Journal of Molecular Liquids 272 (2018) 572–582

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Multiple bio-responsive polymer dispersed liquid crystal composites for sensing applications

Daniela Ailincai *, Daniela Pamfil, Luminita Marin *

"Petru Poni" Institute of Macromolecular Chemistry of Romanian Academy, Iasi, Romania

ARTICLE INFO

Article history:
Received 18 August 2018
Received in revised form 20 September 2018
Accepted 26 September 2018
Available online 27 September 2018

Keywords:
Polymer dispersed liquid crystals
Cholesteric liquid crystals
Polyvinyl alcohol boric acid
Biosensors

ABSTRACT

Polymer dispersed liquid crystal (PDLC) composites were prepared by the encapsulation of cholesteryl acetate (L-ChAc) in polyvinyl alcohol boric acid (PVAB) by microemulsion technique. The supramolecular and morphological peculiarities of the resulted composites were analyzed by polarized optical microscopy, fluorescence microscopy and scanning electron microscopy respectively. The thermal behavior of the systems was evaluated by differential scanning calorimetry and the surface characteristics in terms of wettability and surface free energy were calculated based on contact angle measurements. Circular dichroism was further used to evidence the chiroptical properties of the studied PDLCs and to have an insight on the potential interactions between the components. The ability of the composites to act as sensors for different blood analytes was preliminary tested by POM. The results indicated that PVAB facilitated a uniform distribution of the cholesteric liquid crystal as micrometric droplets with narrow polydispersity and planar anchoring. The obtained PDLCs proved moderate wettability and they showed a selective responsiveness for L or D sugars, amino acids and DNA. All these results indicated the new polymer dispersed liquid crystal systems as promising materials for biosensors building.

1. Introduction

Liquid crystals are a special class of matter combining two traditional incompatible characteristics: the ordering of the crystals with the flow ability of the liquids. They show a specific birefringent texture under polarized light correlated with the degree of ordering and the orientational director. This allows an easy tunability of their optical appearance upon the influence of the external stimuli, which act at the nanometric level. More specific, electrical, magnetical, thermal, chemical or biological events induce an orientational transition of the liquid crystal molecules, which can be easily monitored by the changes of the optical textures [1–7]. Among liquid crystals, the cholesteric ones present a more complicated ordering pattern consisting from helicoidal arrangement of the liquid crystal molecules. This supramolecular arrangement offers a very sensitive responsiveness site: the helix pitch, which can be tuned by the liquid crystal – medium interface, leading to the change of the optical appearance. This creates the premises for the cholesteric liquid crystals to be exploited in a plenty of applications as displays [8], reflective polarizers [9], lasers [10] or sensors [11–13]. On the other hand the advantage of the flow ability, which allows the easy control of the orientational order and consequently of the optical appearance, turns into a challenge in the devices designing. The encapsulation of the liquid crystals as micrometric droplets into a polymeric matrix (polymer dispersed liquid crystals, PDLC) appeared as a reliable strategy to create materials for real life applications. Evidenced by Ferguson in 1984 this strategy was constantly developed in line with the requirements imposed by various applications: displays, smart windows, contact lenses, lasers, holographic systems, sensors and so on [14–28]. Thus, were used various polymer matrices, different liquid crystals or mixtures of liquid crystals, using various encapsulation methods [14–28]. Nematic liquid crystals were used most often due to their good flow ability and thus fast responsiveness in an electric or magnetic field or under the influence of environmental triggers. Recently, the developing of the PDLCs toward the bio-applications revealed the cholesteric liquid crystals as appropriate components, as they usually derive from natural compounds keeping the advantage of biocompatibility and they easily respond under the influence of a wide range of biological analytes [10,29]. To date, the use of cholesteric liquid crystals for sensing applications implies the decoration of their molecules or of the fluid interfaces with recognition elements for the targeted analytes [30]. This make the fabrication of sensing platforms a quite complex and difficult task.

Our studies on the design of polymer dispersed liquid crystals revealed that polyvinyl alcohol boric acid (PVAB) is an excellent matrix for the liquid crystals, both nematic or smectic ones, due to the presence

* Corresponding authors.
E-mail addresses: ailincai.daniela@icmpp.ro (D. Ailincai), lmarin@icmpp.ro (L. Marin).

https://doi.org/10.1016/j.molliq.2018.09.125
0167-7322/

of the electron deficient boron atoms which enable a preferred anchoring of the LC molecules into the micrometric droplets [27,28]. Moreover, the use of the PVAB matrix led to the formation of droplets with the diameter under 5 μm and with a narrow size polydispersity – a desideratum quite difficult to be achieved.

In this context, the goal of the paper was to prepare PDLCs based on PVAB matrix and a cholesteric liquid crystal in view of their testing for sensing applications. To this end, cholesteryl acetate (L-ChAc), a traditional chiral nematic liquid crystal has been encapsulated into the PVAB matrix, by microemulsion technique. The cholesteryl acetate, the first liquid crystal discovered by Reinitzer, has been chosen because it is a natural occurring compound which increases the potential of biocompatibility of the materials containing it [31]. Moreover, its monotropic cholesteric mesophase has a strong thermocromism increasing its potential for sensing applications [32]. PVAB matrix, along with its excellent anchoring properties, combines biocompatibility and nontoxicity properties of PVA [33,34] with the antiseptic and antifungal properties of the boric acid [35] and due to the presence of boron atoms, acts as neutron radiation shields [36]. Moreover, due to the presence of the chiral carbon atoms, PVAB has the potential of cholesteric self-ordering, reaching the possibility of chiral recognition.

