





Vertical Liquid Crystal Alignment of Comb-Like Alkyl Hydroxybenzoate-Substituted Polystyrene

Changha Ju⁺, Shinwoo Kang⁺, Taehyung Kim, Chanhyuk Park and Hyo Kang^{*}

Department of Chemical Engineering, Dong-A University, 37 Nakdong-Daero 550beon-gil, Saha-gu, Busan 49315, Korea; 1771088@donga.ac.kr (C.J.); 1970771@donga.ac.kr (S.K.); xogud1290@donga.ac.kr (T.K.); chan941121@donga.ac.kr (C.P.)

* Correspondence: hkang@dau.ac.kr; Tel.: +82-51-200-7720; Fax: +82-51-200-7728

+ These authors contributed equally to this work.

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Abstract: We investigated the liquid crystal (LC) alignment behaviors of butyl hydroxybenzoate-substituted polystyrene (PBHB#; # = 20, 40, 60, 80, and 100, where # indicates the molar fraction of butyl hydroxybenzoate in the side chain), methyl hydroxybenzoate-substituted polystyrene (PMHB100), and ethyl hydroxybenzoate-substituted polystyrene (PEHB100). Generally, LC cells made employing polymer films having longer alkyl groups in the side chain show vertical LC alignment. For instance, a LC cell fabricated with the PMHB100 film showed random planar LC alignment, while the LC cells made from the PEHB100 and PBHB100 films exhibited vertical LC alignment. Moreover, LC cells prepared from a polymer film having a higher molar content of butyl hydroxybenzoate in the side chain exhibited vertical LC alignment. The observed vertical LC alignment behaviors are closely related to the surface energy of these polymer films. For instance, vertical LC alignment was observed when the surface energy of the alkyl hydroxybenzoate moiety. The LC cell prepared from PBHB100 as the LC alignment layer showed good electro-optical characteristics such as voltage holding ratio, residual DC voltage, and alignment stability at 200 °C.

Keywords: liquid crystal; alignment; vertical; polystyrene; hydroxybenzoate

1. Introduction

Liquid crystals (LCs) are extensively investigated because they have a unique property of showing an intermediate phase with solid- and liquid-like properties [1]. LC molecules are known to have anisotropic physico-chemical characteristics such as optical anisotropy and dielectric anisotropy caused by external stimuli, owing to their special chemical structures [2]. Remarkable progress has been made in a wide range of fields such as information technology [3–5], nanotechnology [6], biotechnology [7], and energy & environment technology [8,9] based on the intriguing physico-chemical characteristics of LCs. For instance, the alignment of LCs has long been an interesting topic in both academia and industry. A technique for aligning LCs in a particular direction on the substrate is considerably important for their various applications [10]. For instance, LC molecules have been extensively used in the display industry, such as in the transmissive mode using nematic LC and in the reflective mode using cholesteric LC, respectively [10]. Because LCs can modify their optical characteristics in response to electrical signals to produce texts and images that one can see, they are a key constituent of displays used in most laptop computers, televisions, and cell phones [11]. One of the LC alignment modes, vertical alignment (VA) mode, can provide outstanding image quality; they can afford a wide viewing angle, minimized light leakage, high contrast ratio, and fast response time [12]. A vertically aligned LC maintains the vertical alignment of the LC molecules well, even when the screen is flexed,

which is also advantageous for curved surfaces [13]. The vertical LC alignment was attributed to steric repulsions between the LC molecules and the polymeric surfaces owing to the incorporation of a nonpolar bulky group in the side chain of the polymer such as in polyhedral oligomeric silsesquioxane, cardanol, and surfactant [14–18]. In order to align the LC molecules, aligning methods such as mechanical rubbing, photoalignment, and ion beam alignment have been mainly investigated in previous studies. The mechanical rubbing of polymeric surfaces is the most widely used technique to achieve consistent alignment of the LC molecules in the production of liquid crystal displays (LCDs) [19–24]. Polyimide derivatives are most commonly employed as LC alignment layers through this rubbing process, since they provide very stable LC alignment [25–33]. Polyimide derivatives with long alkyl or alkyloxy groups, such as semi-flexible copolyimides including *n*-octadecyl side groups and polyimides with (*n*-decyloxy)biphenyloxy side groups, show vertical LC alignment [18,34–36]. Similarly, polystyrene (PS) derivatives with long alkyl or fluoroalkyl chains can also align vertically into LC layers. For instance, LC cells prepared employing a nematic LC and rubbed polymer films of *n*-alkylsulfonylmethyl- and *n*-alkylthiomethyl-substituted polystyrenes consisting of alkyl groups with more than eight carbons showed vertical LC alignment behaviors [37]. Further, LC cells prepared from 4-alkylphenoxymethyl-substituted polystyrenes showed vertical LC alignment behaviors even at a very high rubbing density of 250, irrespective of the length of the alkyl side groups [38].

