurement of enthalpies at that time was not a simple task. As Figure 4 displays, clearing enthalpy values were only available for the para- n -alkoxybenzoic acids [13]. In general, the values displayed by the LCs of this family are rather low (~ 10 kJ/kg) and only the derivatives with $n \geq 14$, and as said above with clearing temperatures lower than 140 °C, have clearing enthalpies around 25 kJ/kg. In view of these data, it seems that this family is not the most appropriate for studying if liquid crystals can be used for thermal storage. Therefore, in order to prove the viability of LCs as phase change materials we decided to prepare some derivatives of 4'- n -alkoxybiphenyl-4-carboxylic acids because they have quite high clearing temperatures for all alkoxy chain lengths (see Figure 4). Other important reasons for choosing this series are the commercial availability of precursors and the simple synthetic route [14]. In this work we present the initial studies on the potential of our idea, which have been carried out on the 4'-decyloxybiphenyl-4-carboxylic acid (10-BPhCOOH). This compound has been characterized by polarized-light microscopy, differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. Additional properties like specific heat capacity (C_p) and dynamic viscosity have also been obtained.

2. Materials and Methods

2.1. Liquid Crystal Preparation

The 4'-decyloxybiphenyl-4-carboxylic acid (10-BPhCOOH) was prepared in two steps, starting from ethyl 4'-hydroxy-4-biphenylcarboxylate, following a synthetic procedure similar to the reported in the literature [14] but with some modifications. As shown in the synthetic scheme of Figure 5, ethyl 4'-hydroxy-4-biphenylcarboxylate was alkylated with decylbromide to give ethyl 4'-decyloxy-4-biphenylcarboxylate. Afterwards, saponification with sodium hydroxide and subsequent acidification with glacial acetic acid produced the desired 4'-decyloxy-4-biphenylcarboxylic acid as a white solid. Full details of synthetic methods, spectroscopic data and elemental analysis are given in the Appendix A.

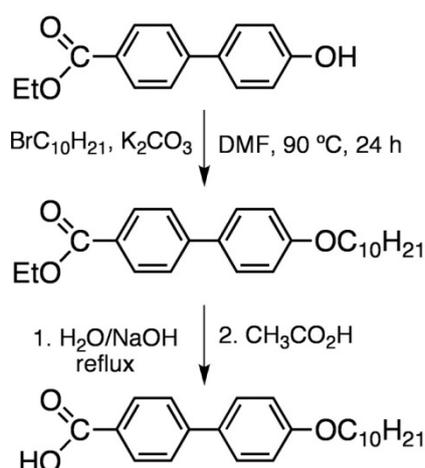


Figure 5. Synthetic route of 4'-decyloxybiphenyl-4-carboxylic acid (10-BPhCOOH).

2.2. Liquid Crystal Characterization

The liquid crystal behavior of the biphenyl acid derivative 10-BPhCOOH was characterized by polarized light microscopy using a Leica DMRB microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor, at 10 °C/min heating rate. As expected, a fan-shaped texture was observed in the temperature range 170 °C–249 °C that can be assigned to a smectic C (SmC) mesophase [17] (see Figure 6a). In addition, just before the clearing point (~249 °C), a nematic (N) mesophase was identified by its characteristic schlieren texture in a very short range of temperatures (0.5 °C) (see Figure 6b). The occurrence of this nematic mesophase was also observed by Gray *et al.* [14]. Consequently, due to the very short temperature range of this mesophase, in DSC scans displayed in section 3 only a peak of the combined transition SmC-N-I is observed.

