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Physicochemical study of silica colloidal liquid crystal

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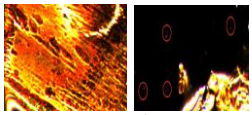
GRAPHICAL ABSTRACT



(a) nematic phase for pure 5CB
(b) Schlieren texture of 5CB liquid crystal

ABSTRACT

A colloidal liquid crystal was prepared by the self-assembly of silica into a nematic liquid crystal, 4-cyano-4'-pentylbiphenyl (5CB). This silica colloidal liquid crystal has massive potential for use in electro-optical device applications such as in developing liquid crystal displays (LCDs). Liquid crystal dispersed with silica have been intensively studied and believed to improve the properties and performance of liquid crystal host. The phases and morphologies of this silica colloidal liquid crystal for two different concentrations, namely 5 and 10 w/v% were characterized by three different techniques which are infrared spectroscopy (IR), polarized optical microscopy (POM) and Raman spectroscopy. IR spectrum showed the functional group of silica colloidal liquid crystal and successfully proved that the 5CB and silica are mixed physically where there is no disruption of the chemical bond of materials. POM revealed the existence of liquid crystal phases which are nematic and isotropic phases. As a result, the presence of Schlieren texture of two and four brushes indicate the nematic liquid crystalline phase during the early stage of cooling process. Raman spectroscopy investigated the chemical fingerprints of the pure liquid crystal and silica liquid crystal that finally been identified.

Keywords: colloidal liquid crystal, 4-cyano-4'-pentylbiphenyl, self-assembly, Schlieren texture

1. INTRODUCTION

Liquid crystal is a unique substance that exhibits an intermediate state of matter that exists between its crystal and liquid states. Liquid crystals are special class of compounds which they neither convert to an isotropic liquid directly upon heating nor revert to a crystalline solid upon cooling from the isotropic liquid state [1]. There are three main types of intermediate state of matter or mesophase of liquid crystal which are nematic, smectic and cholesteric. The nematic phase of liquid crystal has the optical properties of uniaxial crystals and thus it is really useful in the manufacturing of electro-optics device application such as liquid crystal displays (LCDs).

Significantly, electro-optical effects are the change in birefringence and the refractive index where the optical properties of one medium is changed. The change is in response to an electric field that varies slowly compared to the frequency of light. Electro-optic devices are produced in order to modulate properties of light wave consisting phase, polarization, amplitude, frequency and even direction of propagating [2]. Many classes of materials are investigated to design an electro-optic devices such as inorganic crystals, organic crystals and also liquid crystal.

Polymer-dispersed liquid crystals (PDLCs) are one of class materials for manufacturing electro-optic devices with large area displays and switchable windows. However, PDLCs have few practical problems such as high threshold voltage, low contrast ration and slow response time [3]. Major problem of PDLCs is that they are thermally irreversible which caused the reprocessing is impossible. In order to overcome the limitation, thermal-reversible liquid crystals invention was then studied by self-assembly of silica powder in liquid crystal medium via doping to produce a colloidal liquid crystal structures.

Liquid crystal dispersed with silica have been believed to improve the properties behaviour and performance of liquid crystal host. This silica colloidal liquid crystal is widely studied owing to its useful electro-optic properties such as selective light scattering and optical filtering combined with relatively low-cost techniques for their production [4]. The modifying of silica colloidal liquid crystal is reported to reduce dielectric relaxation time and the response time which then gives a better quality of LCDs [5].

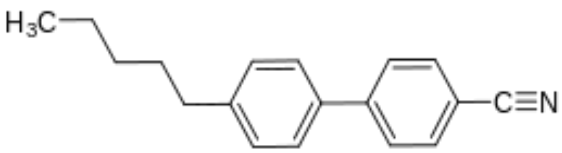


Figure 1 Chemical structures of 5CB

4-cyano-4'-pentylbiphenyl (5CB) is one of the example of liquid crystals with chemical structure shown in Figure 1. In this project, the effect of variety silica concentration and temperature on the electro-optical properties of liquid crystal is studied. The unique behaviour exhibited by this silica colloidal liquid crystal is important for the formation of better LCDs which known that the modulation of alignment of liquid crystal is under influence of an electric field.