Therefore, a series of *p*-hydroxybenzoate derivatives, including methyl 4-hydroxybenzoate, ethyl 4-hydroxybenzoate, propyl 4-hydroxybenzoate, and butyl 4-hydroxybenzoate, is used for preserving foods, cosmetics, and pharmaceuticals, because of their bactericidal and fungicidal features [39–43]. The alkyl length can affect the physico-chemical properties of the alkyl hydroxybenzoate used in several applications. For example, alkyl hydroxybenzoate with shorter alkyl groups that have higher solubility in water are widely used to prepare products using aqueous-based reactions [44]. Taking advantage of these properties, they are commonly used in commercial moisturizers [45] and toothpastes [46]. However, the antimicrobial effect of alkyl hydroxybenzoate can decrease with decreasing carbon chain length of the alkyl group in the alkyl hydroxybenzoate. Alkyl hydroxybenzoate can be used to change surfaces of substrates such as metal and glass using hydroxy groups through primary and secondary bonding for various film applications. The length and content of the alkyl group in the polymer side chain can modulate the wetting characteristics of the substrate surface; therefore, the length and content of the alkyl hydroxybenzoate moiety in the polymer was changed [47,48].

In this study, we synthesized alkyl hydroxybenzoate-substituted polystyrenes (PBHB# (# = 20, 40, 60, 80, and 100, where # means the molar fraction of butyl hydroxybenzoate in the side chain), PMHB100, and PEHB100) to obtain a vertical alignment of LCs and to research the effect of the length and molar contents of the alkyl hydroxybenzoate side groups on the LC alignment behavior for the first time. Further, we also studied the optical and electrical properties of the LC cells prepared employing the polymer films.

2. Materials and Methods

2.1. Materials

4-Chloromethylstyrene, butyl hydroxybenzoate, ethyl hydroxybenzoate, methyl hydroxybenzoate, and potassium carbonate were purchased from Aldrich Chemical. Co. and a nematic LC, MLC-6608 ($n_e = 1.5586$, $n_o = 1.4756$, and $\Delta \varepsilon = -4.2$, where n_e , n_o , and $\Delta \varepsilon$ represent the extraordinary refractive index, ordinary refractive index, and dielectric anisotropy, respectively), was obtained from Merck Co. N,N'-Dimethylacetamide (DMAc) and ethanol were used after dehydrating them using molecular sieves (4 Å). Tetrahydrofuran (THF) was dehydrated by refluxing it with benzophenone and sodium followed by distillation. 4-Chloromethylstyrene was purified by column chromatography on a silica gel column using hexane as the eluent to remove any impurities and inhibitors such as *tert*-butylcatechol and nitroparaffin. 2,2'-Azoisobutyronitrile (AIBN, Junsei Chemical Co., Ltd., Tokyo, Japan) used as

an initiator was purified by crystallizing it from its methanol solution. Poly(4-chloromethylstyrene) (PCMS) was prepared through conventional free radical polymerization of 4-chloromethylstyrene using AIBN at 70 °C for 24 h under a nitrogen atmosphere. All other reagents and solvents were used as received.

2.2. Preparation of Alkyl Hydroxybenzoate-Modified Polystyrene

A typical synthesis of alkyl hydroxybenzoate-substituted polystyrenes is presented for PBHB100 as an example. A solution of PCMS (1 g, 6.56 mmol), butyl hydroxybenzoate (1.91 g, 9.83 mmol, ~150 mol% with respect to PCMS), and potassium carbonate (1.631 g, 11.80 mmol, ~200 mol% with respect to PCMS) dissolved in 50 mL of DMAc was magnetically stirred at 70 °C for 24 h under a nitrogen atmosphere. After polymerization, the mixed solution was cooled gradually to room temperature. Then, it was poured into excess amount of methanol to precipitate a white product, which was collected by filtration. The white precipitate was further purified by reprecipitating it several times from DMAc solution using methanol, and then washed with hot methanol to eliminate potassium carbonate and any residual salts. The PBHB100 was obtained in >80% yield after it was dried overnight in vacuum. The degree of substitution of the chloromethyl group with the butyl hydroxybenzoate group was found to be almost 100% within experimental error.

