

# STRUCTURAL TRANSFORMATION OF POLYSTYRENE NANOSPHERE PRODUCE POSITIVE AND NEGATIVE RESISTS BY CONTROLLED LASER EXPOSURE

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## Abstract

Laser treated polystyrene (PS) thin films were explored for simple, robust, and low-cost polymer based electronic applications. Polystyrene nanospheres of 500 nm were drop coated on silicon wafer before laser treatment was introduced to systematical investigated the structural transformation of treated PS. The relationship between the parameters used and the structural changes of PS, especially for its surface chemistry and the morphological, structural properties were characterized with Attenuated total-reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD) and Field emission electron microscopy (FESEM). It was revealed that the morphological changes observed in the laser treated PS films were the dominant factor for the improvement of modified PS that can be used to tailor functional polymer such as organic light-emitting diodes (OLED), carbonaceous nanostructure, graphene, graphene oxide. Zwitter characteristic of the PS can be clearly observed during laser irradiation; over exposure of laser could be used to tailor different materials on the surface of the PS.

**Keywords:** laser irradiation, polystyrene, zwitter characteristic

## 1. Introduction

Currently there is great interest in developing low cost semiconductor devices by using polymer as precursor. Polymers are large molecules composed of repeating subunits. Such materials are used as electrolytes, dielectrics, semiconductors and have provided significant advantages in replacing the conventional inorganic ones for the same kind of applications. These advantages include high specific energy, high energy density, flexibility, high ionic conductivity or good isolation, wide thermal and electrochemical stability windows, solvent-free condition and easy processing, low weight, and most important costs efficiency<sup>1</sup>. Polymers are often exposed in radiation environments to various kinds of radiations such as laser, gamma rays, X-rays, electrons, photonic and ions, which may affect the chemical structure and physical properties of these materials by atomic or molecular excitation and ionization, resulting in the capture of chemical bonds, intermolecular cross-linking, formation of free radicals and unsaturated bonds, etc. These processes cause defects in the polymer matrices, which are responsible for most of the changes

observed in the physico-chemical properties of polymers<sup>2</sup>. Because polymer surface modification has become an actively studied area recently<sup>1</sup> polystyrene (PS) is widely used polymer in biotechnologies and microfluidic devices, also one of the most important polymers, as it exhibits many good properties, such as good process ability, rigidity, low water absorbability, transparency, and that it can be produced at low cost.

The PS films have wide applications and are mainly employed in surface protection of metals, optical biosensor, and humidity sensor, coatings for biomaterials and barrier films for pharmaceutical packaging. While for PS films, seldom reports have been made on the nanostructure and optical properties of PS films by laser induced CVD<sup>3</sup>. Moreover, PS has a simple chemical structure that consists of both unsaturated aromatic ring and saturated aliphatic chain. Therefore, study on surface modification of PS, especially the chemical reactions occurred at the unsaturated and saturated bonds, is helpful for better understanding the related mechanisms, and for rationally tuning the surface properties of polymeric materials<sup>4</sup>. Although different treatment methods can be used for polymer surface modification, such as the electron beam irradiation<sup>5, 6</sup> plasma treatment<sup>7</sup>. ion beam treatment<sup>8, 9</sup> and laser irradiation<sup>10, 11,12-14 15, 16</sup> laser irradiation is a non-contact clean technique compared with other surface treatment methods. Among the thermoplastic polymer like polystyrene are continues to be a widely used industrial polymer because of its multiple advantages<sup>17</sup>. It is a rigid transparent polymer, having thermal stability, ease of heat fabrication, low specific gravity and excellent thermal and electrical properties for insulating purpose.

