

# Epoxy-Based Organogels for Thermally Reversible Light Scattering Films and Form-Stable Phase Change Materials

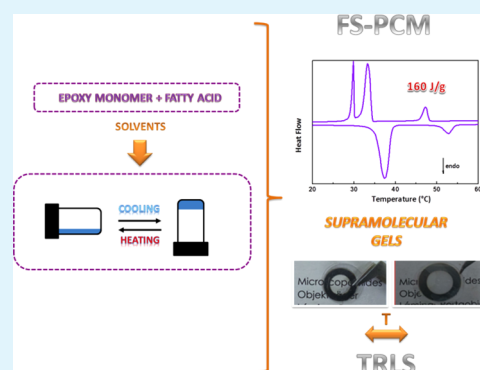
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## Supporting Information

**ABSTRACT:** Alkyl chains of  $\beta$ -hydroxyesters synthesized by the capping of terminal epoxy groups of diglycidylether of bisphenol A (DGEBA) with palmitic (C16), stearic (C18), or behenic (C22) fatty acids self-assemble forming a crystalline phase. Above a particular concentration solutions of these esters in a variety of solvents led to supramolecular (physical) gels below the crystallization temperature of alkyl chains. A form-stable phase change material (FS-PCM) was obtained by blending the ester derived from behenic acid with eicosane. A blend containing 20 wt % ester was stable as a gel up to 53 °C and exhibited a heat storage capacity of 161 J/g, absorbed during the melting of eicosane at 37 °C. Thermally reversible light scattering (TRLS) films were obtained by visible-light photopolymerization of poly(ethylene glycol) dimethacrylate–ester blends (50 wt %) in the gel state at room temperature. The reaction was very fast and not inhibited by oxygen. TRLS films consisted of a cross-linked methacrylic network interpenetrated by the supramolecular network formed by the esters. Above the melting temperature of crystallites formed by alkyl chains, the film was transparent due to the matching between refractive indices of the methacrylic network and the amorphous ester. Below the crystallization temperature, the film was opaque because of light dispersion produced by the organic crystallites uniformly dispersed in the material. Of high significance for application was the fact that the contrast ratio did not depend on heating and cooling rates.

**KEYWORDS:** supramolecular gel, fatty acid, epoxy-acid reaction, form-stable phase change material, thermoreversible light scattering film



## INTRODUCTION

The ability of some low molecular weight organic compounds to form supramolecular (physical) gels in the presence of a variety of solvents has been known and studied for decades.<sup>1–3</sup> These organogelators have the ability to self-assemble into a variety of 3D structures (tapes, fibers, strands, nanotubes, or even nanospheres) that immobilize solvents preventing flow. The origin of this self-assembly lies in specific interactions, such as electrostatic, dipole–dipole, and van der Waals interactions, hydrogen bonding,  $\pi$ – $\pi$  stacking, and metal-to-ligand coordination bonding. The kind of structure is strongly dependent on the gelator structure and is susceptible to changes in temperature, solvent polarity, and aging time, among other variables.<sup>3,4</sup>

The use of organogelators in the generation of new functional materials is the topic of current exciting research due to the new properties and applications that can appear by proper design and selection of the solvent/gelator couple.<sup>4–11</sup> Attractive applications for these molecules and their derived gels have been envisaged, including contaminant removal,<sup>12–14</sup> recognition and catalysis,<sup>15,16</sup> synthesis of tissue scaffolds,<sup>17,18</sup> design of photonically and electronically active soft materials,<sup>6</sup> and creation of surfaces with switchable wettability,<sup>19</sup> among others. Moreover, materials with new properties and enhanced

stability have been obtained by polymerization of the solvent contained in the structure of the physical gel. This approach has already been used to immobilize fibrous structures in acrylic resins,<sup>20</sup> to obtain nanoscale imprinted materials with fibrillary architectures,<sup>21</sup> and for the synthesis of thermochromic films.<sup>22</sup>