2. Experimental

2.1. Materials

Cholesteryl acetate (levorotatory enantiomer) 98%, polyvinyl alcohol boric acid (Mw = 54,000, 4% water content), D-glucose, D-galactose, D-alanine, L-arginine and salmon sperm DNA were purchased from Sigma Aldrich and used as received.

2.2. Experimental protocol for the obtaining of the PDLC composites

PDLC composites have been obtained by the microemulsion technique, mixing a liquid crystal solution in chloroform with PVAB solution in water, in different mass ratios (Table 1), as follows. 0.225 g PVAB have been solved in 3 mL hot water (90 °C) and then gradually cooled down up to room temperature to give a 7.5% solution. A 5% solution of L-ChAc liquid crystal in chloroform has been slowly poured into it, under vigorous magnetic stirring (1000 rot/min), when a fine emulsion has been formed. At each 30 min, the resulted emulsion has been submitted to a vortex for 5 min. The magnetically stirring/vortexing cycles were repeated three times. Finally, the emulsions were casted in Teflon Petri dishes and allowed to slowly evaporate the water for 1 week. For microscopic analyses, small volumes of emulsions were casted on glass lamellas. The final composite films were dried in an oven at 45 °C, for 2 days.

Varying the mass ratios between the two components, from 90:10 to 60:40, a series of four PDLC samples were obtained (Table 1). The resulted films were flexible and were highly adhesive to glass.

A film of PVAB has been prepared in similar conditions, as reference, being demonstrated that its physical properties are strongly related to the manufacture conditions [27,28].

Table 1
Composition of the prepared PDLC composites.

Sample code	S1	S2	S3	S4
% L-ChAc	10	20	30	40
% PVAB	90	80	70	60

2.3. Methods

The thermotropic behavior of the pure liquid crystal and of the PDLC systems were analyzed by polarized optical microscopy (POM), using an Olympus BH-2 microscope equipped with a Linkam THMS 600/HSF9I heating stage and a TMS91 control unit. The samples were observed during a heating/cooling scan, at a heating/cooling rate of 5 °C/min. More detailed POM and fluorescence microimages were obtained on a Leica DM 2500 microscope. Fluorescence microscopy was used in order to have an insight on the real size of the droplets diameter. With this aim, the PDLC films were immersed for 5 min into a water solution of Rhodamine B, which was used as hydrophilic fluorescent marker. A PVAB free standing film was used as a reference.

Differential scanning calorimetry (DSC) was performed on a DSC 200 F3 Maia device (Netzsch, Germany), under nitrogen purge (nitrogen flow 50 mL/min). The temperature scale was calibrated with indium, according to the standard procedures. 5 mg of each PDLC sample was loaded in punched and sealed aluminium crucibles and the DSC curves have been registered on a heating-cooling-heating scan, at a heating/cooling rate of 5 °C min^{-1}. The transition temperatures were read at the top of the endothermic and exothermic peaks.

The morphology of the PDLC composites was monitored with a field emission scanning electron microscope (Scanning Electron Microscope SEM EDAX – Quanta 200) at accelerated electron energy of 10 eV. The morphological observation was carried out for (i) the film samples as resulted by casting and for (ii) the films heated at 120 °C. The droplets size was measured using Image J Software and the resulted values were used in order to build the corresponding histograms using OriginPro 8 software.

The static contact angle for the PDLC, PVAB and L-ChAc films was measured using a CAM-200 instrument from KSV Finland, by the sessile drop method, at room temperature and controlled humidity. The measurements were performed within 10 s after placing 1 μL drop of water on film surface and the contact angle was measured by fitting the drop profile using the Young-Laplace equation [37]. The contact angle was measured 5 times on different places of the surface, and after that the average value was calculated. To calculate the components of the free surface energy and the total free surface energy, the contact angle at equilibrium between the studied surface and three pure liquids – twice distilled water, formamide and diiodomethane – was measured. The total surface free energy (γ_s^{TOT}) and its components were calculated using the acid base approach of van Oss and Good [38].

Circular dichroism (CD) was performed using a Chirascan spectrophotometer. The path length of the cuvette was 0.5 mm. The measurements were performed at room temperature (22 °C).

The response of the PDLC composites at different blood analytes was preliminary determined by POM. For this, solutions of blood analytes with a concentration of 10^{-5} M in 0.9% NaCl (to mimic the physiological conditions) were prepared and dropped on the surface of PDLC composites films deposited on glass lamellas. The contact time was 24 h. The tests were done on three different lamellas, always keeping a reference.

The conformation of the PVAB polymer was simulated by molecular mechanics MM+ using HyperChem software.

3. Results and discussions

Self-standing PDLC composite films have been obtained by the encapsulation of a cholesteric liquid crystal: cholesteryl acetate (L-ChAc) (1) into polyvinyl alcohol boric acid (PVAB) (2), by microemulsion technique. Using different mass ratios between the two components, from 10/90 up to 40/60, a series of four PDLC systems were obtained (Table 1).