However, insulating materials will also play an important role in any organic device structure. Several insulating polymers have been used successfully in organic electronic devices, such as polyvinyl phenol (PVP), polyvinyl acetate (PVAc) and polystyrene (PS). Out of these materials polystyrene shows greater potential for use in future organic electronic devices, due to it having the advantage of superior material characteristics in terms of water absorption and dielectric strength when compared to PVP or PVAc<sup>18</sup>. Furthermore, it is considered to be one of the most stable polymers with respect to the ionizing radiations such as gamma rays, electrons and ion beams, due to the presence of a benzene group in its structural composition<sup>7</sup>. After laser irradiation, photon energy was absorbed by benzene ring of PS and resulted in bound excitation of ring C-H and then the surface radicals were formed. These radicals reacted with oxygen in the air and oxygen-based functional groups were formed on the PS surface. Lu et al .have reported formation of these functional groups on PS<sup>7</sup>. A zwitter polymer is a polymer that is linear or cross-linked, depending on an applied dose of electron-beam irradiation<sup>19</sup>. Zwitter polymers essentially exhibit properties of linear polymer, while zwitter polymers with cross-linked networks induced by irradiation offer the possibility of improving the strength, dimensional stability, and dissolution resistance to solvents at elevated temperatures. Furthermore, zwitter polymers can be used as resists for producing both positive and negative patterns on wafers in semiconductor applications<sup>20</sup>.

Since there is not much report on zwitter characteristics hence in this work, efforts have been made to understand the zwitter characteristics of polystyrene over exposure of laser

irradiation on the structural and chemical properties of polystyrene thin films by employing Fourier Transform Infrared (FTIR), Field Emission Scan Microscopy (FESEM) and X-ray diffraction (XRD).

## 2. Experimental Details

Polystyrene nanospheres with a mean diameter of 500 nm and a concentration of 10 wt% in solution were purchased from Sigma Aldrich and was used without further purification, to achieve a large-area hexagonal close-packed nanosphere monolayer, the PS nanosphere solution was diluted to be 2 wt% with deionized water, silicon wafer ((100) orientation, p-type) were cut into small pieces 1 x 1 cm<sup>2</sup> dimension and thoroughly cleaned, first by sonication in toluene, acetone, ethanol for 10 min respectively and in piranha solution (H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> in the ratio of 3:1) at 80 °C for 40 min to remove organic residues<sup>21, 22</sup>. After each sonication the substrates were rinsed with copious amounts of deionized water and then stored in water until used. Then about 5 μL PS nanosphere suspensions with the concentration of 2 wt% was dropped on silicon wafer and allowed to dry at room temperature before laser treatment. The laser irradiation was performed at room temperature in air atmosphere using He-Ne laser with wavelength 633 nm and a lens (KBX049 Bi-convex (Newport)) used for focusing laser light on samples. Irradiation times were taken as 20, 30, 40, 50 and 60 min. The laser beam was focused at normal incidence to lens placed at a distance of 25 cm from the sample, getting a spot of 1x1 cm<sup>2</sup>. The incident light intensity is 1.6 mW/cm<sup>2</sup>, measured using Newport optical power/energy meter model 842-PE.

FTIR analysis was performed using a Perkin Elmer FTIR Spectrometer LR 64912C, N3896 equipped with a universal Attenuated Total Reflectance (ATR) sample stage and a spectrum express FTIR software V1.3.2 Perkin Elmer LX100877-1. The sample molecular structure is determined within the range of 4000–400 cm<sup>-1</sup> range with a resolution of 4 cm<sup>-1</sup>. The X-ray diffraction pattern of polystyrene films were acquired using a PANalytical XPERT-PRO MPD X-ray diffractometer system with Cu K $\alpha$  line ( $\lambda = 1.54056 \text{ \AA}$ ). The X-ray generator worked at a combination voltage potential and current of 40 kV and 40 mA respectively. The patterns were recorded at 2 $\theta$  angle ranging between 10° to 80° with a step of 0.04°. The measurements were performed for pre and post laser irradiation in order to observed significant change on the sample surface of the polystyrene films. Field emission scanning electron microscope was performed using FE-SEM JEOL JSM-7600F. The samples were carefully loaded on a specific FESEM sample holder then introduced into the FESEM chamber setup on vacuum of about 10x10<sup>-5</sup> Pa. The surface morphology images was then scanned with electron beam of about 2.00 kV, LEI SEM detector mode and scanning wide distance (WD) of about 9.6-9.8 mm. The optimum magnifications scanning is set within 10,000 to 50,000 in order achieved the best images.

