Morphological, Liquid Crystal and Optical Band Energy Properties of Polyphosphates

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Abstract

New metallic liquid crystalline polyphosphates showed thermotropic nematic liquid crystal phases (2.13–2.24 eV). The surface morphology of polyphosphates was examined by the scanning electron microscope and showed rough surface and micro pore structure which an indication of the presence of several crystalline domains. [DOI: 10.22401/ANJS.22.2.03]

Keywords: polyphosphates; polymer liquid crystal; morphology; energy gap.

1. Introduction

Liquid crystalline polymers (LCPs) have attract the attention worldwide due to their interesting properties [1,2]. They have a high chemical resistance, stiffness and strength. In addition, they have a good dimensional stability and low linear thermal expansion coefficient [3–6]. LCPs are of two types that known as side-chain and main-chain based on the location in which mesogenic moieties attached to the backbone of the polymer. The crosslinked LCPs have large spontaneous de-formations [7] in response to changes in temperature [8,9], electric and magnetic fields [10] and light illuminations [11,12], for example. The spontaneous deformation is related to LCPs liquid crystallinity [13]. Materials that have polymeric side-backbone provides the anisotropy properties to liquid crystalline mesogens. While, rigid structures were produced for materials that have polymeric main-chain backbone and leads to high strength and melting temperature. Two common types of LCPs are known as lyotropic and thermotropic LCPs [14,15]. Lyotropic LCPs have liquid crystalline structures in solution and can be fabricated as films or fibers [14]. Thermotropic LCPs have liquid crystalline structures and can be produced upon heating [15] and can be made as three-dimensional structures using injection molding, for example [16]. The modification of the structures and properties of LCPs is of great interest [17–19]. LCPs have high transition temperatures in most cases [20–25]. There are several processes to reduce the tarnation energy by the incorporation of flexible spacers [20], frustrated chain packing [21], nonlinear links [22] and substitution of mesogenic segment [23]. Polymer dispersed liquid crystal materials can be used in building partitions, privacy windows, projection displays, for example [26,27]. Polymer stabilized liquid crystal materials have a uniform oriented polymer networks within the LC matrix [28,29]. The current work investigates the use of new metallic liquid crystal polymers sensing and liquid crystal orientation that is extremely sensitive to the morphology, physical and chemical properties of the surface.

2. Experimental
2.1. Polyphosphates 1–3

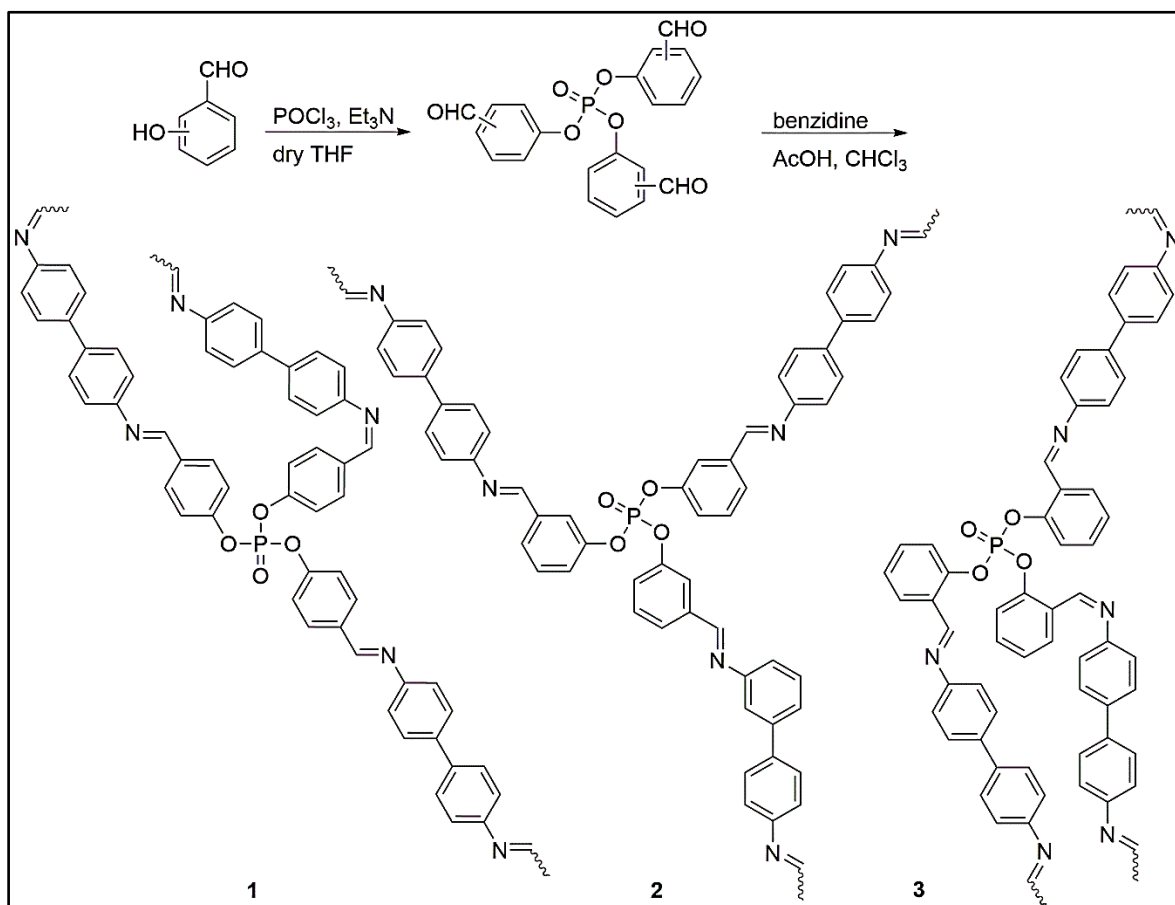Polyphosphates 1–3 Fig.(1) were obtained as previously reported and their structures were confirmed [30,31].