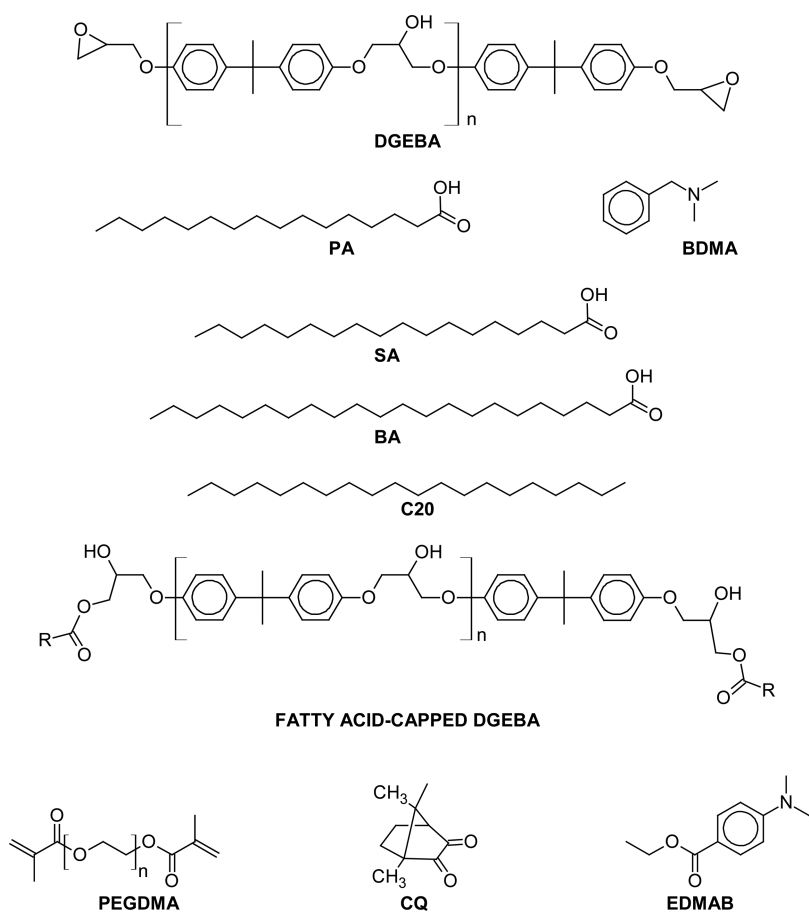
The technological impact of materials based on organogelators strongly depends on the possibility to obtain them through simple, scalable, and economical synthetic routes with low environmental impact. These are aspects of paramount importance in applications requiring considerable scaling up and large mass production, like those related with construction or heat storage.

Recently, the possibility of encapsulating paraffins and other materials with a large latent heat using gelators has been proposed as a way to obtain form-stable phase change materials (FS-PCM).<sup>23</sup> PCMs absorb energy during melting and release energy during crystallization in a way that can be used for storage of thermal energy, e.g., for the increase of the efficiency of energy consumption in buildings<sup>24–26</sup> or for safe transportation of thermo-labile products as vaccines and plasma.<sup>27</sup>

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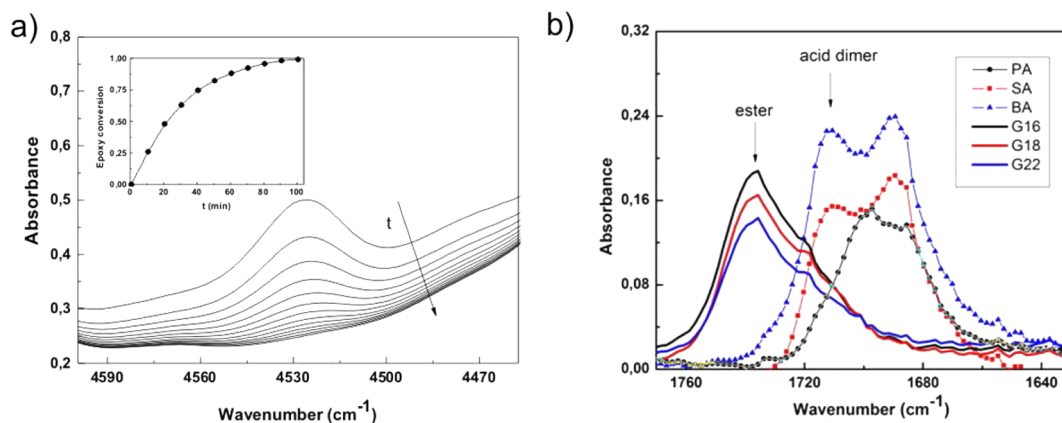
**Figure 1.** Chemical structures of the commercial DGEBA, PA, SA, BA, and BDMA and the synthesized fatty acid-capped DGEBA, C20, PEGDMA, CQ, and EDMAB.

Currently, more than 50 products based on PCMs can be found in the market, most of them using salt hydrates, paraffins, or eutectic salt water solutions.<sup>26</sup> Among them, paraffins have been used in a sustained way probably due to their outstanding properties like availability over a broad temperature range, large heats of fusion, chemical stability, and reliability, among others.<sup>26</sup> Some concerns about the use of paraffins, such as their moderate flammability, have been successfully solved by addition of flame-retardant additives to commercial formulations, especially for applications in building. Concerning transportation applications, various companies have already marketed transportation containers for carrying medicines and food items to field conditions based on the use of low melting temperature PCMs. Inclusion of PCMs in chillers, freezers, and transportable containers is an interesting and promising solution for preservation of biological, food, and other thermo-labile products and to maintain temperatures during power failures, especially in countries with variable climatic conditions, long distances between cities, and energy issues.<sup>27</sup>