PBHB100 ¹H-NMR (CDCl₃): δ = 0.9–1.6 (10H), 4.2–4.4 (2H), 4.8–5.1 (2H), 6.2–6.9 (4H), 7.0–7.2 (2H) 7.8–7.9 (2H).

Other polystyrene derivatives containing alkyl hydroxybenzoate side groups were synthesized using a procedure similar to that of PBHB100 except that the amount of butyl hydroxybenzoate used in the reaction was varied. For example, PBHB80, PBHB60, PBHB40, and PBHB20 were prepared with 1.01 g (5.21 mmol), 0.76 g (3.92 mmol), 0.50 g (2.59 mmol), and 0.25 g (1.30 mmol) of butyl hydroxybenzoate, respectively; a slight excess of potassium carbonate (1.631 g, 11.81 mmol, 180 mol% with respect to PCMS) was used. Methyl hydroxybenzoate-substituted polystyrene (PEHB100) were synthesized following the same procedure, except that methyl hydroxybenzoate and ethyl hydroxybenzoate, respectively, were used instead of butyl hydroxybenzoate.

2.3. Preparation of Films and LC Cell Assembly

Solutions of PBHB#, PMHB100, and PEHB100 in tetrahydrofuran (1 wt.%) were first prepared and filtered through a poly(tetrafluoroethylene) membrane with a pore size of 0.45 μ m. Then, thin films of the polymers were prepared by spin-coating the solutions on glass slides at 2000 rpm for 60 s. LC cells were prepared using the polymer films cast onto glass slides; they were constructed by assembling the films using spacers with thicknesses of 4.25 μ m. Then, the LC cells were filled with nematic LC, MLC-6608. The manufactured LC cells were finally sealed with epoxy glue.

2.4. Instrumentation

Proton nuclear magnetic resonance (¹H-NMR) spectroscopy was carried out on a Bruker AVANCE spectrometer at 300 MHz. The transmittance of the polymer films on the glass slides was determined by ultraviolet-visible (UV-Vis) spectroscopy (Perkin Elmer Lambda 20 spectrometer, Perkin Elmer, Waltham, MA, USA). The contact angles of distilled water and diiodomethane on the polymer films were measured by a Krüss DSA10 contact angle analyzer equipped with drop shape analysis software. The surface energy was calculated using the Owens-Wendt's equation as,

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^{\ d}\gamma_l^{\ d})^{1/2} - 2(\gamma_s^{\ p}\gamma_l^{\ p})^{1/2} \tag{1}$$

where, γ_{sl} is the interfacial energy of the solid/liquid interface, γ_l is the surface energy of the liquid, and γ_s is the surface energy of the solid; while γ_l^d and γ_l^p are known for the test liquids, γ_s^d and γ_s^p can be calculated from the measured static contact angles [49]. The polarized optical microscopy (POM) images of the LC cell were captured using an optical microscope (ECLIPSE E600 POL, Nikon, Tokyo, Japan) equipped with a polarizer and digital camera (COOLPIX995, Nikon, Tokyo, Japan). The voltage holding ratio (VHR) was determined with a VHR measurement system (VHRM 105, Autronic-Melchers, Karlsruhe, Germany) under the following conditions: data voltage, pulse width, and frame frequency of 1.0 V, 64 μ s, and, 60 Hz, respectively. The measurement temperatures were 25 and 60 °C. The residual DC voltage (R-DC) was assessed by the capacitance-voltage (C-V) hysteresis method using Nissan Chemical Industries, Ltd. (Tokyo, Japan).