Fig. (1): Polyphosphates 1–3.

2.2. Spectral analysis

The reflection spectra and band energy for polyphosphate samples (*ca*. 500 μm diameter) were obtained using an unpolarized deuterium-halogen light source (Avantes AvaLight-DH-S, Apeldoorn the Netherlands). The scanning electron microscope (SEM) images (accelerating voltage = 15 Kv) were recorded on Inspect S50 microscope (FEI Company, Czechia, Czech Republic).

3. Results and Discussion
3.1. Liquid crystalline properties

The hot-stage optical polarized light microscope was used to observe the mesophase of thermotropic liquid crystal polyphosphate 3. Fig.(2) shows the crystalline texture of the mesogen in which the phase transition occurred and a nematic texture character was observed at 290 and 350°C. The color of polyphosphate 3 was deep brown, the transition phase from solid to nematic phase (C–N) took place at 290°C, the transition phase from nematic to isotropic phase (N–I) took place at 480°C and the thermal stability of the nematic phase (ΔT) took place at 190°C.
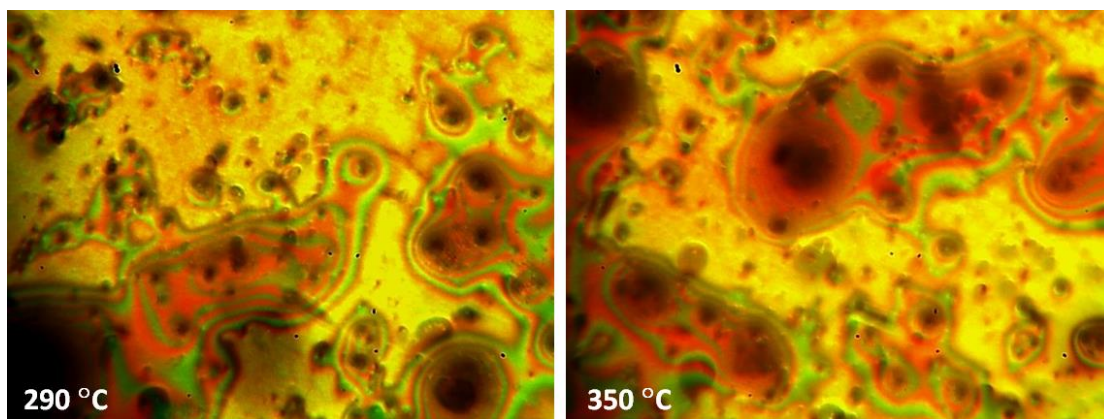
Fig (2): Crystalline texture of the mesogen polyphosphates 3 at 290 and 350 °C (20x).