For practical applications, PCMs are usually encapsulated or packed in special containers to prevent leakage and agglomeration during fusion. Encapsulation can be avoided by using physically or chemically cross-linked systems with the ability to contain large amounts of the PCM.<sup>28</sup> These systems are called form-stable PCMs (FS-PCMs) because they do not suffer changes in their shape during application. Although there are several ways to obtain form-stable PCMs, most of them are based on the incorporation of PCMs within a solid matrix (polymeric, inorganic, etc.). However, as it is evident from the

results included in the excellent review from M. M. Kenisarina and K. M. Kenisarina,<sup>28</sup> one of the main drawbacks associated with this strategy is the limit in the amount of PCM that can be included in these matrices to be effectively used in thermal storage. Incorporation of PCMs amounts above 70 wt % can be a hard issue involving, usually, the use of processing techniques that require high temperatures and shear forces (twin-screw extrusion), the presence of solvents (casting, electrospinning), or special viscosities and low (vacuum infiltration) or high pressures (compression molding). In this framework, advantages of supramolecular gels are several. First, they form stable solids by simple heating the gelator with the PCM above the sol–gel temperature followed by cooling of the sample up to room temperature. The second one is that the amount of PCM that can be included is much higher than the values normally reported for other form-stable PCMs (incorporation of about 85 wt % of PCM is common, and contents higher than 95 wt % could be easily reached by proper selection of the couple PCM/gelator).<sup>23</sup> Hence, low molecular weight substances with the ability to induce gelation of solvents are an interesting choice to stabilize PCMs provided their formulations present a sol–gel transition above the melting temperature of the PCM.

Substances that produce the sol–gel transition through a crystallization/melting process can also be used in the development of thermally reversible light scattering (TRLS) films. TRLS films are materials that reversibly undergo an opaque/transparent transition by cooling/heating across a specific temperature and can be employed in the design of smart windows.<sup>29–31</sup> They are based on the dispersion of a



**Figure 2.** (a) FT-NIR spectra of a stoichiometric formulation DGEBA + BA showing the decrease of the height of the epoxy band. (Inset) Conversion of epoxy groups vs reaction time for the same formulation. (b) FTIR spectra for the three fatty acids and the three gelators in the 1500–1800 cm<sup>-1</sup> range.

crystalline (or liquid crystalline) phase in a polymeric continuous matrix. Efficiency of scattering in the opaque state is related to the size, concentration, and distribution of crystallites used as dispersive centers. Transmittance in the clear state relies on the matching between refractive indexes of the dispersed phase in the amorphous state and the supporting matrix or on its dissolution in the matrix (above the melting temperature) forming a single phase. Keeping both phases immiscible above the melting temperature is the better option because this avoids a strong dependency of the scattering efficiency of the opaque state on the cooling rate.<sup>32</sup> Properties of crystalline gelators can be exploited in the generation of TRLS films by taking advantage of the high efficiency of their percolated crystalline structure as a light-dispersive medium. A reactive solvent immobilized by this gelator can then be transformed in a polymeric matrix to obtain the film, provided polymerization can be carried out below the sol–gel transition. This strategy could help to face some challenges related with current smart windows technologies, like decreasing costs, prolonging lifetime of operation, and expanding temperature ranges of application (in passive controlled systems). In this sense, the use of easily synthesized gelators to stabilize polymeric precursors that can be then transformed in a permanent network by visible light photopolymerization is a clear step toward the development of cheaper, easily manufactured, and more stable smart windows.

In this study, the properties of a new family of crystalline molecules obtained by capping of terminal epoxy groups of diglycidyl ether of bisphenol A (DGEBA) with different fatty acids are described. Applications of these materials for the synthesis of form-stable PCMs and efficient TRLS films are discussed.

## EXPERIMENTAL SECTION

**Materials.** The diepoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA, DER 332, Dow) with a mass per mole of epoxy groups equal to 174.3 g/mol ( $n = 0.03$  in the chemical structure shown in Figure 1). The selected fatty acids were palmitic acid (PA, 16C, Aldrich, 99% purity), stearic acid (SA, 18C, ≥98.5%, Aldrich), and behenic acid (BA, 22C, Aldrich, 99%). Benzyltrimethylammonium chloride (BDMA, ≥99%, Aldrich) was used as catalyst of the epoxy–acid reaction. Eicosane,  $n$ -C<sub>20</sub>H<sub>42</sub> (C20, Aldrich, 99%), was used to develop phase change materials. The selected methacrylic monomer was poly(ethylene glycol) dimethacrylate (PEGDMA, average  $M_n$  550, Aldrich). Camphorquinone (CQ, Aldrich) and ethyl-4-dimethyl

aminobenzoate (EDMAB, Aldrich) were used for photopolymerization. The chemical structures of the different materials are shown in Figure 1. Food-quality vegetable oils (corn and sunflower oils) were obtained from national brands at local food stores. Tetrahydrofuran and isopropanol were P.A. grade and used as received.

