Tanzania Journal of Science 48(1): 140-147, 2022
ISSN 0856-1761, e-ISSN 2507-7961

Synthesis of Polydispersed P(St-MMA-AA) Microspheres and Fabrication of Colloidal Crystals with Non-Compact Morphology

Ikhazuagbe H. Ifijen[1]*, Eribe M. Jonathan[2], Jacob N. Jacob[3], Nyaknno U. Udokpoh[1] and Ukeme D. Archibong[4]

[1]*Department of Research Operations, Rubber Research Institute of Nigeria, Iyanomo, Benin City, Nigeria*

[2]*Department of Chemistry, Benson Idahosa University, Benin City, PMB 1100, Edo State, Nigeria*

[3]*Department of Chemistry, University of Benin, PMB 1154, Benin City, Edo State, Nigeria*

[4]*Department of Science Laboratory Technology, Faculty of Life Science, University of Benin, PMB 1154, Benin City, Edo State, Nigeria*

**Corresponding author, e-mail: larylans4u@yahoo.com*

Received 7 Nov 2021, Revised 22 Mar 2022, Accepted 24 Mar 2022, Published Mar 2022

DOI: https://dx.doi.org/10.4314/tjs.v48i1.13

Abstract

Great attention has been given to the synthesis of monodispersed and uniform colloidal polymer particles with controllable particle sizes. However, investigations on the preparation, characterization and fabrication of polydisperse polymeric particles are very few. Polydisperse polymers are also needed to meet the new demands of the modern markets due to the ease of their synthesis. This study, therefore, synthesized polydispersed poly(styrene-methyl-methacrylate acrylic-acid) (P(St-MMA-AA)) via emulsion polymerization synthetic approach under unstable reaction conditions. The synthesized P(St-MMA-AA) microparticles were characterized using Fourier transform infrared spectroscopy (FTIR), dynamic light scattering (DLS), a thermo-gravimetric analyzer (TGA) and scanning electron microscope (SEM). The DLS results revealed a highly polydispersed P(St-MMA-AA) microparticles with an average particle diameter of 803.4 nm. SEM, TEM (transmission electron microscopy) and AFM (atomic force microscopy) analyses showed that the particles were spherical and polydispersed. The unequal diameters and non-compact nature of the fabricated colloidal crystals may have affected its possible uses in some specific applications such as decorative coatings, biomedical and sensing applications. However, other materials can be incorporated into the polydispersed prepared P(St-MMA-AA) colloidal microspheres to improve their properties and possible applications.

Keywords: Emulsion polymerization; Polydispersed; Polymer; P(St-MMA-AA).

Introduction

A polydisperse polymer can be defined as a polymer with a non-uniform nature and chains of unequal lengths, and so its molecular weight does not have a single value (De Vos and Leermakers 2009). The existence of the polymer is usually in the form of distributed molecular weights and chain lengths (De Vos and Leermakers 2009). The reason for unequal chain lengths and shapes can be ascribed to the non-uniform nature of the degree of polymerization that may have resulted from unstable reaction conditions (Ifijen and Ikhuoria 2020, Ifijen et al. 2019a). In comparison to polydisperse polymers, monodispersed polymers are uniform, i.e., polymers in which all molecules have the equivalent degree of polymerization or relative molecular mass. Many biopolymers, especially proteins, are

monodisperse (Omorogbe et al. 2019, Ifijen et al. 2019b).

Colloidal stability is a vital requirement that must be reached before polymeric colloidal materials can be put into use (Ifijen et al. 2019c). Polydispersed polymers do not usually meet the aforementioned colloidal stability requirement. As such, they tend to coagulate or agglomerate faster than monodispersed particles. Agglomeration or coagulation is encountered in several natural or industrial processes, like the growth of aerosol particles in the atmosphere and during material synthesis or even flocculation of suspensions, granulation, crystallization and colloidal particle processing. These particles collide by different mechanisms and stick together forming irregular particles of different shapes and sizes. Lee and Chen (1984) analytically examined the coagulation rate of suspended particles, taking into consideration the impacts of both the size spread and particle size. The results of the analysis revealed that the coagulation rate of polydisperse particles is significantly more elevated than the monodisperse counterparts (Lee and Chen 1984). Eggersdorfer and Pratsinis (2012) showed that polydisperse primary particles tend to generate agglomerated structures more than monodisperse particles. The problems associated with polydispersed colloidal polymeric particles have made monodispersed polymer spheres attracted so much relevance due to their fascinating utilization in areas such as combinatorial synthesis, diagnostics, security coating and drug delivery (Sultan et al. 2021, Kovtun et al. 2021, Baudis and Behl 2021).