3.2. Scanning electron microscopy (SEM)

The surface morphology of 1–3 was examined by the SEM at accelerating voltage of 15 kV. The SEM images are shown in Figs.(3–5).
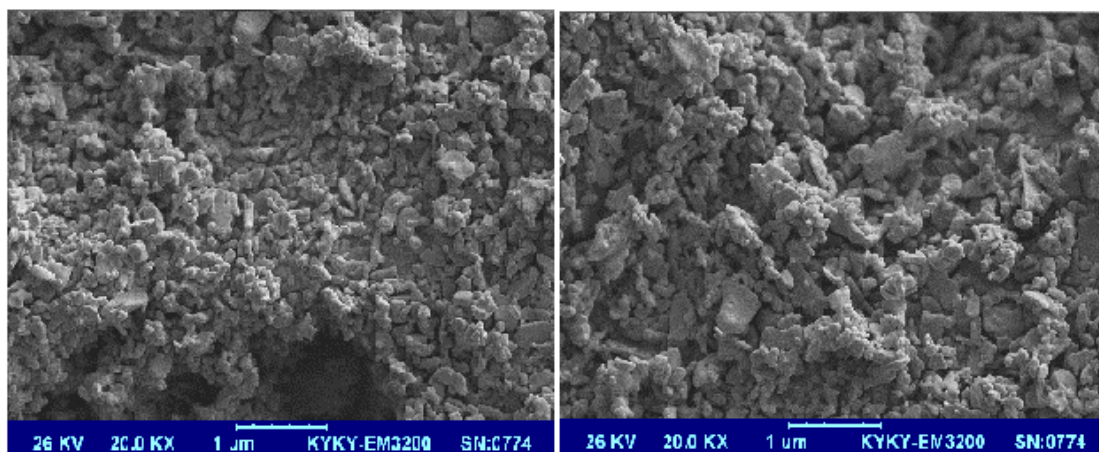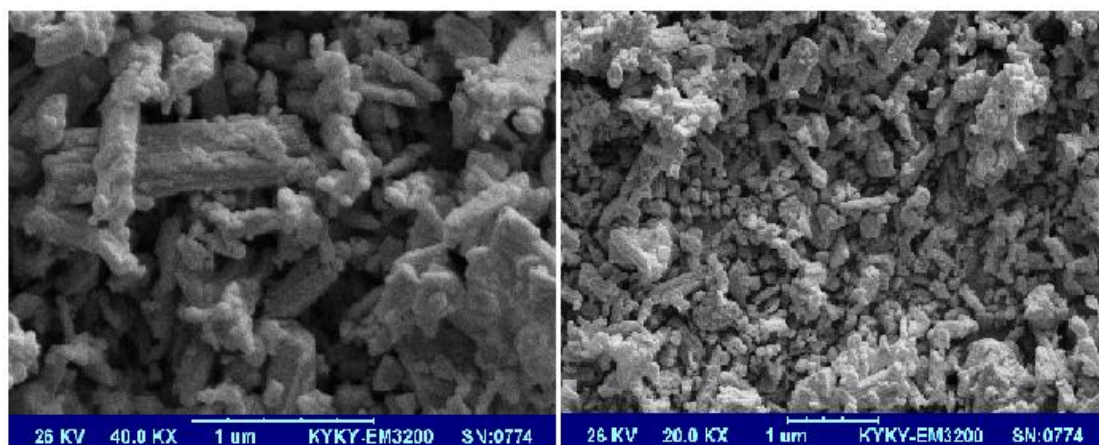

Fig.(3): SEM images of polyphosphate 1.

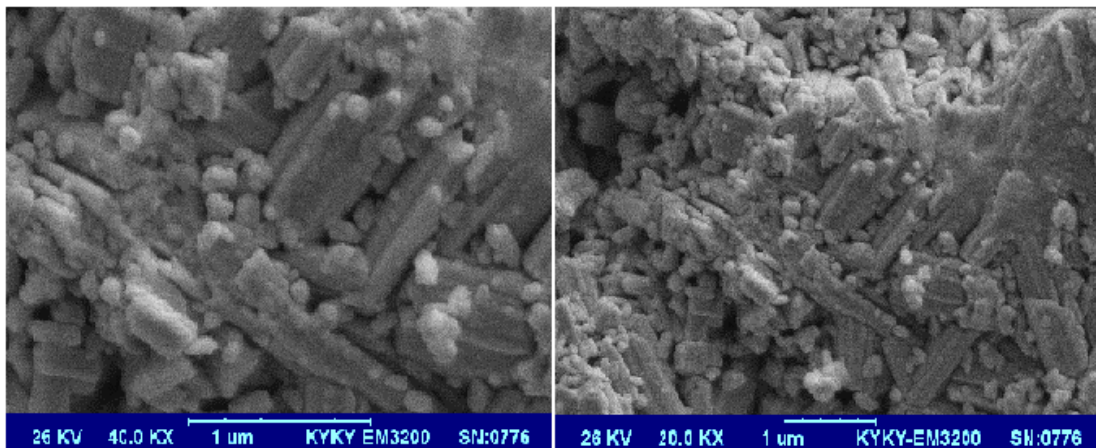*Fig.(4): SEM images of polyphosphate 2.*

Fig.(5): SEM images of polyphosphate 3.

