Journal of Photochemistry and Photobiology A: Chemistry 278 (2014) 19–24

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Thermal and photo reversible gel–sol transition of azobenzene based liquid crystalline organogel

Subramanian Balamurugan[a], Guan-Yeow Yeap[a,*], Wan Ahmad Kamil Mahmood[a], Pi-Lin Tan[b], Kuan-Yew Cheong[b]

[a] Liquid Crystal Research Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
[b] School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:
Received 7 September 2013
Received in revised form
24 November 2013
Accepted 16 December 2013
Available online 7 January 2014

Keywords:
Liquid crystal
Nematic phase
Homeotropic alignment
Organogel
Azobenzene

ABSTRACT

Azobenzene based photoresponsive gelator, 1,2-bis[4-(4-(10-decyloxy)phenylazo)]-benzoylhydrazine showing selective gelation in alcoholic solvent is described. Whilst their thermodynamic behaviors are investigated by polarized optical microscopy and differential scanning calorimetry, the related layer arrangement is measured by X-ray diffraction techniques in which the organogel shows monotropic liquid crystalline phase. Present work shows that the non-liquid crystalline gelator can be converted into liquid crystalline organogel in the presence of alcoholic solvent in which the *trans-cis* isomerization of the azobenzene moiety disrupts the entanglement of gel fibers of self-assembly resulting in gel–sol transition. The present result also shows that the organogel is capable of the thermal and photo induced transition from gel–sol and vice versa.

1. Introduction

The design and self-assembly of low molar mass component into supramolecular aggregation have been one of the main areas of research in supramolecular chemistry [1–4]. Intermolecular non-covalent interactions such as H-bonding, Van der Waals, π–π stacking, solvophobic effect, charge-transfer and metal–ligand coordination are the driving forces responsible for supramolecular assembly. Among these the hydrogen bonding (H-bonding) is considered as an ultimate non-covalent interaction to construct supramolecular architecture since it is highly selective and directional oriented [5–8]. Besides, the inter and intra-molecular H-bonding play a vital role in synthetic [9], biological [10,11] and material chemistry [12]. It has been claimed as one of the key factors toward the formation of organogel. Low molecular weight organogelators (LMOGs) are growing interest in the area of academic research owing to their potential uses as templates for material synthesis [13,14], drug delivery cosmetics [15], separations [16], sensors [17–20] and biomimetics [21]. Moreover, the gel retains the anisotropic nature of the liquid crystal (LC) property.

Organogels have been considered as a new class of dynamic functional materials since they are macroscopically soft solids and display improved electro-optical, photo-driven and electronic properties [22–25]. Recently, many reports on the organic gelators with various derivatives of urea [26–29] and peptides [30–32] have been documented. Among them chromophore based gelators have received more attentions as the thermal reversible property accompanied by interesting spectral variation can be observed in the corresponding gel–sol phase transition [33–35].

In the present work, we report the H-bonding induced self-assembly of a photo switchable azobenzene based liquid crystalline organogel. In the course of study the mesomorphic properties of non-liquid crystalline behavior of the gelator was converted into liquid crystalline gel in the presence of alcoholic solvents. The driving force for molecular aggregation has been attributed to the H-bonding of molecule. It is also understood that the target organogel is capable of undergoing thermal and photo reversible transition from gel–sol and viz. *versa*. Under UV irradiation, photoisomerization of azobenzene (*trans-cis* isomer) disrupts the molecular aggregation between the molecules leading to gel–sol transitions of the system.

2. Experimental

2.1. Materials and methods

The chemicals were obtained from Sigma Aldrich Chemicals (St. Louis, MO, USA) and Merck (Darmstadt, Germany). All the solvents

---

* Corresponding author. Fax: +60 4 6534075.
E-mail address: gyyeap@usm.my (G.-Y. Yeap).

1010-6030/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jphotochem.2013.12.013

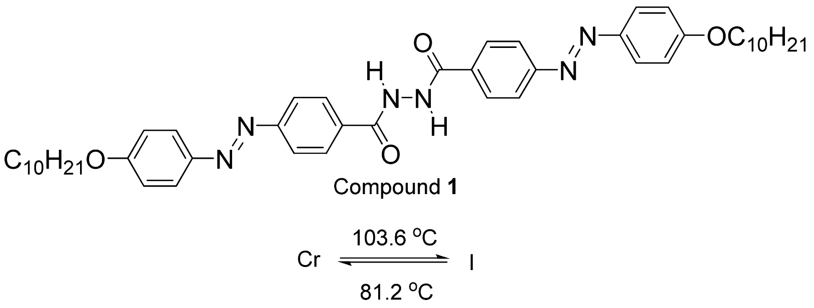

Fig. 1. Molecular structure of 1,2-bis[4-(4-(10-decyloxy)phenylazo)]benzoylhydrazine (**1**).

were purified and dried by standard methods and the crude samples were purified by column chromatographic technique using silica gel (230–400 mesh) as a stationary phase. Thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel (Merch, Kieselgel 60, F254). The infrared (IR) spectra for all compounds were recorded in the range 4000–400 cm^{-1} using a Perkin Elmer 2000 FTIR spectrophotometer with the samples embedded in KBr discs. The ^{1}H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz Ultra-Shield spectrometer. $CDCl_3$ and DMSO-d_6 were used as solvents and TMS as the internal standard. CHN microanalyses were carried out on a Perkin Elmer 2400 LS Series CHNS/O Analyzer. The liquid crystalline textures were observed under a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Linkam TMS94 temperature controller and a LTS350 hot stage. The transition temperatures and enthalpy changes were measured by a differential scanning calorimeter TA Q200 at a rate of 5 °C min^{-1} for both heating and cooling.