From an experimental point of view, based on our experience, polydispersed polymers are usually easier to synthesize than monodispersed polymers because their synthetic approaches do not involve any specific reaction conditions unlike that of their monodispersed counterparts. Research on polydispersed colloidal polymers has not been thoroughly investigated because of several setbacks associated with their applications. Notwithstanding, these polymers are also needed to meet the new demands of the modern markets due to the ease of their synthesis. This study, therefore, investigated the synthesis and characterization of polydispersed poly (styrene-methyl-methacrylate acrylic acid) (P(St-MMA-AA)) microspheres. Its use in the generation of colloidal crystals was also examined.

Materials and Methods

Materials

Methyl-methacrylate (MMA), sodium hydroxide, acrylic acid (AA), ammonium bicarbonate, sodium dodecylbenzene sulfonate (SDBS) and ammonium per-sulfate and styrene were used in this study. They were all obtained from Sigma Aldrich Inc. (USA) and were of analytical grade.

Synthesis of polydispersed poly-(styrene-methylmethacrylate- acrylic-acid) microspheres

Polydispersed poly-(styrene-methyl-methacrylate acrylic-acid) (P(St-MMA-AA)) colloidal solution was prepared via batch emulsion polymerization method (Wang et al. 2016) with slight modifications. In a conventional synthesis, 0.0042 g of sodium dodecylbenzene-sulfonate (SDBS) emulsifier (0.012 mmol), 0.735 g of methyl-methacrylate (MMA) (7.34 mmol), 3.17 g of styrene (30.4 mmol), 0.62 g of acrylic acid (AA) (8.61 mmol), 16.5 g of de-ionized water (917 mmol) and 0.085 g of ammonium carbonate $NH_4)_2CO_3$ buffer agent (1.076 mmol) were dispersed into a 50 ml two-neck flask and then agitated with a magnetic stirrer (410 rpm) for 20 minutes at 80 ^oC. Pure nitrogen was injected into the system to completely purge the vessel of oxygen. Afterwards, initiation of the polymerization process was initiated by the addition of 0.08 g of ammonium persulfate (APS) (0.35 mmol).

Characterization techniques

Scanning electron microscope (JEOL-JSM 5600LV), high-resolution transmission electron microscopy (TECNAI F2 G20 HRTEM), atomic force microscope in the tapping mode (Bruker Multimode, Germany) were used to view the microscopic structure

of the generated P(St-MMA-AA) microspheres. Dynamic light scattering (DLS) (Nano-Zetasizer, Malvern Instruments) was used to determine the average particle diameter and polydispersity index (PDI) at 25 °C under the scattering angle of 173° at 6333 nm wavelength.

The appearance of several functional groups is displayed by the FTIR spectra of the synthesized poly(styrene-methylmethacrylate-acrylic acid) (P(St-MMA-AA)) (Figure 1). The emergence of the absorbance peaks at 1490 cm^{-1} and 1596 cm^{-1} are ascribed to the aromatic C=C-C stretching vibration (Ifijen and Ikhuoria 2019). Aromatic -C-H out-of-plane bending vibrations were seen at 698 cm^{-1} and 770 cm^{-1} (Ifijen and Ikhuoria 2020). This is suggestive of the fact that the non-polar core-interior structure of the P(St-MMA-AA) latex displayed by the transmission electron micrographs consists of a phenyl ring. The justification of the broad peak at 1345-1040 cm^{-1} can be established with the C-O (ester bond) stretching vibration (Ifijen et al. 2020). The appearance of the carboxylic functional group can be ascribed to the sharp intense peak at 1731 cm^{-1}. Furthermore, the occurrence of the non-bonded hydroxyl group is due to the broad absorbance peak at 3500 cm^{-1}. This may be due to the absorption of water molecules from the surrounding.