The SEM images of 1−3 showed a porous amorphous structure as a result of the azomethane (-CH=N-) linked networks (Figs. (6–8)). Polyphosphates 1–3 have nano-sized particles in most cases and their dimensions were *ca*. 40–165, 28–806 and 30–598 nm for 1, 2 and 3, respectively. The SEM indicated that the agglomerated particles of polyphosphates 1 and 2 arranged side by side to produce a topographical microporous structures forming clusters as a result of the high surface energy Figs.(6) and (7). While, the SEM images of 3 revealed an irregular morphology with rod-like mesogens Fig. (8) which can be used as building blocks to construct liquid crystal with optical properties [32].
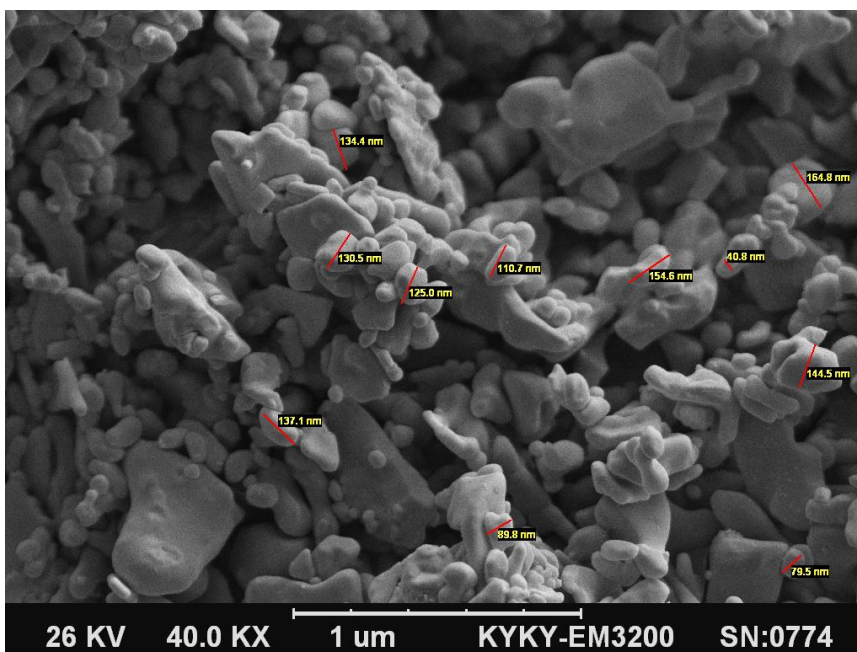

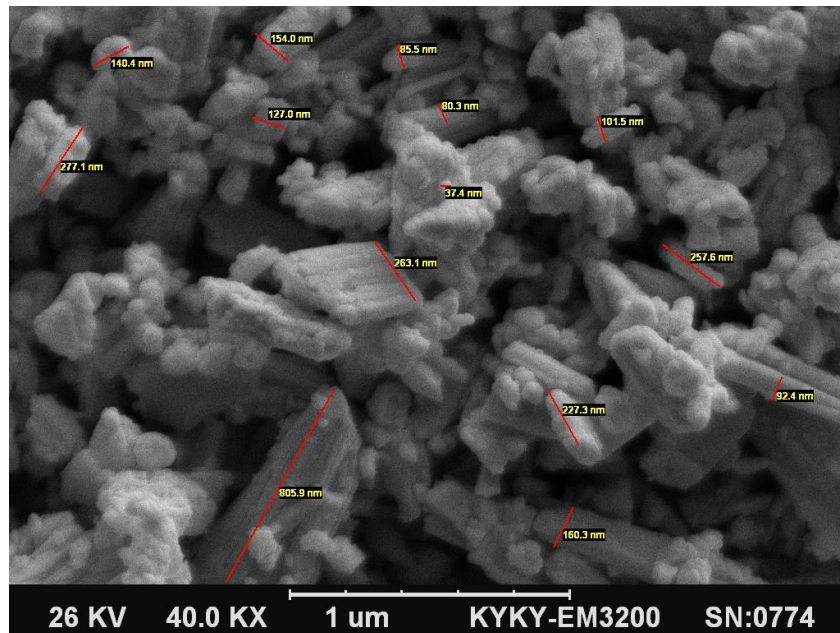*Fig.(6): SEM images with dimension range of polyphosphate 1.*