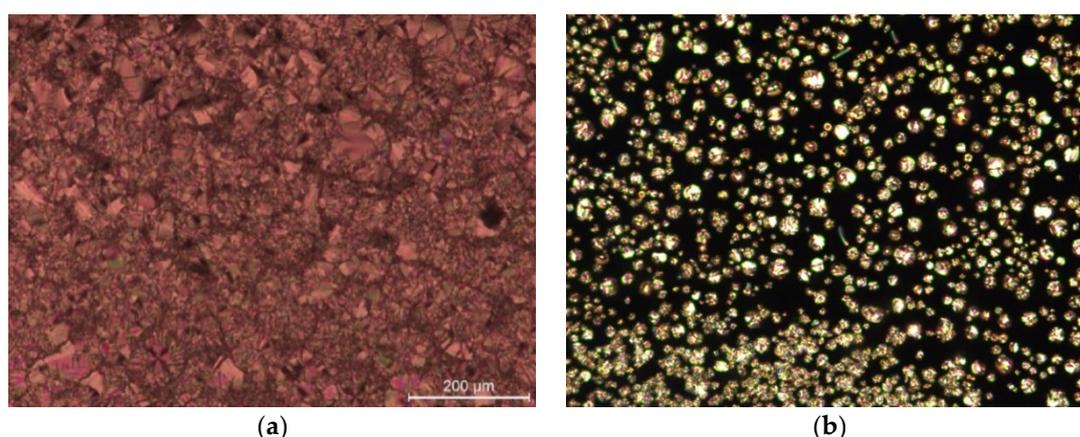


Figure 6. Mesophase textures observed for 10-BPhCOOH under polarized light upon cooling from isotropic liquid. (a) Smectic C mesophase between 170 °C and 249 °C; (b) Nematic mesophase at $T = 249$ °C.

10-BPhCOOH was further characterized by differential scanning calorimetry (DSC) with a Q100 DSC of TA Instruments (TA-Instruments Walters L.L.C., New Castle, DE, USA), performing heating/cooling ramps between 60 °C and 270 °C both at 10 °C/min rate. Other scan rates were not tested because this material is crystalline and hence strong variations in thermal parameters (*i.e.*, temperature and enthalpy of transitions) were not expected. Also thermogravimetric (TG) analyses were carried out with a Setaran Setsys Evolution TGA Thermobalance (SERATAM Instrumentation, Caluire-et-Cuire, Lyon, France) at increasing temperature from 25 °C to 550 °C at 10 °C/min constant rate by using Ar as inert gas at 50 mL/min. Heat capacity measurements were obtained by Temperature-Modulated Differential Scanning Calorimetry method using a DSC Q2000 V24 of TA Instruments (TA-Instruments Walters L.L.C., New Castle, DE, USA) and sapphire as reference. The technical details of the procedure are reported elsewhere [18] and the measurement conditions were as follows. At each single determination, the sample was first stabilized at the desired temperature for 5 min and then all heat inside the probe cell was removed. Afterwards, the sample was subjected to a modulated temperature with 0.5 K amplitude and 80 s angular frequency modulation period, during 45 min.

The dynamic viscosity of 10-BPhCOOH was measured using an Advanced Air Bearing Rheometer from Malvern Instruments Ltd., Malvern, Worcestershire UK, Model: Bohlin Gemini 2. The rheometer allows different sample geometries and integrates an oven for performing measurements up to 300 °C. In our case, the 10-BPhCOOH sample was placed between two stainless steel parallel plates with 40 mm diameter and 1000 μm plate spacing and a shear rate ramp from 0 to 70 s⁻¹ was applied. Measurements were carried out at two different temperatures: 225 °C for obtaining the mesophase viscosity and 270 °C for the isotropic liquid viscosity.

3. Results and Discussion

In order to determine the temperatures of all phase transitions occurring in 10-BPhCOOH together with their corresponding enthalpy values, DSC scans were performed from 60 °C to 270 °C. In Figure 7, the scans of the first and second heating/cooling cycles are displayed. As we can see, this compound has a solid/mesophase transition at around 170 °C with 35 kJ/kg melting enthalpy and a mesophase/isotropic liquid transition at 251 °C with 55 kJ/kg clearing enthalpy. These temperatures are in full agreement with the values reported in the literature (see Figure 4 [14]). In addition, two crystal-to-crystal transitions (at 90 °C and 166 °C) are observed before melting. The one occurring at 90 °C can be seen during both heating and cooling process; however, the one at 166 °C can be clearly observed during heating whereas in the cooling only a very smooth shoulder can be appreciated after freezing. The second DSC cycle reproduces exactly the first one, and this reversibility is a promising indication of thermal stability.

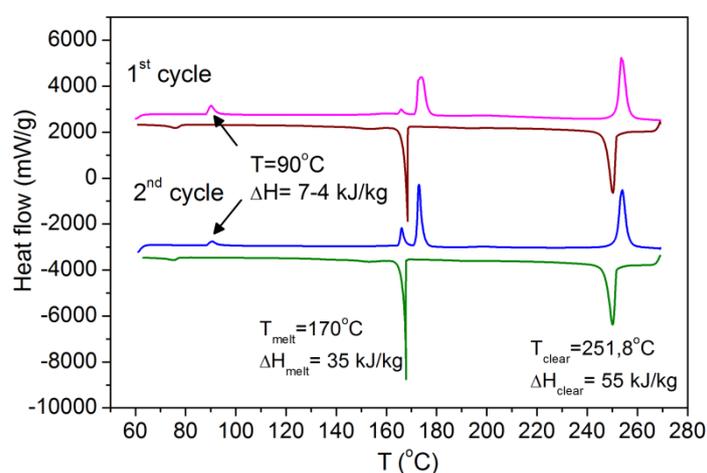


Figure 7. Differential scanning calorimetry (DSC) scans of first and second heating/cooling cycle for 10-BPhCOOH.