## 3. Results and Discussion

FTIR spectral analysis of polystyrene films was performed to confirm the molecular structure for pre and post laser irradiation. The formation of the carbonyl groups is observed from the ATR-FTIR spectra for both pre and post laser irradiation as shown in Figure 1(a-f). Before the irradiation, one can observe that the main peaks appearing at 1300-1000 cm<sup>-1</sup>, 1500-1450 cm<sup>-1</sup>, 1600 cm<sup>-1</sup>, 2800–3000 cm<sup>-1</sup>, and 3000–3100 cm<sup>-1</sup>, which corresponds to the C-O stretching, C=C Asymmetric stretching of aromatic ring, C=C Symmetric stretching of aromatic ring, C-H stretching of aliphatic ring, and C-H stretching of aromatic ring, respectively<sup>5,21,23</sup>. After

irradiation, figure 1(b-f) it is clearly shown that the intensity of absorption was also found to increase with time of irradiation increases and change the shape of the spectra at longer wavelength, thus indicating a possibility of photo degradation of polymer chains. The spectra for 40 min irradiated sample, shows a predominant absorption associated with creation of carbonyl compounds at  $1737\text{ cm}^{-1}$ . In addition, the observed increase in the intensities of the carbonyl and hydroxyl regions of the ATR-FT-IR spectra, have provided an evidence for the photo degradation as well as photo-oxidation of polymeric chains. This indicates the carbonyl groups were formed on the PS nanospheres by laser irradiation because of photon energy was absorbed by benzene ring<sup>24</sup>. It is observe that the intensity of the peaks for C-H bonds of aliphatic ring and aromatic ring are reduced and increases after irradiation while the intensity of the peak for C=C bonds also changes. The new small peaks at  $3200\text{--}3500\text{ cm}^{-1}$  resulting from the hydro peroxides were also observed. This verifies that laser irradiation in normal atmosphere leads to the decomposition of C-H bonds with the subsequent formation of the carbonyl groups<sup>23</sup>. Therefore, the white emission can be clearly attributed to the formation of the carbonyl groups on the surface of the PS nanospheres.

Figure 2. Show XRD pattern for both per and post laser irradiation. It is well known that most polymers are not entirely crystalline, because the chains or parts of chains have no order to the arrangement of their chains. A polymer has two phases, the crystalline portion and the amorphous portion. The existence of amorphous portion leads to the appearance of characteristic amorphous halos in the diffraction pattern. It is clear show that broad peak at  $19.7^\circ$  of pre-laser irradiation is due to amorphous polystyrene and is assigned to the diffraction pattern of (002) which is agreement with findings in reference<sup>25</sup>. There is an initial decrease in intensity and subsequent disappearance of the broad amorphous peak with increase in laser irradiation time which indicates the films have improved in crystallinity. Additionally new peaks appeared in PS films when irradiated with laser for 30 – 60 min. There is an appearance of sharp (002) peak which is corresponding to the diffraction angle  $2\theta = 56.12^\circ$  (ICSD card No. 98-016-3828) for samples irradiated at 30, 50 and 60 min laser irradiation time. At 40 min and 60 min laser irradiation sharp peaks appear at  $53.63^\circ$  corresponding to (022) reflection planes. The peak at  $56.12^\circ$  for the 40 min laser irradiated sample is less prominent compared to same peak for 30, 50 and 60 min samples. This indicates a dominant disordered atomic structure and therefore destruction of crystalline structure of the samples. For the 50 min irradiated sample a sharp, low intensity peak is observed at  $52.31^\circ$  (ICSD card No. 98-008-8821) which correspond to (112) plane. Also at 60 min sample there are two prominent peaks appeared at  $53.63^\circ$  and  $56.12^\circ$  which assigned to the (022) and (002) reflection planes. These peaks might be attributed to the increase in the laser irradiation which could lead to cross linking. Any significant change appears in the peak intensity after irradiation leads to changes in the structure of the materials and gradual decrease in the integral intensity occurs with increasing the laser irradiation. This decrease can be explained by the decrease in the amount of crystalline phase in the irradiated samples, and consequently, destruction in the crystalline structure. Also can be explained by the formation of new bonds between the neighboring chains which could be attributed to the change in the regularity arrangement of the crystallites into disorders, as a result of cross linking of the molecular chains<sup>26,27</sup>. The corresponding peaks are indicating sizes of the particles in nano-range with average grain size of 0.998 nm. The Debye–Scherer diffraction formula has been applied to calculate the average size of nanoparticles by using Full Width at Half Maximum (FWHM) on the basis of (002) diffraction.