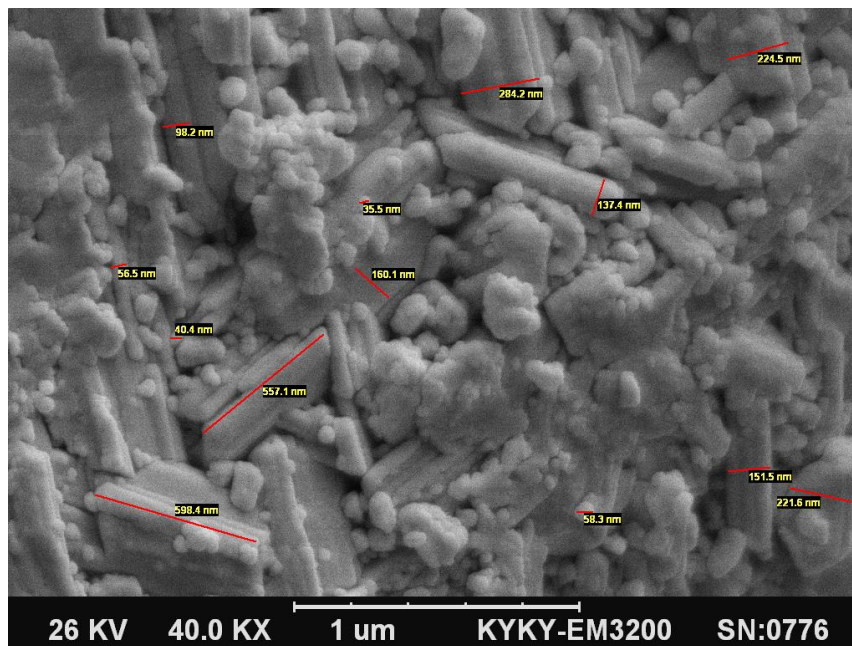*Fig.(7): SEM images with dimension range of polyphosphate 2.*

Fig.(8): SEM images with dimension range of polyphosphate 3.

3.3. Photonic properties

The absorption band edge can be used as a useful tool to investigate optically the induced transition. Photons with energy higher than the band gap energy (Eg) should be absorbed [33].

In crystalline and non-crystalline materials, the electronic transitions between the valence and conduction bands start at the absorption edge. The absorption edge or Eg is the minimum energy difference between the lowest minimum of the conduction band and the highest maximum of the valence band. The changes in the optical absorption spectra of 1–3 with a high energy proton beam (2.13–2.24 eV) are shown in Figs.(9–11). From the band energy (Eg), it has been observed the polyphosphate 3 was the best in terms of semiconductor properties which is a determining factor for the structural stability [34].
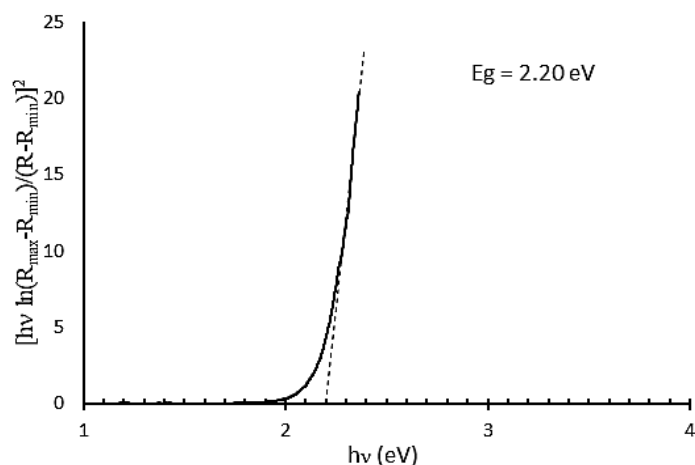
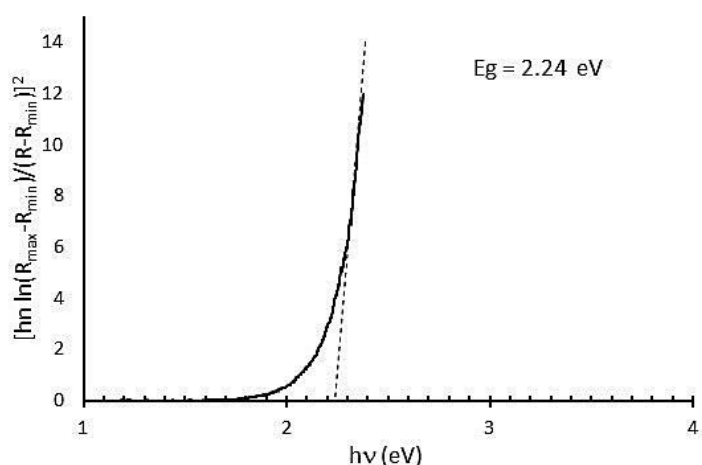**Fig.(9): Plot of [hvln(Rmax-Rmin)/(R-Rmin)]²vs. hv for polyphosphate 1.**