In relation to the transition energies, it is worth remarking that the clearing enthalpy is much higher than melting enthalpy (55 kJ/kg *vs.* 35 kJ/kg), which confirms that intermolecular forces in the mesophase are fairly strong as we expected from the involvement of H-bonds [19]. For comparison, the esters from these acids do not exhibit mesomorphic behavior probably due to their inability to form a dimeric molecule via H-bonding [14].

It is also interesting to note that 10-BPhCOOH displays a wide mesophase range (80 °C), which would largely prevent its freezing in case of an eventual temperature decrease due to undesired thermal losses. Therefore, these DSC results confirm the potential of 4'-*n*-alkoxybiphenyl-4-carboxylic acids as liquid phase change materials. In this way it is worth preparing some other derivatives of this family for determining the influence of the alkoxy chain length in the thermal properties.

In order to have an idea of 10-BPhCOOH stability upon thermal cycling, some preliminary studies were carried out with DSC apparatus. For this purpose, up to 11 consecutive heating/cooling cycles were performed between 230 °C and 270 °C, *i.e.*, 20 °C below and above its clearing temperature. From DSC scans, clearing temperatures were recorded and enthalpies were calculated for both heating and cooling processes. The values obtained for each cycle are represented in the graph of Figure 8.

As we can see, clearing temperature remains constant during the cycling for both heating and cooling processes. However, clearing enthalpies tend to decrease with cycling from about 55 kJ/kg in the first cycle to around 50 kJ/kg after 11 cycles. Hence it seems that some degradation takes place in 10-BPhCOOH upon cycling. Such degradation at high temperatures may be due to the decarboxylation from aluminum benzoate formed by reaction of the carboxylic acid with the aluminum pan used in

the DSC study. However, 10-BPhCOOH could also undergo some kind of degradation under the storage system service conditions. Therefore, further long-term thermal cycles under conditions as close as possible to the real working conditions (*i.e.*, furnace cycles in different atmospheres) should be performed to this compound, in order to assess its viability as latent storage material.

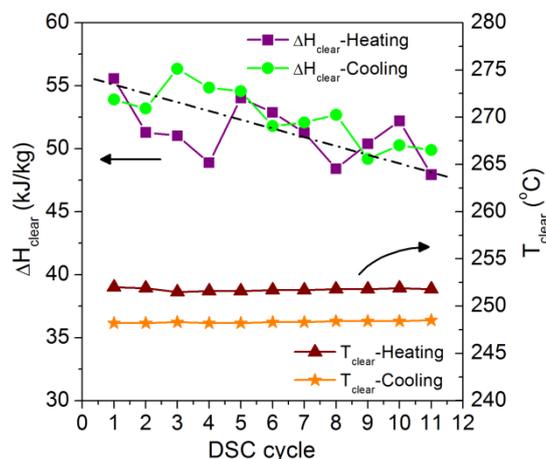


Figure 8. Clearing temperatures and enthalpies obtained for each DSC heating and cooling cycle performed to 10-BPhCOOH.

Heat capacity is another important thermal parameter that should be measured for liquid crystals that are going to be used as PCMs since they could storage also sensible heat in both mesophase and isotropic states. While storing sensible heat in the mesophase state would avoid the need of a preheating storage system, storing sensible heat in the isotropic state would avoid the need of a superheating storage system. Therefore, specific heat capacity (C_p) of 10-BPhCOOH was measured at three different temperatures within the mesophase range. In Table 1, C_p values obtained for each temperature have been recorded. It is clear that C_p slightly increases with temperature but a mean value of 2.4 kJ/kgK can be estimated for the heat capacity in the mesophase range of 10-BPhCOOH.

Table 1. Specific heat capacity (C_p) values for three temperatures of mesophase interval of 10-BPhCOOH.