**Synthesis of  $\beta$ -Hydroxyesters (gelators).** Stoichiometric amounts of a fatty acid (2 mol) and DGEBA (1 mol) were mixed at 100 °C until a homogeneous solution was obtained. After cooling to room temperature, BDMA was added (0.06 mol/mol of epoxy groups). Temperature was increased to 90 °C while stirring and the reaction was performed at 90 °C in an oven for 2 h. Products of these reactions will be referred to as gelators and identified as  $G_m$  (where  $m$  is the number of carbon atoms of the fatty acid,  $m = 16, 18,$  and  $22$ ).

Critical gelation concentrations (CGC) were obtained by dissolving different amounts of the  $G_m$  in a number of solvents (isopropanol, corn and sunflower oils, and PEGDMA) using a test tube inversion method. The vial containing adequate amounts of gelator and solvent was heated until a homogeneous solution was obtained and then slowly cooled to room temperature. Values were determined as the lowest concentrations of  $G_m$  required to avoid fluency of the solvent by inversion of the vial containing the solution.

**Synthesis of FS-PCMs.** Blends of G22 and eicosane were weighed in a vial, heated with stirring until a transparent solution was formed, and cooled to room temperature.

**Synthesis of TRLS Films.** A solution formed by PEGDMA and 50 wt %  $G_m$  ( $m = 16, 18,$  or  $22$ ) was heated above the melting temperature until a transparent solution was formed. Then 2 wt % CQ and 2 wt % EDMAB (with respect to PEGDMA) were added, and the mixture was heated again up to the transparent state. Films were obtained by casting the solution immediately between glass covers using a steel spacer of 200  $\mu$ m thickness. The films were irradiated at room temperature with a light-emitting diode (LED) array (irradiance  $I = 600$  mW/cm<sup>2</sup> in the wavelength range 410–530 nm) for consecutive periods of 30 s until complete conversion was attained (2 or 3 irradiation cycles were required).

**Techniques.** Differential scanning calorimetry (DSC, Pyris 1, PerkinElmer and Shimadzu DSC-50) was used to determine parameters related to the melting and crystallization of gelators and FS-PCMs. Dynamic scans were performed at 10 °C/min under nitrogen flow.

Fourier-transformed infrared spectroscopy (FTIR, Nicolet 6700, provided with a heated transmission cell HT-32, Spectra Tech, and a temperature controller CAL 9500P, Spectra Tech) was used to determine the conversion of epoxy groups during the synthesis of gelators and the conversion of methacrylate groups during photopolymerization. The blend of DGEBA and the fatty acid was placed between glass windows using a rubber spacer of 1.4 mm. Kinetics at 90 °C was followed by measuring the height of the absorption band at 4530 cm<sup>-1</sup> (assigned to the conjugated epoxy CH<sub>2</sub> deformation band

with the aromatic CH fundamental stretch) with respect to the height of a reference band at  $4621\text{ cm}^{-1}$  (assigned to a combination band of the aromatic conjugated C=C stretch with aromatic CH fundamental stretch).<sup>33</sup> The conversion in the photopolymerization reaction was determined as follows. The blend of PEGDMA and Gm was coated onto a glass slide and irradiated with the cycle described in the previous section. Spectra were collected at different exposure times, following the height of the absorption band at  $6165\text{ cm}^{-1}$  (first overtone of the =C–H stretching of the methacrylate group).

Gelators were characterized by size exclusion chromatography (SEC) using a Knauer K-501 device provided with a Waters HR 4E column and an RI Knauer K-2301 detector. THF was employed as a carrier at a flow rate of 1 mL/min.

Transmittance measurements of samples polymerized between two glass covers were determined by transmission optical microscopy (TOM) in the wavelength range of visible light. A Leica DMLB optical microscope incorporating a photodetector in its optical path and equipped with a programmable hot stage (Linkam THMS 600) was employed. Optical micrographs of gelled samples were obtained using the same microscope. Scanning electron microscopy (SEM, JEOL JSM-6460LV) was used to determine the morphology of cryogenically fractured samples. Samples were previously coated with a fine layer of Au–Pd.