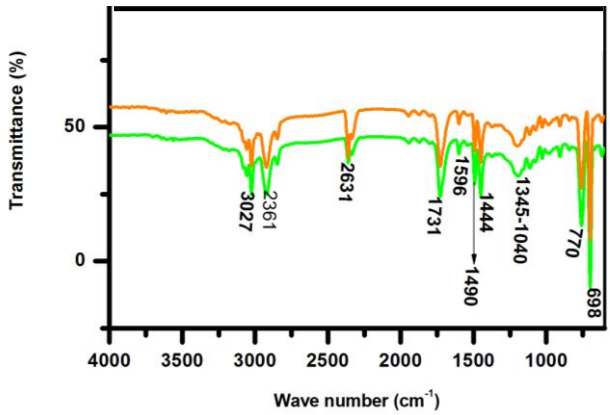

Figure 1: FTIR of the synthesized P(St-MMA-AA) colloidal microspheres.

Particle sizes and their distributions

It is a well-known fact that polymer colloidal solutions are usually composed of particles of varying sizes. The variation between the polymer colloidal particle sizes may be negligibly small or significant depending on the synthetic approach employed during their synthesis. It was therefore, necessary to obtain the average size and size distributions of the synthesized P(St-MMA-AA) polymer particles before exposing them to an evaporation induced self-assembly approach. Figure 2 (a and b) shows typical size distribution histograms of the produced terpolymer nano-particles synthesized using SDS (surfactant). The average particle size of 804.3 nm was estimated from the dynamic light scattering graph (Figure 2b). The reported size is in agreement with that estimated by the size distribution histogram. The polydispersity index (PDI) was estimated to be 1. PDI is used to indicate the distribution of polymer chain molecular weights in a given polymer sample. As the PDI value increases the heterogeneity in cross-linking, network formation, chain length, branching, hyper branching will have a more random arrangement. The polymer is said to be polydispersed (polymer particles with a non-uniform nature and chains of unequal length) when the PDI > 0.5 and monodispersed when PDI < 0.5. According to the dynamic light scattering analysis (DLS), the observed PDI of the synthesized P(St-MMA-AA) is greater than 0.5. This is an indication that the particles are highly polydispersed. This observation is in line with the difference in

sizes reported by the scanning electron and atomic force images in Figure 3 (a, b and c) and Figure 4(a and b). The polydispersed nature of the synthesized P(St-MMA-AA) terpolymer can be attributed to several unstable reaction conditions. Reaction conditions like concentrations of reactants, stirring speed, temperature and humidity are some of the major factors that determine the morphology of polymeric colloidal microspheres.