3. Results and Discussion

The synthetic routes used for preparing the alkyl hydroxybenzoate-substituted polystyrene derivatives (PMHB100, PEHB100, and PBHB100) and copolymers (PBHB80, PBHB60, PBHB40, and PBHB20) are shown in Figure 1. The copolymers having different substitution ratios (%) were obtained by varying the molar ratio of butyl hydroxybenzoate in the reaction mixture. Almost 100% conversions from chloromethyl to oxymethyl were obtained when 150 mol% of methyl hydroxybenzoate, ethyl hydroxybenzoate, and butyl hydroxybenzoate were reacted with PCMS at 75 °C for 24 h.



Figure 1. Synthetic route to butyl hydroxybenzoate (PBHB#, n = 4) and methyl hydroxybenzoate (PMHB100, n = 1) and ethyl hydroxybenzoate-substituted polystyrene (PEHB100, n = 2), where # represent the molar fraction of butyl hydroxybenzoate containing monomeric units in the polymer.

The chemical structures of the substituted polymers were confirmed by ¹H-NMR spectroscopy. For example, the ¹H-NMR spectrum of PBHB100 indicates the existence of protons from the phenyl ring of the styrene backbone (δ = 7.0–7.2, 7.8–7.9 ppm). Further, the proton peaks from the butyl hydroxybenzoate side chains and polymer backbone (δ = 4.2–4.4, 0.9–1.6 ppm) indicate the inclusion of butyl hydroxybenzoate moieties in the polymer. The content of butyl hydroxybenzoate group could be calculated by comparing the integrated peak intensities of the proton peaks of the butyl hydroxybenzoate (δ = 4.2–4.4 ppm) and chloromethyl side chains (δ = 4.8–5.1 ppm). Similar integrations and calculations for PMHB100, PEHB100, PBHB80, PBHB60, PBHB40, and PBHB20 were performed and the results were generally within ± 10% of the values expected for stoichiometric reactions.

We examined the thermal properties of these polymers using differential scanning calorimetry (DSC). All the polymers were found to be amorphous; only one glass transition was observed in their DSC thermograms (Figure 2). As the number of carbon atoms in the alkyl moiety of the alkyl hydroxybenzoate side group is increased from 1 to 4, the T_g value decreased from 87.1 °C for PMHB100 to 48.3 °C for PBHB100 (Table 1). Moreover, as the molar content of the butyl hydroxybenzoate side group is increased from 20 to 100%, the T_g value decreased from 83.2 °C for PBHB20 to 48.3 °C for

PBHB100. This means that the incorporation of a bulky side group, such as alkyl hydroxybenzoate, can reduce the flexibility of the polymer backbone. A decrease in the T_g value of the polystyrene derivative having increased alkyl chain length and molar content of the alkyl hydroxybenzoate side group has been reported owing to the increase in the free volume of the polymer; polymers with larger free volumes have lower T_g values [50].



Figure 2. DSC (Differential scanning calorimetry) thermogram of PBHB# (PBHB20, PBHB40, PBHB60, PBHB80, and PBHB100) and PMHB100 and PEHB100.

Table 1. Reaction conditions and results for the synthesis of the PCMS and PBHB# and PMHB100and PEHB100.

Polymer Designation	Alkyl hydroxybenzoate (mol%)	Degree of Substitution (%)	T_{g}
PCMS	-	-	106
PBHB20	20	20	83.2
PBHB40	40	40	79.9
PBHB60	60	60	58.7
PBHB80	80	80	55.7
PBHB100	150	100	48.3
PMHB100	150	100	87.1
PEHB100	150	100	70.3

To investigate the possibility of using the prepared polymers in surface coating applications, quantitative analysis of the transparency of PBHB#, PMHB100, and PEHB100 films was carried out using UV-Vis spectroscopy (Figure 3). The transmittance of the glass slides coated with PBHB#, PMHB100, and PEHB100 films was found to be in the range of 98.4–99.6% at 550 nm; this transmittance is higher than that (86.3%) of the commonly used polyimide (PI) film, which has some problems of connatural yellowish coloration associated with the conjugation of di-imide fragments in the LC alignment layer [51–53]. This result suggests that the optical transparencies of the PBHB#, PMHB100, and PEHB100 films in the visible light region are sufficient for their use as optical materials in display devices.