Fig.(10): Plot of [hvln(Rmax-Rmin)/(R-Rmin)]²vs. hv for polyphosphate 2.
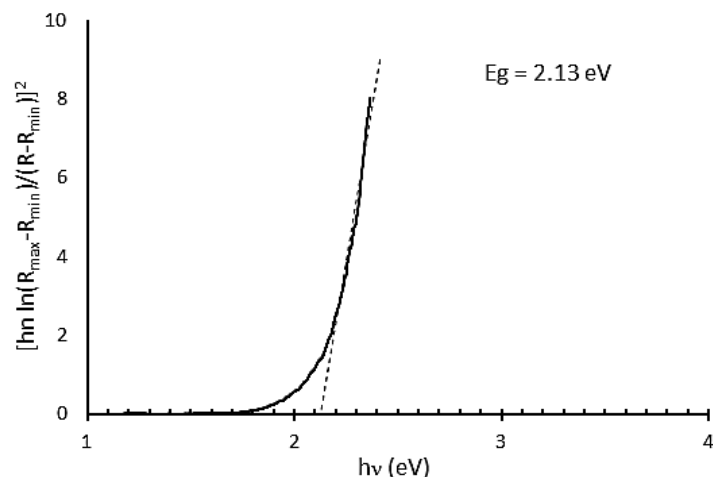
Fig.(11): Plot of [hvln(Rmax-Rmin)/(R-Rmin)]²vs. hv for polyphosphate 3.

The polarizing force of the –CH=N- bonds and the resonance effect within the aromatic rings can have an effect on the formation of liquid crystal phases and their stability. Polyphosphate 3 gave a liquid crystal phases possibly as a result of the strong polarization effect of the –CH=N- bonds of the *ortho*-substitution compared with the *meta*- (2) and the *para*-substitution (1). Polyphosphate 3 showed liquid crystalline phase properties at 50–400 and 440–460 nm regions with a light reflectance percentage of 18, and 26%, respectively due to the high the irregularity of the internal arrangement of 3 compared to 1 and 2 Fig.(12).
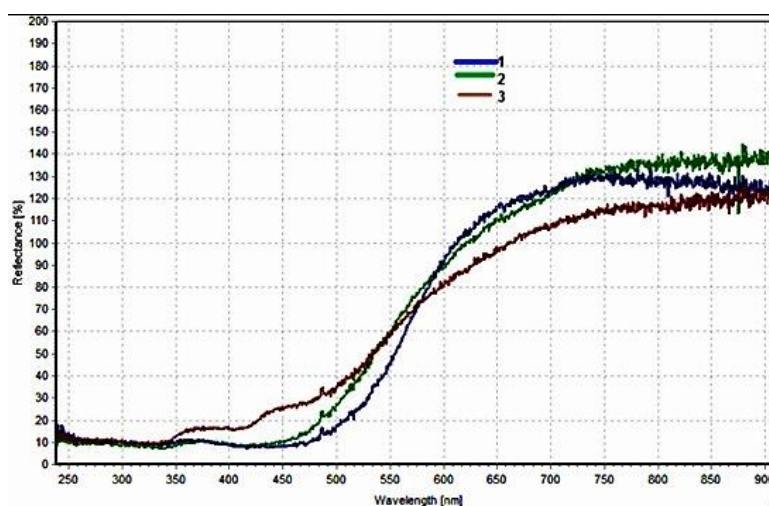
Fig.(12): Reflectance of polyphosphates 1–3.

4. Conclusion

New metallic crystalline liquid polyphosphates were developed and could be used to adsorb gas molecule efficiently in range of 2.13–2.24 eV. The *ortho*-substituted polyphosphate 3 was found to be the most efficient liquid crystal.

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