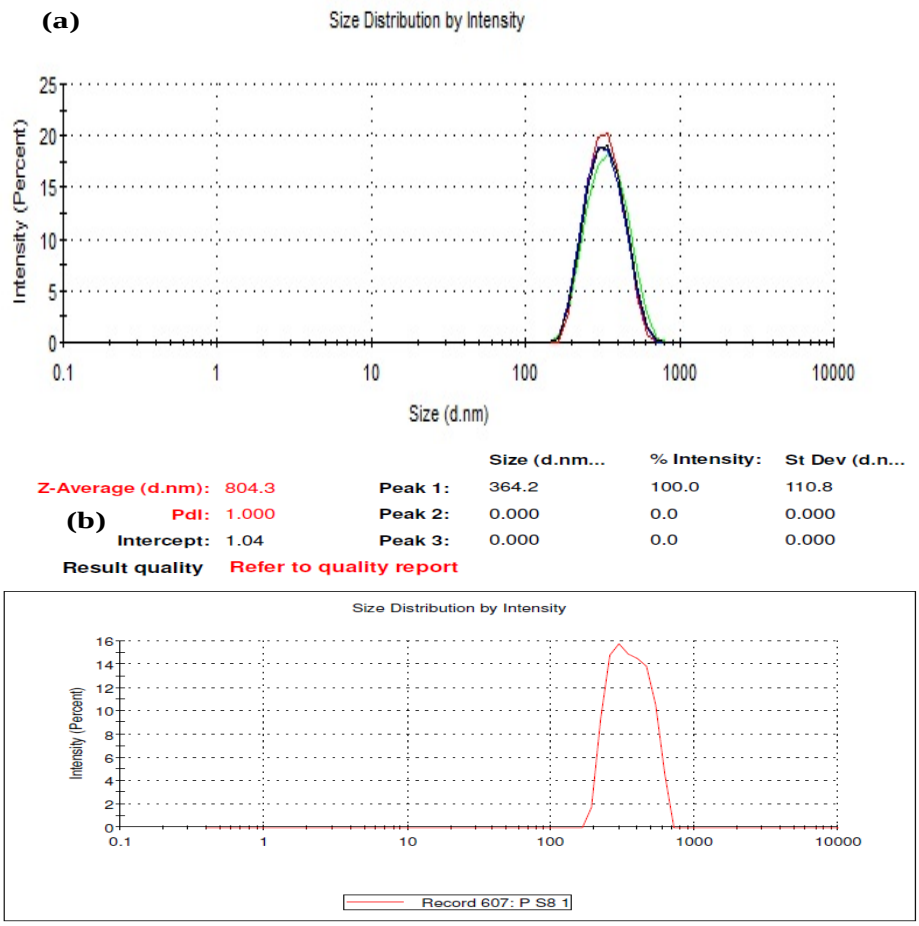

Figure 2: (a) size distribution intensity (b) dynamic light scattering graph.

Microscopic analysis of the generated colloidal crystals

An attempt was made to fabricate colloidal photonic crystals on glass substrates using the synthesized P(St-MMA-AA) microspheres having an average particle diameter of 804.3 nm via the vertical deposition technique. The self-assembly technique is spurred by the capillary forces in the meniscus between the interconnecting phase of the glass substrate and the convective force instigated from the evaporation of the solvent (Boles et al. 2016, Díaz-Marín et al. 2021, Perkins-Howard et al. 2022). Self-assembly of the colloidal particles was performed at 55 °C for 24 hr in a water bath. Figure 3 (a, b and c) shows the scanning electron micrographs of the generated photonic crystals self-assembled with the P(St-MMA-AA) core-shell microspheres on a glass substrate. The self-assembled P(St-MMA-AA) microspheres were observed to be polydispersed. This observation is in agreement with that

recorded by the dynamic light scattering, SEM and TEM analyses. The obtained P(St-MMA-AA) colloidal photonic crystals did not display any form of colour as the observation angles changed. This may be due to the obstruction of the light diffraction caused by the polydispersed nature of the P(St-MMA-AA) particles. The photonic bandgap of the P(St-MMA-AA) colloidal photonic crystal which is a function of its crystal lattice and periodicity may have been adversely affected by the polydispersed nature of the terpolymer particles, thereby hindering the emergence of structural colour on the generated film (Rong et al. 2011). Ifijen and Ikhuoria (2020) fabricated terpolymer colloidal crystals that displayed colour that changed from red to green with viewing angles using the vertical deposition technique. They attributed the formation of colours to the occurrence of scattering and light diffraction due to the combined effects of the superior level of dispersity, intrinsic small sizes and the well-ordered arrangements of particles of the terpolymer particles. It was also established that a more uniform distribution of particle sizes produces colour with higher intensity (Ifijen and Ikhuoria 2020).

The morphology of the P(St-MMA-AA) colloidal particles was viewed through a transmission electron microscope (Figure 3(a & b)). The microscopic analysis of the synthesized P(St-MMA-AA) colloidal microsphere revealed the existence of two separate regions (dark and light regions) which indicate a core-shell morphology. The dark layer is composed of polystyrene (PS) core interior. The appearance of a core-shell structure could be ascribed to the polar MMA/AA shell and the non-polar PS core which resulted in huge polarity disparity in the P(St-MMA-AA) latex, while the light region is made up of methyl-methacrylate/acrylic acid shell exterior (MMA/AA) (Zhang et al. 2007). The carboxyl groups existing upon the surface of latex spheres is the major reason for the formation of hydrogen bonds among the latex spheres. The TEM images show that the diameters of synthesized P(St-MMA-AA) microspheres are unequal, signifying a high degree of polydisperse microspheres. The observed result is in agreement with the SEM, TEM and dynamic light scattering results.