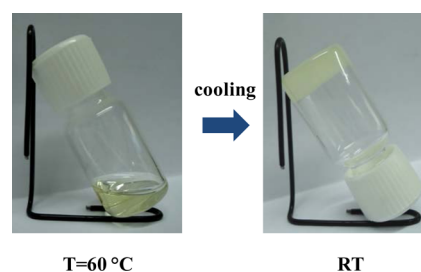
## RESULTS AND DISCUSSION

**Synthesis of  $\beta$ -Hydroxyesters (gelators).** Evolution of the reaction between fatty acids and DGEBA, at  $90\text{ }^\circ\text{C}$ , was followed by FTIR (Figure 2). Conversion of epoxy groups was monitored with the band at  $4530\text{ cm}^{-1}$  (conjugated epoxy  $\text{CH}_2$  deformation band with the aromatic CH fundamental stretch).<sup>33</sup> Complete conversion of epoxy groups was reached after about 100 min (inset in Figure 2a). At the same time, the peak located at  $1710\text{ cm}^{-1}$ , characteristic of a carboxylic acid dimer, showed a significant decrease, whereas the peak of the ester group produced by reaction, located at about  $1736\text{ cm}^{-1}$ ,<sup>34</sup> was generated and increased in height (Figure 2b). The position of strong symmetric (d+) and antisymmetric (d-)  $\text{CH}_2$  stretching bands, with peak maxima at  $2847$  and  $2916\text{ cm}^{-1}$ , was characteristic of an extended all-trans conformation of alkyl chains<sup>35</sup> (Figure S1). This evidence that a fraction of alkyl chains of the gelator is present in a crystalline phase at room temperature.

**Characterization of  $\beta$ -Hydroxyesters.** SEC analysis performed for DGEBA and the three gelators (Figure S2) shows that the main peak corresponds to a DGEBA molecule capped with fatty acids at both extremes.<sup>36</sup> This  $\beta$ -hydroxyester is the main product expected for the stoichiometric reaction between a carboxylic acid and the epoxy monomer under basic catalytic conditions.

Products of the reaction between DGEBA and fatty acids were white, hydrophobic, waxy solids that easily dissolved in solvents like THF or isopropanol when added at low mass concentrations (typically lower than 15 wt %). Further increase in concentration produced gelation by formation of a crystalline network that percolated through the solvent. Gelation was evidenced by immobilization of the solvent and the absence of flow observed when the vial containing the solution was inverted as it is shown for a sample containing 3 wt % of G22 in corn oil (Figure 3).

It is interesting to note that the use of fatty acids presenting alkyl chains of different lengths makes it possible to easily tune the sol–gel transition temperature of solids obtained by mixing the gelator with a solvent. In general terms, for each gelator, the maximum available sol–gel temperature will be given by its melting temperature. Variation of the sol–gel temperatures can



**Figure 3.** Optical photographs showing the gelation process evidenced by the test tube inversion method for a sample with 3 wt % of G22 in corn oil.

be explained by considering the energy involved to form the supramolecular network. A possible explanation for the formation of this network can be found in the self-assembly of the long alkyl chains bonded to the stiff segments of DGEBA. Hydrogen bonding between secondary hydroxyl groups of  $\beta$ -hydroxyesters could also favor formation of this tridimensional structure. It is expected that a higher number of interactions between alkyl groups can occur for longer chains, explaining the highest melting and sol–gel temperature observed for the behenic acid derivative.

TOM images of a solvent (corn oil) gelled by 3 wt % of G22 reveal a clear micrometric structure formed by crystalline domains of the gelator below the sol–gel temperature (Figure S3).

The minimum concentration required to obtain a gel strongly depended on the kind of solvent, varying from 3 to 5 wt % for vegetable oils up to 10–15 wt % for the case of isopropanol or paraffin waxes (Table 1). Although it did not

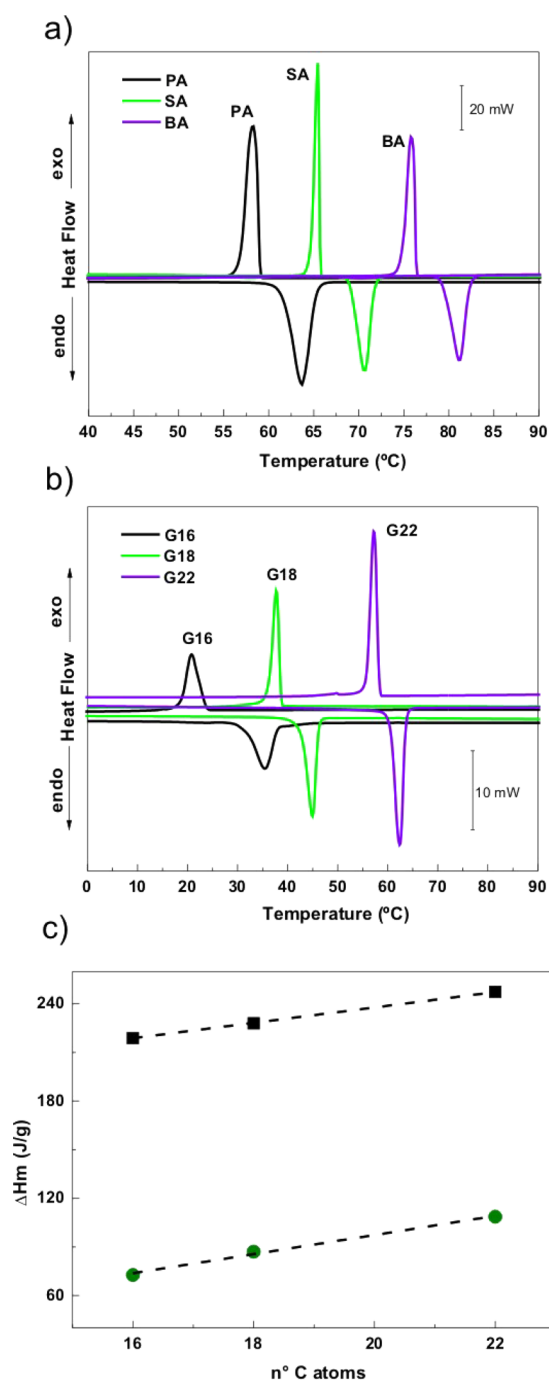
**Table 1.** Minimum Concentrations of Gelator (in wt %) Required for Gelation of Different Solvents at Room Temperature