Figure 4 shows the photographs of the LC cells made from the alkyl hydroxybenzoate-substituted polystyrenes (PBHB#, PMHB100, and PEHB100). Initially, a random planar LC alignment was observed for the LC cells based on the PMHB100 films, while the LC cells made from the PEHB100 and PBHB100 films exhibited vertical LC alignment behavior. The LC cells prepared from the PBHB# films made

of polymers with less than ~20 mol% butyl hydroxybenzoate side group (PBHB20) partially showed LC textures with birefringence, while good uniformity of the vertical LC alignment was observed for the LC cells prepared from polymer films made of polymers with greater than ~40 mol% butyl hydroxybenzoate side group (PBHB40, PBHB60, PBHB80, and PBHB100) in the whole area in the photographs. All the PBHB40, PBHB60, PBHB80, and PBHB100 films were able to produce stable vertically aligned LC layers and the vertical LC alignment was maintained for at least more than one year since the preparation of the LC cells. Therefore, as the alkyl chain length and molar fraction of the alkyl hydroxybenzoate side groups increase, the vertical LC alignment capability of the LC cell increases.



Figure 3. UV-Vis transmittance spectra of PBHB# and PMHB100 and PEHB100 and polyimide alignment layers onto quartz substrates.



Figure 4. Photograph images of the LC cells fabricated with PBHB# and PMHB100 and PEHB100 films.

The LC alignment behaviors of the LC cells fabricated with the alkyl hydroxybenzoate-substituted polystyrenes (PBHB#, PMHB100, and PEHB100) films were investigated by observing their POM images (Figure 5). On one hand, the LC cells prepared from the PMHB100 film showed random planar LC alignment with birefringence in the conoscopic images. On the other hand, the LC cells fabricated with the PEHB100 and PBHB100 films exhibited vertical LC alignment. When the molar fraction of the butyl hydroxybenzoate containing monomeric unit in the PBHB# was less than 20%, the LC cells prepared from the PBHB# film showed random planar LC alignment with birefringence in conoscopic

images. In contrast, PBHB40, PBHB60, PBHB80, and PBHB100 films were able to provide stable vertically aligned LC layers. The distinguishable difference between the LC orientations on PBHB# films with vertical LC aligning ability according to the molar fraction of the butyl hydroxybenzoate in the side groups cannot be observed through Maltese cross pattern in the conoscopic POM images. Based on the results obtained for the LC alignment behavior, we found a universal trend that the polymers having longer alkyl groups and higher molar contents of the alkyl hydroxybenzoate in the side groups have preference for vertical LC alignment.



Figure 5. POM images of the LC cells made from PBHB# (PBHB20, PBHB40, PBHB60, PBHB80, and PBHB100) and PMHB100 and PEHB100 films.

The surface energies of polymer films such as PMHB, PEHB, and PBHB# are shown in Figure 6 and Table 2; the values are based on the static contact angles of water and diiodomethane. The total surface energy was calculated using the Owens-Wendt's equation, and the value is a summation of the polar and dispersion components. The vertical LC alignment was observed for the PEHB100, PBHB40, PBHB60, PBHB80, and PBHB100 films. The total surface energies of these polymers are 43.86, 43.99, 42.83, 39.55, and 33.99 mJ/m², whereas the other polymers with total surface energies larger than ~45.82 mJ/m² (for example, PBHB20 (45.82 mJ/m²) and PMHB100 (46.45 mJ/m²)) did not show vertical LC alignment behavior. Therefore, the vertical LC alignment behavior correlates well with the total surface energy of the polymer with a value smaller than ~43.86 mJ/m² (critical surface energy of the polymer films to induce vertical LC alignment).

Table 2. Surface energy values and LC (liquid crystal) alignment properties of the polymers.

Polymer Designation —	Contact Angle (°) ^a		Surface Energy (mJ/m ²) ^b			
	Water	Diiodomethane	Polar	Dispersion	Total	LC Aligning Ability
PCMS	70.9	35.4	8.83	36.86	45.69	х
PBHB20	84.6	26.4	2.26	43.56	45.82	х
PBHB40	87.6	30.7	1.70	42.29	43.99	0
PBHB60	89.2	33.3	1.46	41.37	42.83	0
PBHB80	91.0	40.2	1.45	38.10	39.55	0
PBHB100	93.0	50.8	1.76	32.23	33.99	0
PMHB100	76.0	28.7	5.55	40.90	46.45	х
PEHB100	79.6	33.6	4.51	39.35	43.86	0

^a Measured from static contact angles. ^b Calculated from Owens-Wendt's equation. ^c Circle (O) and cross (X) indicate polymer film have vertical and planar LC aligning ability, respectively.



