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The decomposition process and kinetic analysis of benzene-based liquid crystal in hydrothermal system

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HIGHLIGHTS

- Hydrothermal method can effectively decompose EMOPE into innocuous products.
- Reaction kinetic of EMOPE under optimized conditions is studied.
- Two possible decomposition processes of EMOPE are proposed.
- The mixture of EMOPE and OCBPh can be hydrothermally treated together sufficiently.

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ABSTRACT

Liquid crystal, while being a core component in liquid crystal displays, also has potential harmful effects on ecosystems and human health, especially when it is not treated properly. In this study, a hydrothermal process is proposed to dispose liquid crystal of 1-ethyl-4-[(4-methoxyphenyl)ethynyl]benzene (EMOPE) and mixed liquid crystal of EMOPE and 4-octoxy-4′-cyanobiphenyl (OCBPh). The effect of reaction time, reaction temperature, oxidant addition and solid-to-liquid ratio on decomposition ratio is evaluated. Products from hydrothermal decomposition of EMOPE are characterized, and two possible hydrothermal decomposition pathways are proposed. To get complete decomposition of 4 mg of EMOPE, the conditions required are: 0.3 mL of H_2O_2 addition, 3.5 mL of water supply, 275 °C and 5 min. The decomposition kinetic analysis of EMOPE indicates that its decomposition process fits the apparent first-order reaction model. For the mixture's decomposition, given conditions of 275 °C, reaction time of 6 min, 3.5 mL of water supply, and 1.5 time of oxidant addition, the decomposition ratio of OCBPh reaches to 99.75%, and EMOPE can be completely decomposed.

1. Introduction

Liquid Crystal Displays (LCDs) are more and more popular and renowned for their excellent properties, such as space-saving, low power consumption, soft rendering, and so on [1]. The global output of LCDs in 2016 is estimated to be around 255 million units and LCD panel is the main form of visual display technology [2,3]. On average, the lifespan of a LCD is approximately 3–5 years in notebooks and 8–10 years in TVs [4]. Besides, products updating is shortening the lifespan of LCD devices, thus contributing even more to the huge generation of waste LCDs.

The core component of LCD is liquid crystal which is pressed between the two glass substrates of LCD panel. In general, liquid crystal in LCD devices is the mixture of 10 to 25 different kinds of liquid crystal compounds [5,6]. These compounds are mostly aromatic-based polymers which are non-biodegradable and bio-accumulative thus necessitating for proper treatment [7–9]. In the conventional disposal, liquid crystal and other organic parts in waste LCD panel are incinerated together [8,10,11]. However, in these processes, considerable emissions of undesirable air pollutants have been monitored, such as polycyclic aromatic hydrocarbons (PAHs) [12] which are in the American EPA list of priority pollutants [13]. Therefore alternative options for proper disposal of waste liquid crystal are an urgent need in order to cope with the removal of these pollutants.

Hydrothermal degradation method has been effectively adopted for hazardous waste [14–16] and organic waste [17,18] treatment using water as reaction medium at elevated temperature and pressure, as well as hazardous waste disposal. For example, the radioactivity and toxicity of radioactive ion exchange

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Nomenclature

EMOPE	1-ethyl-4-[(4-methoxyphenyl)ethynyl]benzene	2MP2MB	2-Methylphenyl 2-methoxybenzoate
OCBPh	4-octoxy-4′-cyanobiphenyl	4MP	4′-Methoxypropiophenone
TPE	1-[4-(2-p-Tolylvinyl)phenyl]ethanone	DMBn	4,4′-Dimethoxybenzil
4EP4MB	4-Ethylphenyl 4-methoxybenzoate	MPPED	1-(4-Methoxyphenyl)-2-phenyl-1,2-ethanedione
DP4EB	3,5-Dimethylphenyl 4-ethylbenzoate	EMB	Ethyl 4-methoxybenzoate

resins can be effectively eliminated through hydrothermal process [19], and it is also reported as an efficient way to treat and recover brominated wastes [20,21]. Under hydrothermal conditions, these organic materials can be chemically converted to non-toxic products by the superheated water, which is known by several reaction steps, including direct hydrothermal liquefaction and hydrous pyrolysis [22].