	isopropanol	PEGDMA	corn oil	sunflower oil	eicosane
G18			4	4	
G22	11	5	3	3	15

constitute a problem for applications considered in this work, it is true that these values are well above what is considered a low gelation concentration for typical, purified organic gelators. This could be attributed to the weaker nature of interactions between  $\beta$ -hydroxyester molecules when compared with other types of molecules and/or to the presence of low contents of additional products that could decrease the purity of the obtained material (e.g., minimal amounts of transesterification products or  $\beta$ -hydroxyesters formed by reaction of fatty acids with low contents of oligomers of DGEBA present in the commercial monomer). Minimum gelation concentrations were lower for longer alkyl chains, which is expected when considering that self-assembly of the tridimensional structure should be favored with a higher number of interactions between alkyl chains.

DSC thermograms of the fatty acids (Figure 4a) and the  $\beta$ -hydroxyesters (Figure 4b) show single melting and crystallization peaks. Thermal transitions of the gelators appeared at lower temperatures than those of the fatty acids. Melting heats were also lower for gelators than for the fatty acids (Figure 4c).

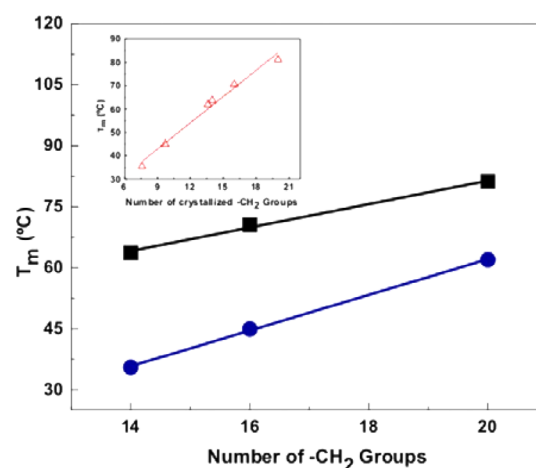
The fraction of crystallized  $\text{CH}_2$  groups in every gelator was also calculated (Table S1). The melting enthalpy of gelators may be expressed per unit mass of  $\text{CH}_2$  groups supplied by the



**Figure 4.** DSC thermograms: (a) melting and crystallization of the fatty acids; (b) melting and crystallization of gelators; (c) enthalpy of melting as a function of the number of carbon atoms for fatty acids (squares) and gelators (circles). Lines serve only to guide the eye.

fatty acid. The resulting values may be compared with the value reported for the heat of fusion of a polyethylene crystal, equal to 293 J/g.<sup>37</sup> About 6 CH<sub>2</sub> groups (presumably those next to the ester group) of every fatty acid chain were not able to take part of crystalline domains. This explains the lower values of both melting enthalpies and temperatures observed for gelators compared with those of fatty acids.

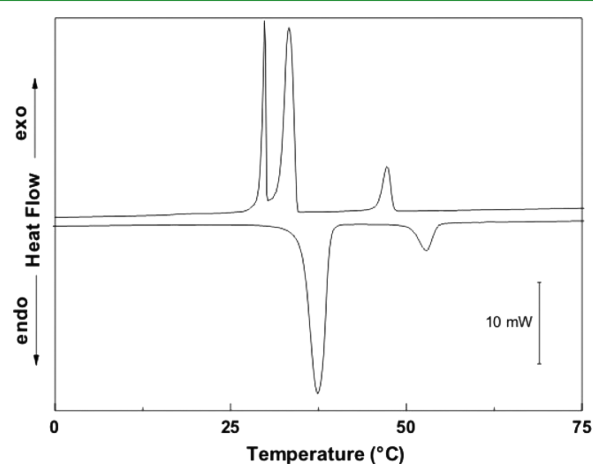
Melting temperatures of fatty acids and gelators as a function of the number of methylene groups (instead of total C atoms) per fatty acid chain are plotted in Figure 5. Melting temperatures varied from 35.5 °C for G16 to 62 °C for G22.