3. Results and discussion

The target compound 1,2-bis[4-(4-(10-decyloxy)phenylazo)] benzoylhydrazine (**1**) was synthesized as reported in our earlier publication [36]. Compound **1** (Fig. 1) was soluble in polar solvents such as acetone, acetonitrile, dioxane, EtOAc, THF, $CHCl_3$, CH_2Cl_2, THF and DMSO. It forms gels in most of the alcoholic solvents except isopropanol.

For preliminary study a weighted amount of gelator and a measured volume of selected pure organic solvent were placed in a sealed glass bottle and the solution was heated until the solid was dissolved. The solution was allowed to stand at room temperature, and the state of the mixture was evaluated by the 'stable to inversion of a test tube' method [30]. The low critical gelation concentration (CGC) of the gelator was summarized in Table 1[1] wherein the CGC concentration was observed as 10 mM in 1-propanol. The result thus obtained indicates that the intermolecular H-bonding between —NH and —C=O in compound **1** facilitates the gelation.

The phase transition behavior of the compound **1** and its gel were investigated by polarizing microscopy, DSC and XRD studies. The transition temperatures were obtained from DSC measurements of the second heating and cooling cycles at a rate of ±5 °C min^{-1}. Sandwich type clean glass slides were employed to identify the mesophase. The compound **1** possesses a sharp melting at 104.7 °C corresponding to crystal to isotropic melting. It does not show other transition on heating and cooling processes hence it fails to form mesophase (Fig. 2). The H-bonding increases the intermolecular interaction between the layers which have contributed to the increase in the rigidity (Fig. S1). The DSC thermogram has also suggested the monotropic liquid crystalline behavior of organogel (Fig. 3). On heating it shows one broad exotherm at 83 °C while on cooling it exhibits three transition peaks. To identify the mesophase, the gel is placed in between two glass slides. Microscopy observation revealed that the gel possesses crystalline to isotropic transition on heating run. However, on cooling the birefringence was observed from the isotropic liquid wherein the homogeneous alignment of nematic phase was first developed at 83 °C (Fig. 4a). Further cooling has led to

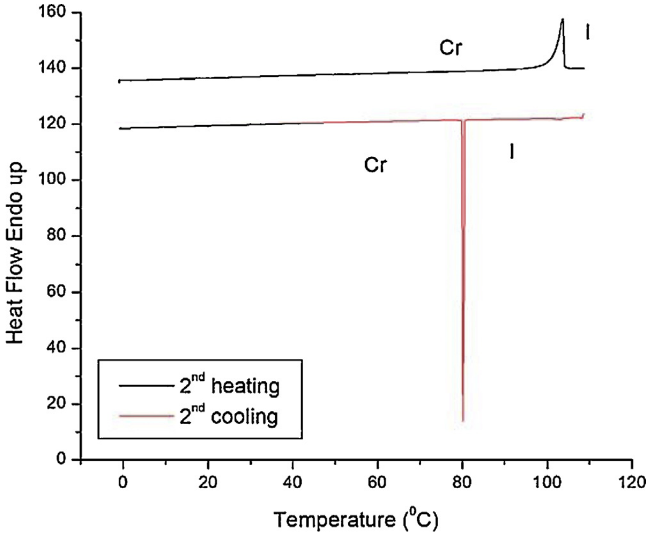

Fig. 2. DSC thermogram of compound **1**.

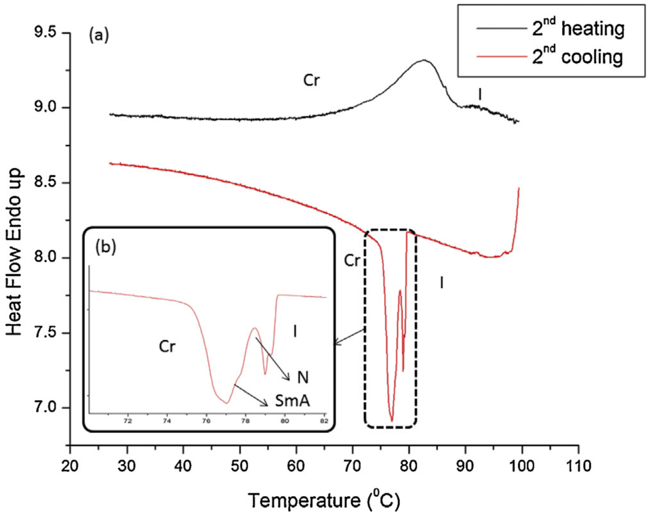

Fig. 3. DSC thermogram of organogel in 1-propanol (10 mM).

---

[1] Electronic supplementary information (ESI) available for the techniques and gelation ability in different solvents.