T (°C)	C_p (kJ/kg K)
180	2.31
200	2.44
220	2.59

For studying the thermal stability of 10-BPhCOOH, thermogravimetric (TG) analysis was performed in a thermobalance by heating it up to 550 °C under Ar and monitoring its mass variation during the process. In Figure 9, the mass variation percentage (left axis) recorded during the experiment together with the corresponding differential curve (dTG in right axis) are displayed.

dTG curve indicates that two main degradation processes take place: one at around 386 °C and another one at around 435 °C. Actually, according to mass variation (left axis), only 1% mass is lost at 290 °C, which indicates that 10-BPhCOOH is expected to be stable under Ar at least up to 40 °C above its clearing temperature (251 °C). However, as we observed for other PCMs [20], TG analyses performed at increasing temperature are not enough for thermal stability assessment and, in our opinion, they should at least be combined with TG studies at different constant temperatures.

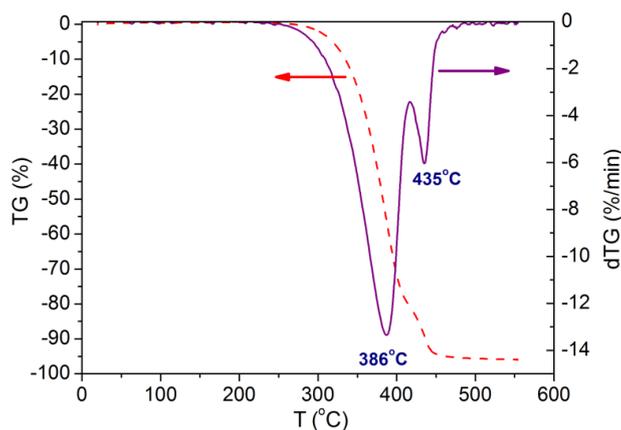


Figure 9. Thermogravimetric (TG) and differential (dTG) curves of 10-BPhCOOH in Ar atmosphere.

Finally, since liquid crystals used as PCMs are meant to move during phase changing, the viscosity values of both mesophase and isotropic states should be a primary concern. Therefore, the viscosity of 10-BPhCOOH was measured with the help of a rheometer using the parallel-plates configuration which requires only a little amount of sample to be deposited between the plates. The whole set-up is located inside an oven so that the experiments can be performed at constant temperature. In our case, dynamic viscosity measurements were carried out at 225 °C and 270 °C, *i.e.*, 26 °C below and 14 °C above the clearing point and hence in both mesophase and isotropic states. In Figure 10, the variation of dynamic viscosity with shear rate is represented for both temperatures. As we can see, 10-BPhCOOH behaves as a pseudo plastic fluid in both mesophase (@ 225 °C) and isotropic state (@ 270 °C). In the first case a constant viscosity of about 0.6 Pas is obtained for shear rates higher than 20 s⁻¹, whereas the isotropic liquid attains 0.18 Pas constant viscosity already at 7 s⁻¹. These values are low enough to allow the liquid crystal pumping inside a conventional circuit.

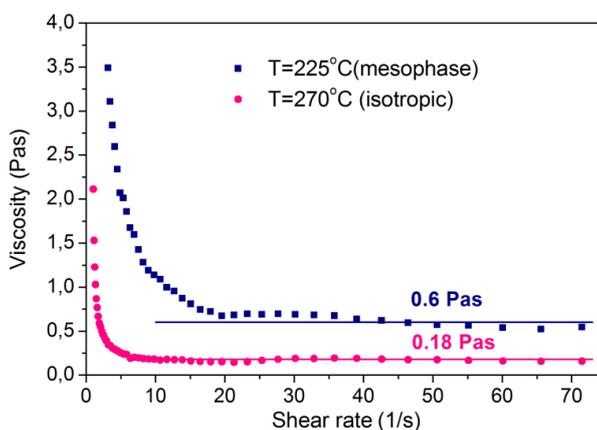


Figure 10. Dynamic viscosity of 10-BPhCOOH for the mesophase (@ 225 °C) and the isotropic state (@ 270 °C).

4. Conclusions

In this paper we propose the use of thermotropic liquid crystals based on aromatic carboxylic acid derivatives with intermolecular H-bonds as phase change materials for latent heat storage. From the data found in the literature, liquid crystals based on alkoxy-derivatives of benzoic, biphenylbenzoic, cinnamic and naphtoic acids seem to be adequate in terms of clearing phase change temperature. In this way, we present the preliminary results of preparation and characterization of 4'-decyloxybiphenyl-4-carboxylic acid. This compound fulfills quite well the requirements

for being used as latent storage medium for applications in which steam is involved. It has a mesophase/isotropic transition temperature in the range of 251 °C, high enough clearing enthalpy (55 kJ/kg), good heat capacity (~2.4 kJ/kg) and low dynamic viscosity (<0.6 Pas). Although more characterization in terms of long-term thermal stability is required, these preliminary results are very promising and further studies on other liquid crystals with carboxylic acid as functional group are underway.