This research emphasized on preparation and characterization of 5CB doped silica of varied w/v% forming silica colloidal liquid crystal structures. Technically, 5CB was doped with silica at 5 and 10 w/v% concentrations to study their phase properties and morphologies. Resulting colloidal liquid crystal at both concentrations were compared to pure 5CB. Good distribution, well-ordered assembly and better morphologies are pursued and achieved by 10 w/v% silica colloidal liquid crystal.

2. EXPERIMENTAL

2.1 Synthesis of colloidal liquid crystal

The first stage was focused on the synthesized of silica colloidal liquid crystal via self-assembly technique. The pure 5CB was purchased from Sigma Aldrich Co. (USA). The suspensions of 5CB doped with silica came together with various concentrations which were 5 and 10 w/v%. After that, the mixture was heated with different temperatures which were 25.0°C, 35.0°C and 50.0°C. The holding time for each temperature was programmed to 1 minute respectively before the image being captured.

2.2 Characterization of colloidal liquid crystal

Pure 5CB together with prepared 5 and 10 w/v% colloidal liquid crystal were characterized using Attenuated Total Reflectance-Infrared (ATR-IR) method on a Perkin Elmer spectrophotometer fitted with ATR accessory. The phases of pure 5CB and both colloidal liquid crystals were determined using polarized optical microscopy (POM) and the images were captured by using a LEICA polarized optical microscope. The chemical fingerprints and morphologies of pure 5CB and both colloidal liquid crystals were collected using a Raman spectroscopy on HORIBA XploRA PLUS Raman microscope. The laser wavelength used in this analyser was 532 nm indicated solid state laser in green.

3. RESULTS AND DISCUSSION

3.1. Characterization of SiO_2/5CB using Infrared Spectroscopy

ATR-IR was used for physical characterization methods. The spectra of pure 5CB, 5 w/v% and 10% silica colloidal liquid crystal are shown in Figure 2. All the spectra showed intense peaks within range 2856.62 until 2955.81 cm^{-1} which indicated the peaks of alkane group (C-H) stretching bond. The spectrum of pure 5CB and silica colloidal liquid crystals showed absorption band of nitrile group (C≡N) at 2226.16 cm^{-1}. The spectrum also showed stretching vibration bonds of (C=C) in the benzene rings of 5CB molecule. Spectrum data collected for pure 5CB, 5 w/v% and 10 w/v% of silica colloidal liquid crystal showed not much differences [6]. All of the functional groups have been identified successfully. The mixtures with various concentrations have similar spectrum as pure 5CB showed that the mixture between silica and 5CB was physically combined not chemically united. The self-assembly of this silica colloidal liquid crystal was proven that the compounds was still pure as received as it does not change the mesoscopic behaviour of the mixture.

3.2. Characterization of SiO_2/5CB using Polarized Optical Microscopy

The phases of pure 5CB, 5 w/v% and 10 w/v% silica colloidal liquid crystal were observed throughout the heating and cooling process using polarized optical microscopy method. All images were collected using the microscope. In this part of study, temperature was varied at 25.0°C, 35.0°C and 50.0°C respectively. Firstly, the pure 5CB was placed under microscope and each phase characterization in heating and cooling process can be observed which is denoted in Figure 3.

Before the heating scan, at 25.0°C the pure 5CB showed the nematic phase with a bright domain between the cross polarizer and this confirmed the birefringence of sample [7]. Clear image was captured as shown in Figure 3 (a). When the heating scan reached 35.0°C, the 5CB material started to show thermal scenario. The nematic-isotropic transition temperature (T_{NI}) can be found here with image captured revealing and proving this transition temperature as in Figure 3 (b). At this transition temperature, 5CB showed full transformation of phase with uniformly dark image occured slowly. At the high temperature of 50.0°C, the axes of 5CB randomly orient and resulting in the isotropic phase. As in Figure 3 (c), the microscope captured image of total dark background since the incident light could not be rotated by the isotropic medium across the crossed polarizers.