**Figure 5.** Melting temperatures of fatty acids (squares) and gelators (circles) as a function of the total number of -CH<sub>2</sub> groups per fatty acid chain. (Inset) All data merged in the same curve when they are plotted as a function of the number of crystallized -CH<sub>2</sub> groups per fatty acid chain (lines serve only to guide the eye).

Interestingly, when melting temperatures are plotted as a function of crystallized CH<sub>2</sub> groups per fatty acid chain, they merged in the same curve (inset in Figure 5). This simply indicates that melting temperatures depend on the crystal thickness that, in turn, depends on the number of crystallized CH<sub>2</sub> groups.

**G22–Eicosane Blends as Form-Stable Phase Change Materials (FS-PCMs).** Due to its convenient melting point, G22 was useful for the encapsulation of eicosane, a paraffin with a melting temperature of 37 °C that can be used for heat storage near room temperature.<sup>32</sup> The minimum amount of G22 to form a gel with eicosane was 15 wt %. The thermal behavior of a blend with 20 wt % G22 is shown in Figure 6.



**Figure 6.** DSC thermograms obtained during heating (below) and cooling scans (above) for a G22–eicosane blend containing 20 wt % G22.

The peak at high temperature in the cooling scan corresponds to crystallization of G22. The following peak is produced by crystallization of eicosane, and the third peak, at about 30 °C, arises from a solid–solid transition in crystalline eicosane.<sup>38</sup> The heat absorbed during the melting of eicosane, related to the efficiency as a phase change material, was 161 J/g (the evolution of the morphology during heating can be

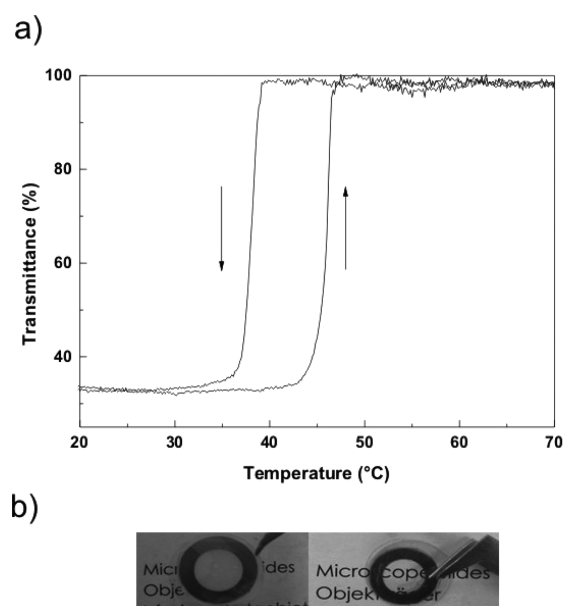
observed in Figure S4). As the melting enthalpy of eicosane is 248 J/g, the expected value for the G22–eicosane blend was  $0.80 \times 248 = 198.4$  J/g. This means that the fraction of crystallized eicosane in the blend was around 81%, a reasonable value considering practical applications as FS-PCM. The curve in Figure 6 also shows the absence of extensive undercooling for this formulation, which is of paramount importance for actual applications.

Vegetable oils have also been considered like a “green” alternative to the use of other organic FS-PCM materials when a low temperature is required. Results found in this work showed that stabilization of vegetable oils as form-stable PCMs is possible for concentrations of gelator as low as 3 wt %. Figure 3 shows a photograph of a sample containing 3 wt % of G22 and 97 wt % of corn oil at room temperature. The sol–gel temperature of this sample was 52 °C as determined by DSC (Figure S5). The melting heat of the oil in the gelled phase reached about 90% of the value determined in its pure form (59 J/g). Although still preliminary, this result showed that the use of this new family of  $\beta$ -hydroxyesters could be expanded to the stabilization of PCMs with applications in a wide temperature range.

**Synthesis of TRLS Films.** Different methacrylic monomers were tested to find a cross-linked polymer with a refractive index similar to that of the melted gelators. This is a necessary condition to attain transparency above the transition temperature of a TRLS. PEGDMA (Figure 1) satisfied this requirement. TRLS films were prepared by dissolving 50 wt % gelator (G16, G18 or G22) in PEGDMA and adding 2 wt % CQ (Figure 1) and 2 wt % EDMAB (Figure 1). Visible light photopolymerization was carried out at room temperature in the gel state. After irradiating for 60 s, complete consumption of dimethacrylate groups (band at  $6165\text{ cm}^{-1}$  in NIR spectra) was confirmed (an example is shown in Figure S6). Interestingly, for the neat PEGDMA monomer the photopolymerization reaction rate was very slow due to the known inhibition by oxygen. The fast rate observed for the blend can be assigned to the oxygen barrier produced by the gelator that encapsulates the monomer. This is important to produce TRLS coatings in an industrial scale. Typical SEM micrographs of photopolymerized samples can be observed in Figures S7 and S8.