Figure 6. (a) Water, (c) diiodomethane contact angle, and (e) surface energy of polymer films according to the molar content of the butyl hydroxybenzoate moiety in the side groups and (b) water, (d) diiodomethane contact angle, and (f) surface energy of polymer films according to the number of carbons in the alkyl benzoate side chains.

The reliability of the LC cells made from the polymer films was investigated by analyzing the stability of the LC alignment under severe conditions such as high temperatures and ultraviolet (UV) energies. To evaluate the thermal and UV stability, an LC cell made from the PBHB100 film was heated for 10 min at 100, 150, and 200 °C, and then supplied with UV energy at 5, 10, and 15 J/cm². Subsequently, POM images of the cell were obtained. As shown in Figure 7, the vertical LC alignment capability of the PBHB100 LC cell was preserved even when heated at a high temperature and supplied with UV energy, indicating no difference in the LC alignment as determined by the Maltese cross pattern in the conoscopic images. The electro-optical (E-O) performance of the LC cell prepared from the

PBHB100 film was evaluated for its possible practical LC display application. The LC cell exhibited a voltage holding ratio (VHR) above 99% at 25 °C and this value was maintained at 60 °C. It is sufficiently high for its pragmatic application as an LC alignment layer in a thin film transistor addressed LCD [16]. The residual DC voltage (R-DC) of the LC cell measured using the capacitance-voltage (C-V) hysteresis method was found to be very low at less than 10 mV, which is even smaller than those of commercial polyimides [16]. The outstanding thermal stability, VHR, and R-DC of the LC cell prepared from PBHB100 film can be attributed to the connatural property of the hydrocarbonated polymer, such as its good thermal stability and low dielectric constant.



Figure 7. Conoscopic POM images of the LC cells made PBHB# films, after thermal treatment at 100, 150, and 200 °C for 10 min and UV treatment at 5, 10, and 15 J/cm², respectively.

Considerable effort is required to develop plastic substrates for flexible LC displays. All the LC cells prepared from the PBHB# films on polyethylene terephthalate (PET) substrates exhibited LC alignment behaviors comparable to those observed with the LC cells made from the same polymer films on glass substrates (as shown in Figures 5 and 8). We found that the LC cells prepared from the polymer films having a monomeric unit larger than ~40 mol% (PBHB40, PBHB60, PBHB80, and PBHB100) on PET substrates also showed vertical LC alignment behaviors. Therefore, the LC cells fabricated from PBHB40, PBHB60, PBHB80, and PBHB100 films can be considered to be good candidates for application as LC alignment layers in flexible LC displays.



Figure 8. Conoscopic POM images of the LC cells made from PBHB# films on polyethylene terephthalate substrates according to the molar content of alkyl benzoate moiety ((**a**) PBHB20, (**b**) PBHB40, (**c**) PBHB60, (**d**) PBHB80, and (**e**) PBHB100).

4. Conclusions

A series of butyl hydroxybenzoate-substituted polystyrene (PBHB#), and methyl hydroxybenzoate-substituted polystyrene (PEHB100) were synthesized to evaluate the liquid crystal (LC) alignment behaviors of their films. The vertical LC alignment behavior was observed for LC cells made from polymers having longer alkyl chains and higher molar contents of the alkyl hydroxybenzoate side groups. For example, LC cells prepared from polymer films having greater than ~40 mol% of butyl hydroxybenzoate (PBHB40, PBHB60, PBHB80, and PBHB100) showed vertical LC alignment, while the LC cells prepared from PBHB# films having smaller than 20 mol% of butyl hydroxybenzoate exhibited random planar LC alignment. The series of alkyl hydroxybenzoate-substituted polystyrene films exhibited outstanding optical transparency in the visible light region (400–700 nm). For instance, the transmittance (98.4–99.6%) of the PBHB#, PMHB100, and PEHB100 films coated on glass slides at 550 nm is superior to that (86.3%) of the polyimide film, the most frequently used LC alignment layer. The vertical LC alignment behavior correlated well with the total surface energy of the polymer with a value smaller than ~43.86 mJ/m² which is due to the long alkyl groups in the alkyl hydroxybenzoate moiety.

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