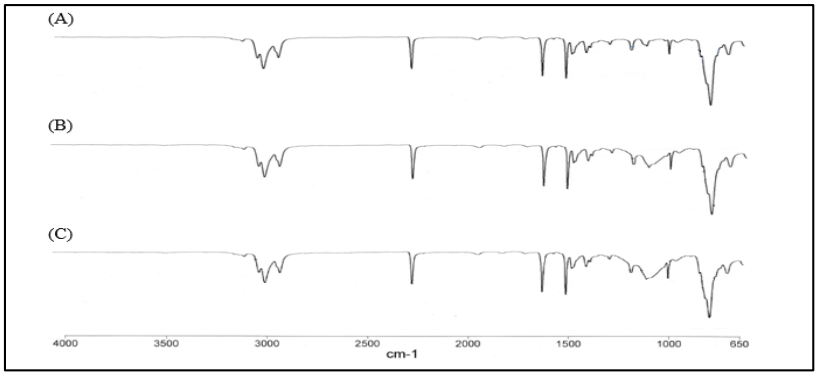


Figure 2 ATR-IR spectra of (A) pure 5CB (B) 5 w/v% SiO_2/5CB (C) 10 w/v% SiO_2/5CB

For comparison, the cooling process of pure 5CB was observed as well. During cooling scan, the isotropic-nematic phase transition became domain as denoted in Figure 3 (d). The schlieren texture was observed and formed in the earlier stage of cooling process [8]. The black bands indicated the four-brushes of the schlieren texture.