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where  $D$  is the mean size of the ordered (crystalline) domains,  $k$  is a dimensionless shape factor,  $\lambda$ -is the X-ray wavelength,  $\beta$ -is the line broadening at half the maximum intensity (FWHM),  $\theta$ -is the Bragg angle <sup>28</sup>.

Figure 3 (a-f) show top views of a FESEM images for both pre and post laser irradiation respectively. Here, a detail of carbonaceous substance species on the sample surface is revealed. As reported in previous work, the carbonization of polymers will produce volatile gases and the volume of polymers will decrease obviously due to loss of atoms, so an effective way to study carbonization in overexposure process is to monitor the morphological evolution of the PS films <sup>6</sup>. Figure 2a shows the evolution of the surface morphologies of the PS film for per-laser irradiation. It can be seen that a self-assembled monolayer of PS coated clearly formed in hexagonal shape arrangement on the silicon. As the laser bombardment proceeds from 20 min to 60 min there is evolution of the gap between each polystyrene beads as illustrated in Figure 2(b-f). The average diameter of the individual PS beads was reduced in size and shape. However the original hexagonal lattice was maintained and become more carbonaceous material due to fragmentation formed between PS beads

#### 4. Conclusion

In this work, overexposure process of PS by laser irradiation was systematically studied. We found that PS films at irradiation of 40 min shows a predominant absorption associated with carbonyl group created. In addition, the observed increase in the intensities of the carbonyl and hydroxyl regions of the FT-IR spectra, have provided an evidence for the photo degradation and zwitter characteristics as well as photo-oxidation of polymeric chains. This indicates that the carbonyl groups were formed on the PS nanospheres by laser irradiation. We also found, by analyzing the evaluation of surface morphologies and composite of PS films under overexposure that the transformation of PS from negative to positive resist was as a result of carbonization process. The residuals after overexposure could be further carbonized by high temperature treatment. Further work should be considered by laser treatment of metal nanoparticles embedded in polystyrene and to study electrical and chemical properties of the prepared composite.