In view of its excellent properties and successful applications, hydrothermal method can be applied to treat liquid crystal. There are two important kinds of liquid crystal widely used in today's market: the twisted nematic liquid crystal and super twisted nematic liquid crystal [23]. In a previous study led by our research group, it has been proven that the typical twisted nematic liquid crystal of OCBPh can be effectively decomposed by hydrothermal method and the decomposition pathway was analyzed [6]. However, there is still some work that needs to be done on the decomposition of super twisted nematic liquid crystal and especially on the decomposition of a mixture of these two kinds of liquid crystal, as it is common case to dispose together different kinds of waste LCDs. Therefore, this study focuses on hydrothermal decomposition of one typical super twisted nematic liquid crystal of EMOPE, also known as para ethyl methoxyl diphenylacetylene, which is widely applied in LCDs. Laboratory experiments are conducted to evaluate the effect of different reaction factors on decomposition ratio with the aim to optimize operating conditions for hydrothermal decomposition of EMOPE. Moving forward, the decomposition kinetic of EMOPE under optimized conditions is analyzed on the basis of experimental results. Products from EMOPE decomposition are characterized to propose two different decomposition pathways. At last, the decomposition of EMOPE and OCBPh mixture is investigated to give proper operation parameters for their joint treatment.

2. Materials and methods

2.1. Materials and chemicals

Liquid crystal of EMOPE and OCBPh were purchased from Hebei Maison Chemical Co., Ltd and their properties are shown in Table 1. Hydrogen peroxide solution (30% of H_2O_2) was purchased from Sino-pharm Chemical Reagent Co., Ltd (Shanghai, China). Chromatographically pure acetonitrile from Fisher Scientific is used for HPLC analysis. Water used in this study is deionized.

2.2. Experimental apparatus and procedures

In order to get instant and uniform heating, a cylindrical reactor with wall thickness of 1 mm is used throughout the experiments. This tubular reactor is made of a piece of stainless steel 316 tubing and two ends fitting (Swagelok), providing an inner volume of 5.7 mL. A salt bath is used for heating the reactor. The batch reactor is rinsed with ethanol and water before performing experiment. 4 mg of liquid crystal is used in the whole study. The reactor is submerged into the salt bath which is preheated to the desired temperature. When the reaction is over, it is taken out of the salt bath and immediately put into a cold-water bath to quench the reaction. Reaction time is defined as the duration for which the reactor is submerged in the salt bath. In order to get precise data, each reaction is repeated for three times, and all reported quantitative data are averages of analytical results from three samples. The whole experimental process is shown in Fig. S1 in Supplemental file.

2.3. Analytical methods

Thermo-gravimetric analysis (TGA, Q60, TA, US) is used to analyze raw materials. Gas Chromatography Mass Spectrometry (GC–MS, QP 2010, Shimadzu, Japan) is used to characterize liquid products. High Performance Liquid Chromatography (HPLC, e2695, Waters) is used to quantify EMOPE and OCBPh in liquid samples.

The decomposition ratio of liquid crystal in this study is defined as the ratio of decomposed amount in water to its initial quantity (Eq. (1)).

$$\eta(\text{wt.\%}) = \frac{m_0 - m_t}{m_0} \times 100\% \quad (1)$$

where η is decomposition ratio. m_0 is the quantity of liquid crystal compound before hydrothermal treatment (mg) and m_t is the remaining quantity in liquid sample after treatment.

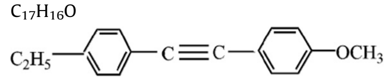
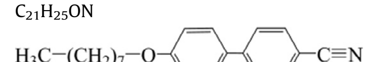
3. Results and discussion

3.1. Investigation of different reaction factors

3.1.1. Effect of reaction temperature and time on EMOPE decomposition

The thermal-gravimetric analysis shows that EMOPE is thermally instable from the temperature of 150 °C and the mass loss

Table 1
Chemical and physical properties of EMOPE and OCBPh.

Liquid crystal compounds	EMOPE	OCBPh
Molecular formula	$C_{17}H_{16}O$	$C_{21}H_{25}ON$
Chemical structure		
Average mass	236.31	307.43
Melting point	74 °C	51–77 °C