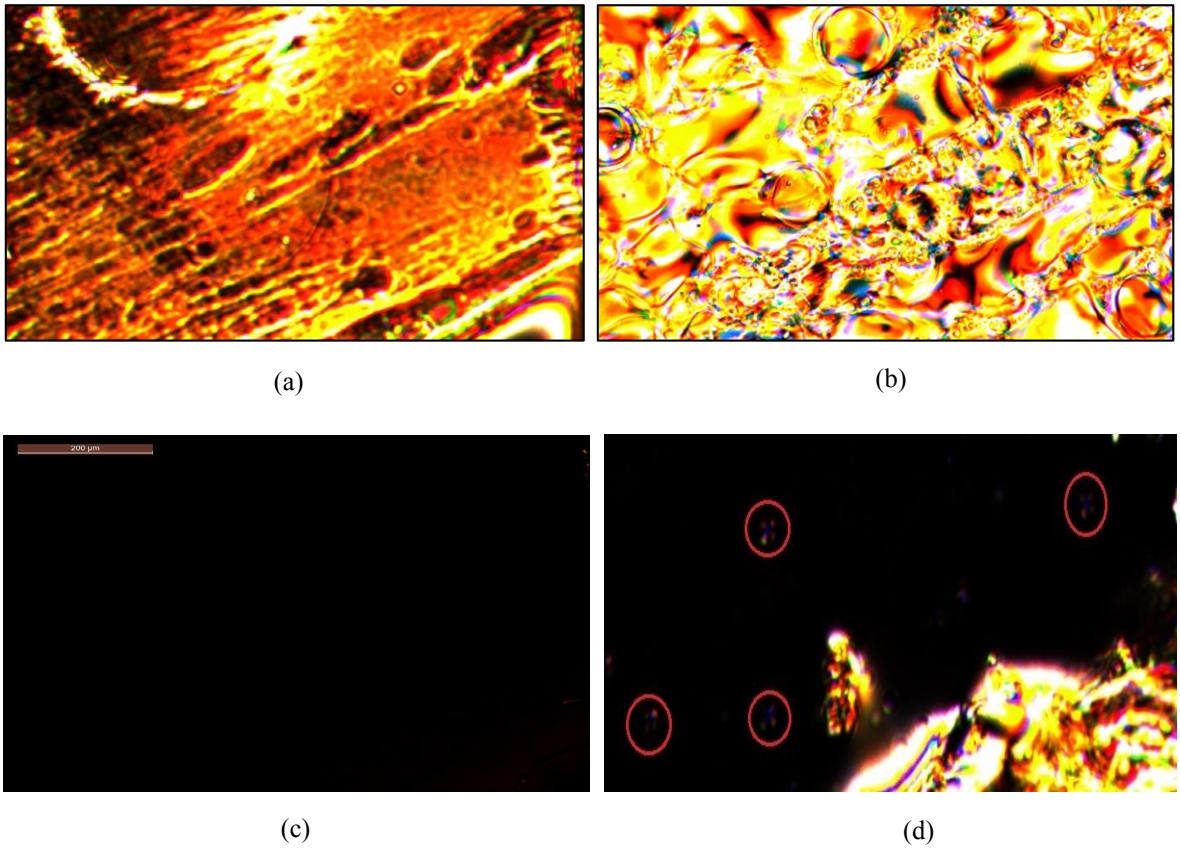


Figure 3 5CB showing thermal scenario during heating and cooling process: (a) nematic phase at 25.0°C (b) nematic-isotropic phase at 35.0°C (heating) (c) dark region of isotropic phase (d) isotropic-nematic phase at 35.0°C (cooling)

Secondly, the phase characterization of 5 w/v% silica colloidal liquid crystal were investigated from the heating to cooling scan. At temperature of 25.0°C, a bright image of nematic phase is observed and confirmed the birefringent of liquid crystalline as shown in Figure 4 (a). The thermal behaviour at temperature 35.0°C exhibited dark region which started to form and indicated the nematic-isotropic phase. The difference between nematic and nematic-isotropic phase is clearly shown in Figure 4 (b). Heating process was continued until 50.0°C, and a total dark region represented isotropic phase was formed in Figure 4 (c).

The image during cooling process is illustrated in Figure 4 (d). At 35.0°C, sample slowly cooled down from isotropic back to nematic phase. Here, the schlieren texture and high strength of singularities of two and four brushes were captured in isotropic-nematic phase.