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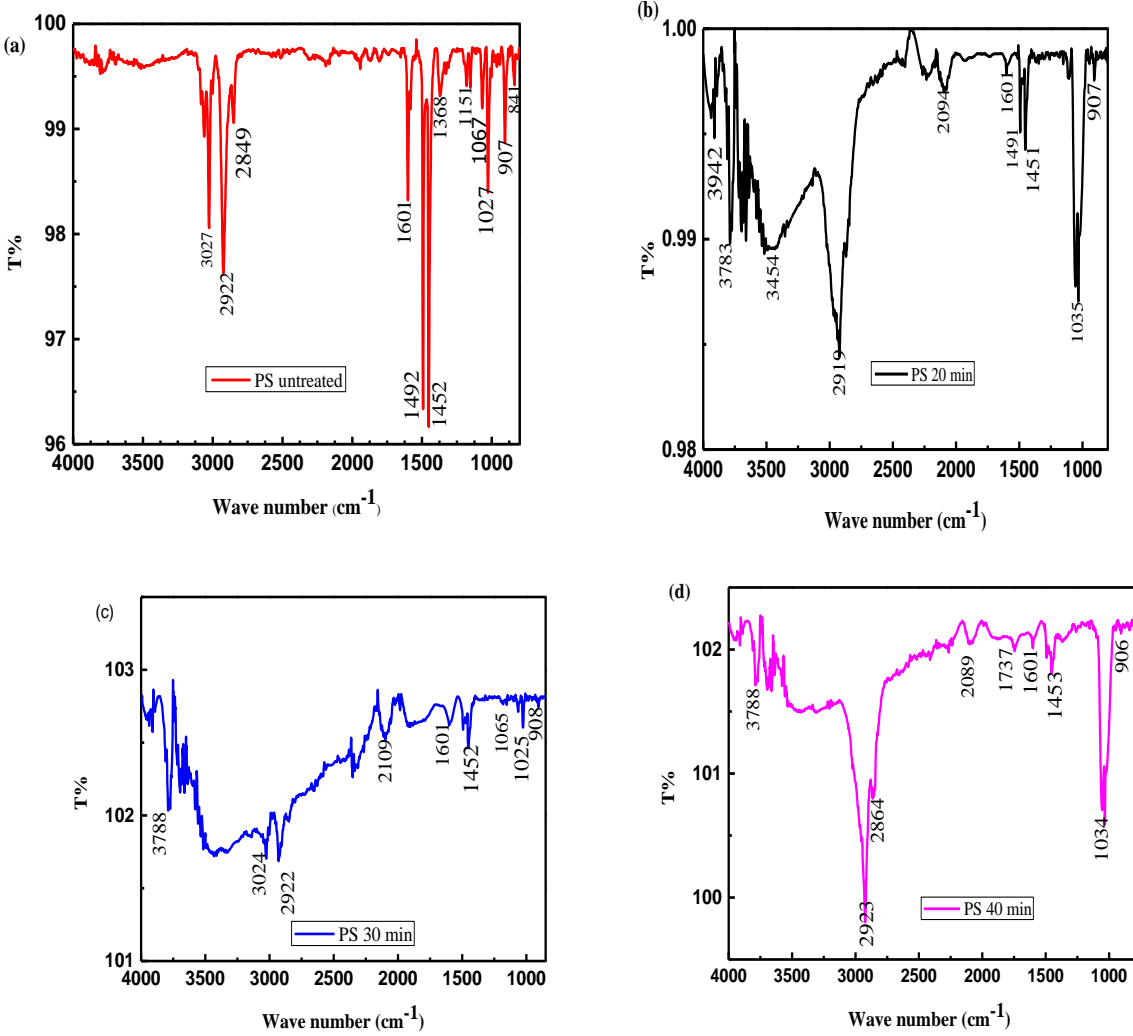
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## Figure captions

Figure 1. FTIR spectra for both pre and post laser irradiation

Figure 2. X-ray diffraction patterns for both pre and post laser irradiation polystyrene