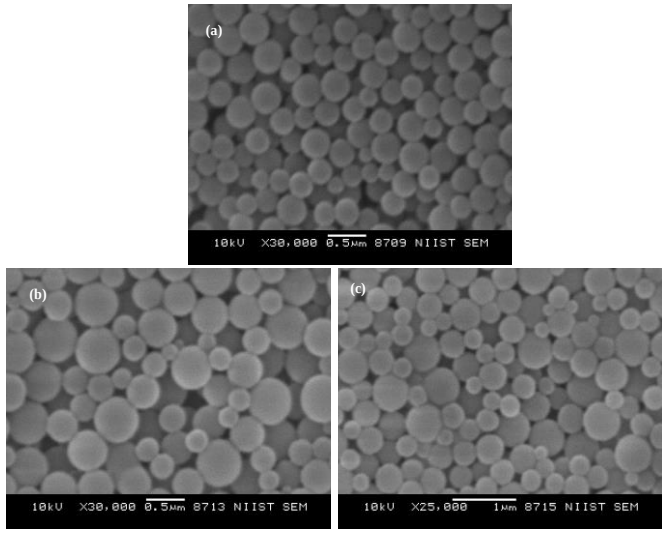

Figure 3: (a, b & c) scanning electron micrographs of the synthesized P(St-MMA-AA) colloidal crystals.

An atomic force microscope (AFM) was employed in viewing the P(St-MMA–AA) colloidal microspheres in a tapping mode at room temperature. The micrographs represent different magnification views of the colloidal microspheres. Figures 5 (a) and (b) are lower magnification images compared to Figures 5(c) and 5(d). Figures 5(a), (b), (c) and (d) show three dimensional (3D) images of the P(St-MMA–AA) colloidal microspheres. The observed morphology is similar to the scanning electron micrograph (SEM) displayed in Figure 3 (a, b and c). The AFM images revealed a non-closed-packed colloidal disordered particle with spherical shapes and a high degree of polydispersed particles. The observed average particle diameter, particle height and surface roughness are 795.4 nm, 32 nm and 11. 4 nm, respectively.

This non-compact and unequal nature of the colloidal crystals obtained by vertically depositing the synthesized polydispersed P(St-MMA-AA) colloidal microspheres on a glass slide (Figures 3, 4 and 5) is contrary to the periodic ordered self-assembled coloured colloidal crystals obtained by several other studies that fabricated colloidal crystals using monodispersed terpolymer colloidal solutions (Zhang et al. 2007, Rong et al. 2011, Ikhuoria et al. 2018, Ifijen and Ikhuoria 2020). The properties observed for the fabricated polydispersed colloidal crystals in this study would affect its possible uses in decorative coatings and anti-counterfeiting applications. However, this crystal film may find uses as a promising building block in constructing superhydrophobic coatings, super hydrophilic films, optical devices, etc (Ikhuoria et al. 2018). A wider application range can be obtained for the studied polydispersed P(St-MMA-AA) colloidal microspheres by incorporating other functional materials into their matrix.

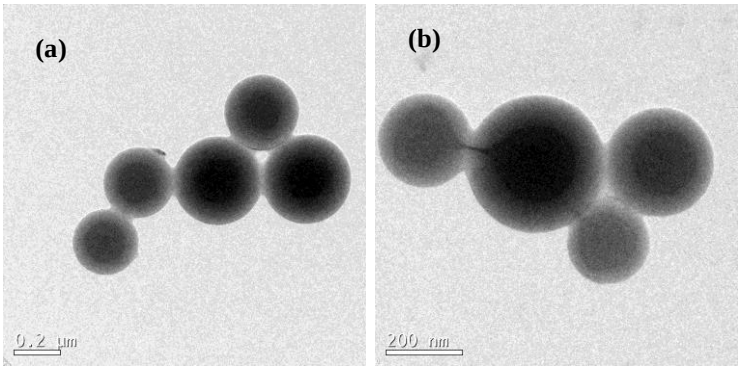

Figure 4: (a & b) Transmission electron micrographs of the synthesized P(St-MMA-AA) colloidal microspheres.