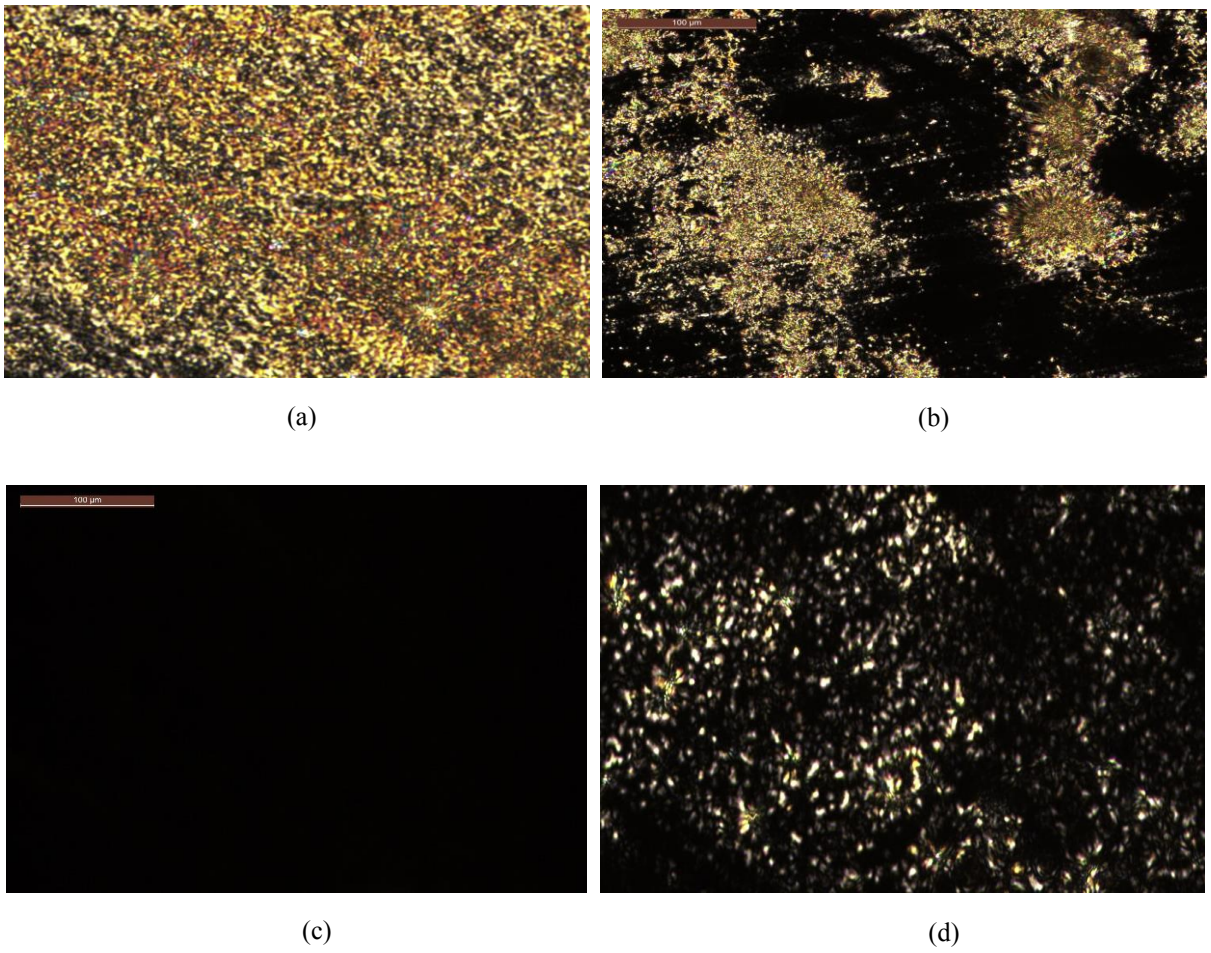


Figure 4 5 w/v% of SiO_2/5CB showing thermal scenario during heating and cooling process: (a) nematic phase at 25.0°C (b) nematic-isotropic phase at 35.0°C (heating) (c) dark region of isotropic phase (d) isotropic-nematic phase at 35.0°C (cooling)

Lastly, 10 w/v% silica colloidal liquid crystal was used to study the phases characterization which exhibited through heating and cooling process. The textures with changing temperatures trend were observed on this higher concentration of guest material. During heating scan at 25.0°C, much brighter image was shown in Figure 5 (a). In this nematic phase, the texture of birefringence region was clearly seen compared to the texture formed in 5 w/v% concentration. The nematic-isotropic phase as in Figure 5 (b) was observed at temperature 35.0°C with dark region started to form. A complete isotropic phase with total dark region background was captured at temperature 50.0°C as denoted in Figure 5 (c).

Further cooling process of this 10 w/v% silica colloidal liquid crystal exhibited a high strength of disclination with two dimensional of mesogenic units. Figure 5 (d) confirmed the existence of schlieren texture possessing both singularities of two and four brushes in the isotropic-nematic phase.

3.3 Characterization of SiO_2/5CB using Raman Spectroscopy

The vibration spectra of pure 5CB and 10 w/v% silica colloidal liquid crystal have been studied by using Raman spectroscopy. The shifts for both samples were compared and revealed that all shifts were quite similar. However, some small shifts were discovered in some peak positions as the molecular structure of dispersion of silica into 5CB recorded in Figure 6. Both shifts showed intense peaks at 1179.14 cm^{-1}, 1281.52 cm^{-1} and 2222.68 cm^{-1} [9]. 1179.14 cm^{-1} represented the C-C stretching while 1281.52 cm^{-1} was for C-H stretching (aromatic). C≡N stretching was indicated by the peak at 2222.68 cm^{-1}.