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Author Contributions: Rocío Bayón and Esther Rojas conceived the concept, performed the literature review, designed characterization strategy and coordinated the work between institutions; María Barcenilla, Silverio Coco and Pablo Espinet designed the synthetic route, prepared the liquid crystal and performed some characterization (preliminary DSC measurements, IR spectra, elemental analysis, ¹H NMR and polarized light microscopy); Gorka Imbuluzqueta performed DSC scans and cycles and also TG analysis; Jokín Hidalgo performed viscosity measurements; Rocío Bayón wrote the paper and the rest of authors contributed with corrections and comments.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

PCM	phase change material
LC	liquid crystal
10-BPhCOOH	4'- <i>n</i> -decyloxybiphenyl-4-carboxylic acid
DSC	differential scanning calorimetry
TG	thermogravimetry
dTG	differential thermogravimetry
C _p	specific heat capacity

Appendix A

Unless otherwise stated, all reagents and solvents were obtained from commercial suppliers and used without further purification. Combustion analyses were made with a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded in a Perkin-Elmer Frontier spectrometer coupled to a Pike GladiATR-210 accessory and ¹H NMR spectra on Bruker AV-400 (400.13 MHz) or Varian 500 (499.73 Hz) instruments in CDCl₃.

Preparation of ethyl 4'-decyloxy-4-biphenylcarboxylate. Anhydrous K₂CO₃ (1 g, 7.235 mmol) was added to a solution of ethyl 4'-hydroxy-4-biphenylcarboxylate (0.2 g, 0.826 mmol) and decylbromide (0.185 mL, 0.826 mmol) in 15 ml of dry *N,N*-dimethylformamide. The mixture was heated in an oil bath at 100 °C under N₂ for 24 h. and then was allowed to cool to room temperature. The resulting white solid was filtered off, washed with water (3 × 15 mL) and dried under vacuum (0.225 g, 71% yield). IR: ν(C=O): 1712 cm⁻¹. ¹H NMR (CDCl₃): δ₁ 8.08, δ₂ 7.61, AA'XX' spin system (³J_{1,2} + ⁵J_{1,2} = 8.55 Hz), δ₃ 7.56, δ₄ 6.98, AA'XX' spin system (³J_{3,4} + ⁵J_{3,4} = 8.84 Hz), 4.39 (q, 2H, J = 7.29 Hz, O-CH₂-CH₃), 3.99 (t, 2H, J = 6.39 Hz, O-CH₂-CH₂-), 1.81 (m, 2H, O-CH₂-CH₂-), 1.51–1.28 (m, 17H, alkyl chain and O-CH₂-CH₃), 0.88 (t, 3H, J = 6.39 Hz, -CH₂-CH₂-CH₃).

Preparation of 4'-decyloxy-4-biphenylcarboxylic acid. To a solution of ethyl 4'-decyloxy-4-biphenylcarboxylate (0.2 g, 0.523 mmol) in 15 mL of ethanol was added NaOH (0.2 g, 4.88 mmol) dissolved in 1.5 mL of water. After refluxing for 2 hours, the solution was allowed to cool to room temperature affording the sodium 4'-decyloxy-4-biphenylcarboxylate salt as a white solid, which was filtered off and washed with water (3 × 100 mL). The dried material was then refluxed with glacial acetic acid (20 mL) for 30 min. After cooling the solution to room temperature, the resulting

acid appears as a white precipitate, which was washed with water and dried under vacuum. (0.180 g, 88% yield). IR: $\nu(\text{C}=\text{O})$: 1685 cm^{-1} . ^1H NMR (DMSO- d_6): δ_1 12.97 (s, 1H, OH), δ_2 7.93, δ_3 7.68, AA'XX' spin system ($^3J_{1,2} + ^5J_{1,2} = 8.42$ Hz), δ_4 7.63, δ_5 7.00, AA'XX' spin system ($^3J_{3,4} + ^5J_{3,4} = 8.66$ Hz), 3.98 (t, 2H, $J = 6.52$ Hz, O-CH₂-CH₂-), 1.69–1.22 (m, 20H, alkyl chain), 0.81 (t, 3H, $J = 6.64$ Hz, -CH₃). Anal. Calcd. for C₂₃H₃₀O₃: C, 77.93%; H, 8.53%. Found: C, 77.68%; H, 8.29%.

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