Figure 3. FESEM images obtained for both pre and post laser irradiation



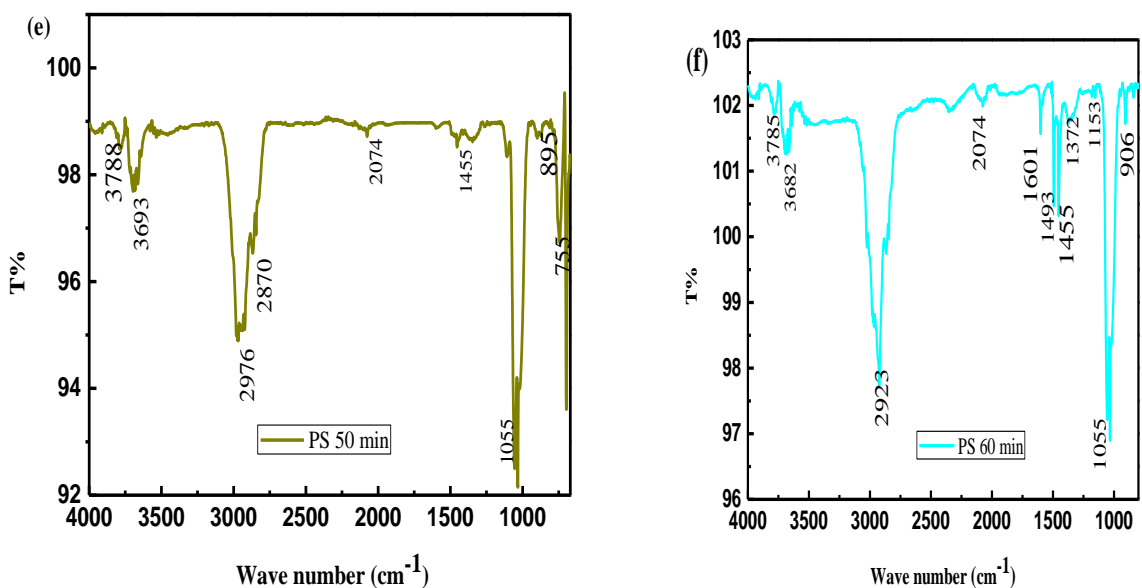


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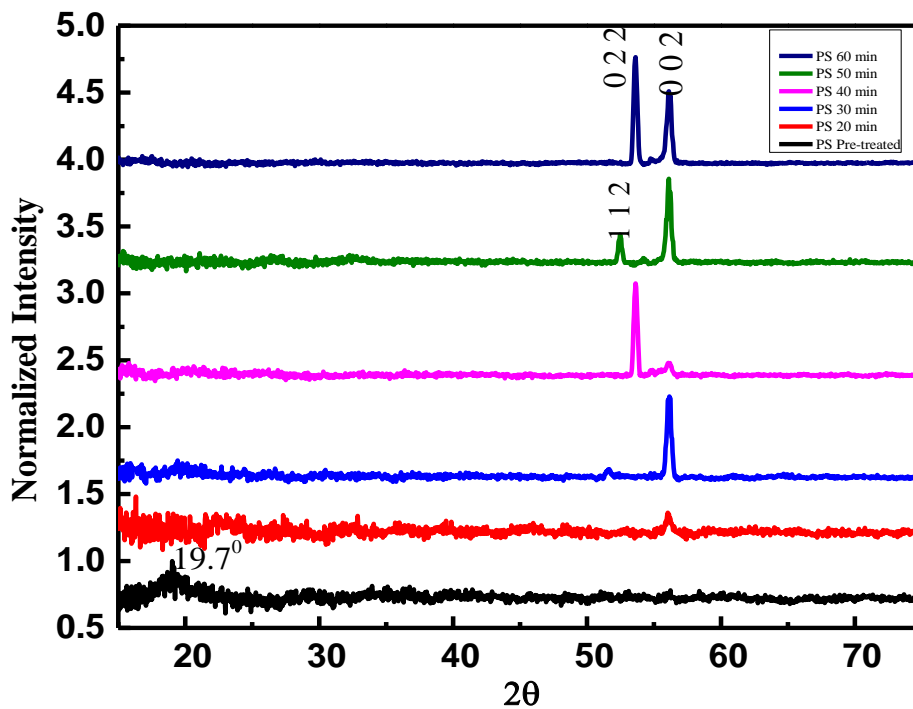