The optical transmittance of 200  $\mu\text{m}$  TRLS films was monitored as a function of temperature. As an example, Figure 7a shows heating and cooling cycles for the blend with 50 wt % G18. At high temperature (above 48 °C for the film made with G18), gelator was melted and optical transmittance of the films approached 100% because of the matching between refractive indices of the amorphous gelator and the polymeric matrix. At low temperature (below 37 °C for the film made with G18), the gelator crystallized and transmittance dropped to about 35%. As shown in Figure 7b, at this transmittance value the film can be regarded as opaque for practical purposes. The behavior could be reproduced in several consecutive cycles.

Optical contrast increased with the length of the alkyl chain. Transmittance above melting was higher than 90% for all samples; however, in the opaque state it was 72% for G16, 35% for G18 (as shown in Figure 7a), and 25% for G22. The decrease in opacity for shorter chains could be attributed to both a decrease in the total concentration of the crystalline phase in the film (a lower amount of methylene groups crystallized in gelators obtained with shorter fatty acids) and a change in the size of crystallites of the percolated structure.



**Figure 7.** (a) Optical transmittance as a function of temperature for a 200  $\mu\text{m}$  thick photopolymerized PEGDMA film containing 50 wt % G18, submitted to a heating/cooling cycle at 20 °C/min. (b) Optical images of the TRLS films in the opaque (left) and transparent (right) states.

The influence of heating and cooling rates on the optical contrast and temperature transition of TRLS films was determined for films containing 50 wt % G22. Interestingly, the optical contrast was not affected by the cooling rate (Figure S9), which indicates that the spatial location of the gelator did not change (crystallization occurred from the melted gelator phase and not from a phase formed by the cross-linked methacrylic polymer swollen by the melted gelator). This is a very convenient property for practical applications. Transition temperatures showed a slight variation with cooling and heating rates as expected from a crystallization/melting process.

The polymer network obtained by photopolymerization reached complete conversion after a very short time of irradiation. Once completely cured, the chemically cross-linked structure of this matrix remains stable, explaining its stability and the absence of leakage even after several heating–cooling cycles.

## CONCLUSIONS

Alkyl chains of  $\beta$ -hydroxyesters synthesized by the capping of terminal epoxy groups of diglycidyl ether of bisphenol A (DGEBA) with palmitic (C16), stearic (C18), or behenic (C22) fatty acids self-assemble forming a crystalline phase. Above a particular concentration, solutions of these esters in a variety of solvents led to supramolecular (physical) gels below the crystallization temperature of alkyl chains, i.e., they acted as gelators. This property was used to develop a form-stable phase change material (FS-PCM) and thermally reversible light scattering films (TRLS). A FS-PCM was obtained by blending G22 with eicosane. A blend containing 20 wt % G22 was stable as a gel up to 53 °C and exhibited a heat storage capacity of 161 J/g, absorbed during the melting of eicosane at 37 °C. Thermally reversible light scattering (TRLS) films were obtained by visible light photopolymerization of poly(ethylene glycol) dimethacrylate–gelator blends in the gel stage. The reaction was very fast and took place in air at room

temperature. An interesting result was that oxygen inhibition, observed for the photopolymerization of the neat dimethacrylate, did not occur in the blends due to the oxygen barrier properties of the gelator. TRLS films consisted of a cross-linked methacrylic network interpenetrated by the network formed by the gelator. Above the melting temperature of alkyl chains, the film was transparent due to the matching between refractive indices of the methacrylic network and the amorphous organogelator. Below the crystallization temperature, the film was opaque because of light dispersion produced by organic crystallites. The optical contrast was not affected by the cooling rate, which indicates that the spatial location of the gelator did not change (crystallization occurred from the melted gelator phase and not from a phase formed by the cross-linked methacrylic polymer swollen by the melted gelator). This is a very convenient property for practical applications.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b00086.

FTIR and SEC spectra for the three gelators; optical transmission micrograph of 3 wt % G22 and corn oil; fraction of crystallized and noncrystallized CH<sub>2</sub> groups in every gelator; sequence of optical micrographs during heating of a sample with 20 wt % of G22 and 80 wt % of eicosane; DSC thermogram for a G22-corn oil blend; FT-NIR spectra for a PEGDMA-G22 blend (50 wt % G22); SEM micrographs of G22 and G18/resin samples; optical transmittance as a function of temperature at different heating/cooling rates for a photopolymerized PEGDMA film (50 wt % G22) (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

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