Another peak at 1522.28 cm^{-1} also represented C-C stretching for aromatic ring which was asymmetric. For 10 w/v% silica colloidal liquid crystal, several peaks obtained between 100 until 900 cm^{-1} confirmed the existence of silica in the 5CB [10]. Peaks at 100.70 and 407.10 cm^{-1} proved the Si-O-Si stretching of silica. Plus, the Si-O stretching arise at the peak 634.49 and 808.02 cm^{-1}.

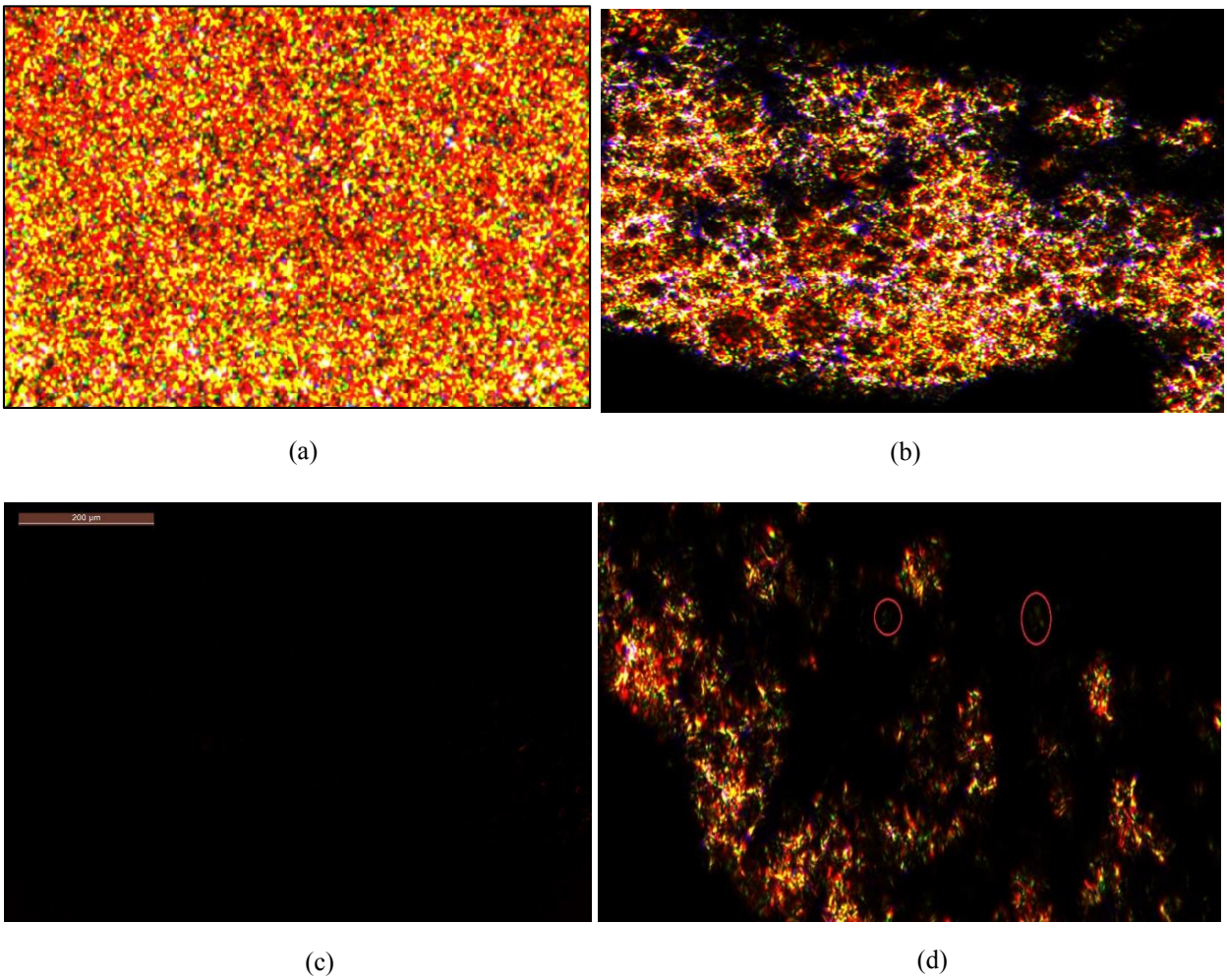


Figure 5 10 w/v% of SiO_2/5CB showing thermal scenario during heating and cooling process: (a) nematic phase at 25.0°C (b) nematic-isotropic phase at 35.0°C (heating) (c) dark region of isotropic phase (d) isotropic-nematic phase at 35.0°C (cooling)

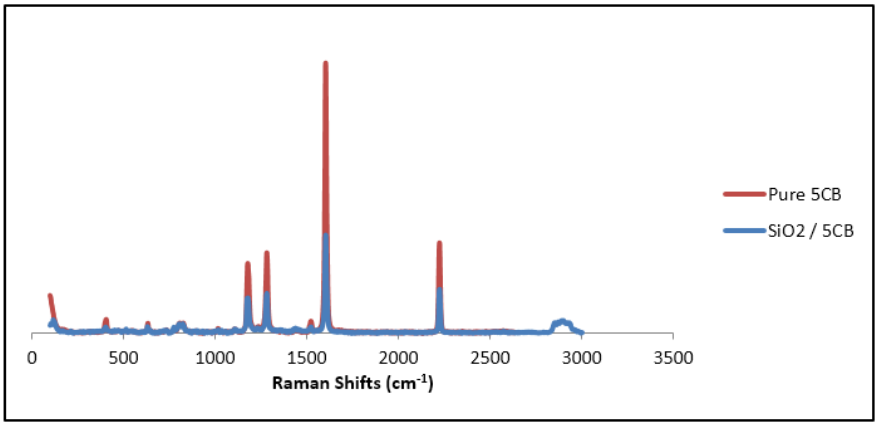


Figure 6 Raman shifts for pure 5CB and 10 w/v% SiO_2/5CB

4. CONCLUSION

The self-assembly of the guest material, silica in 4-cyano-4'-pentylbiphenyl (5CB) nematic liquid crystal facilitaes the formation of the silica colloidal liquid crystal. The phase characterization highly dependent on the various concentration of silica in liquid crystal host. The colloidal liquid crystal was successfully produced in two different concentrations which were 5 w/v% and 10 w/v%. The phase and morphologies were characterized using ATR-IR, POM and Raman spectroscopy. Based on ATR-IR analysis, colloidal liquid crystals with 5 w/v% and 10 w/v% doped of silica give similar spectrum plotted as compared to pure 5CB. It proved that the 5CB and silica was physically combined as there is no disruption on the chemical bond of the materials. On the other hand, phases of pure 5CB and silica colloidal liquid crystal with various concentrations were studied using POM according to different temperature and concentration dependence. The phase varience shows the presence of isotropic-nematic liquid crystalline phase with the existence of schlieren textures. At higher concentration of colloidal liquid crystal doped with silica revealed a brighter image of all phases and clearer image of two and four brushes of schlieren textures. Raman spectroscopy studies suggested that at 10 w/v% silica colloidal liquid crystal showed additional peaks in their shifts plotted when compared to the pure 5CB shifts. The additional peaks obtained between 100 until 900 cm^{-1} confirms the existence of silica dispersed in the liquid crystal host. In conclusion, the set of characterization of higher concentration at 10 w/v% of silica colloidal liquid crystal produced a better images of all phases and good morphologies are obtained.

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