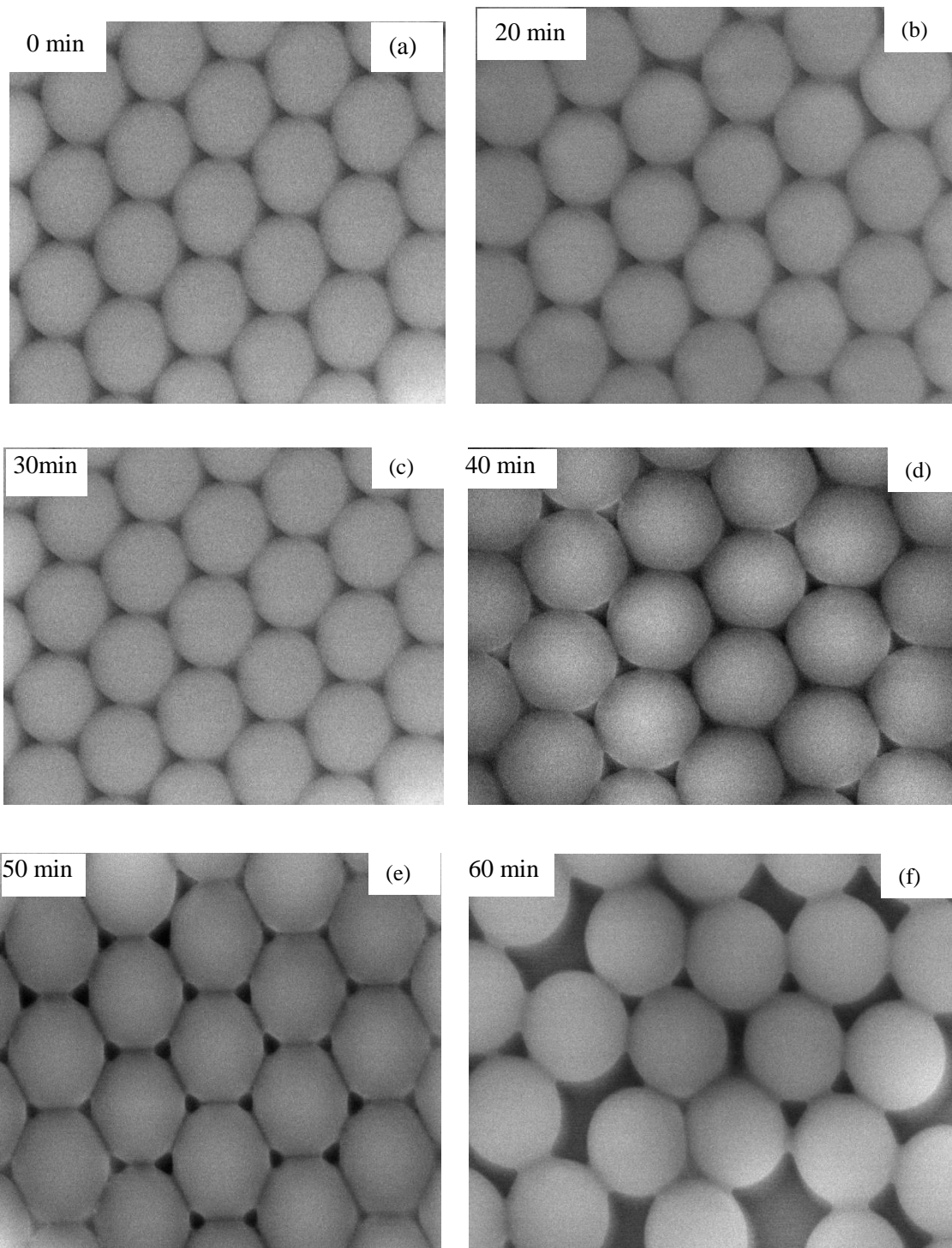


Figure 2. X-ray diffraction patterns for both pre and post laser irradiation polystyrene





**Figure 3. FESEM images obtained for both pre and post laser irradiation**