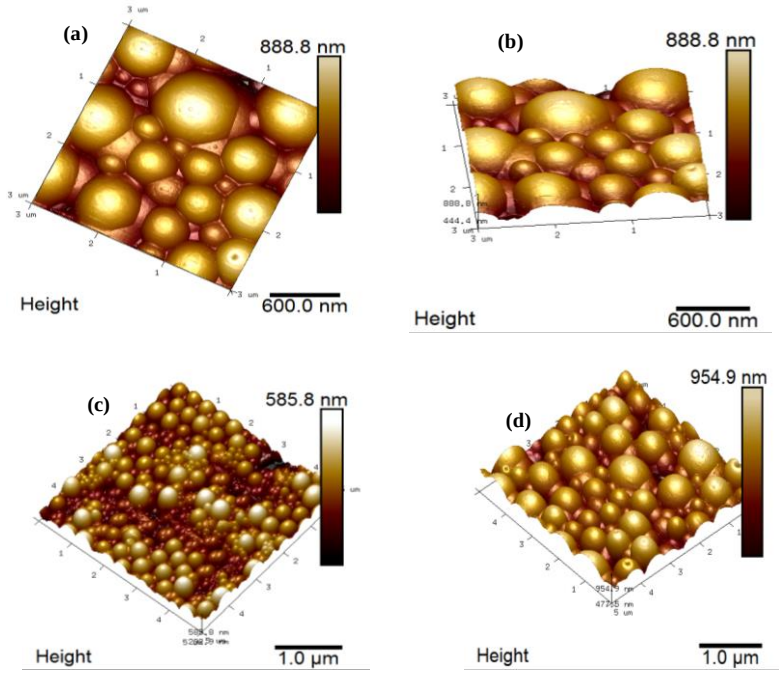

Figure 5: (a, b, c & d) Three dimensional (3D) images of P(St-MMA–AA) colloidal crystals viewed by atomic force microscope.

Conclusion

This study demonstrated the fabrication of non-compact colloidal crystals using polydispersed as-prepared P(St-MMA-AA) colloidal microspheres. SEM, TEM and AFEM analyses of the generated colloidal crystals revealed self–assembled non-compact polydispersed particles. The unequal diameters and non-compact nature of the fabricated colloidal crystals could affect its possible uses in decorative coatings, anti-counterfeiting, sensing applications. However, the possible applications of P(St-MMA-AA) colloidal microspheres can be improved upon by incorporating other functional materials into them. We recommend that more studies on the modification of the studied polydispersed terpolymer microspheres with varying types of functional materials for the improvement of their possible applications be carried out.

Competing Interests: Authors declare that no competing interests exist.

References

Baudis S and Behl M 2021 High-throughput and combinatorial approaches for the development of multifunctional polymers. *Macromol. Rapid Commun.* 2100400: 1-20.

Boles MA, Engel M and Talapin DV 2016 Self-assembly of colloidal nanocrystals: from intricate structures to functional materials. *Chem. Rev.* 116(18): 11220-11289.

De Vos WM and Leermakers FAM 2009 Modeling the structure of a polydisperse polymer brush. *Polym.* 50(1): 305-316.

Díaz-Marín CD, Shetty RM, Cheung S, Vaartstra G, Gopinath A and Wang EN 2021 Rational fabrication of nano-to-microsphere polycrystalline opals using slope self-assembly. *Langmuir* 37(43): 12568-12576.

Eggersdorfer ML and SE Pratsinis 2012 The structure of agglomerates consisting of polydisperse particles. *Aerosol Sci. Technol.* 46(3): 347-353.

Ifijen IH and Ikhuoria EU 2020 Monodisperse polystyrene microspheres:

studies on the effects of reaction parameters on particle diameter. *Tanz. J. Sci.* 46(1): 19-30.

Ifijen IH, Ikhuoria EU and Omorogbe SO 2019a Correlative studies on the fabrication of poly(styrene-methyl-methacrylate-acrylic acid) colloidal crystal films. *J. Dispers. Sci. Technol.* 40(7): 1023-1030.

Ifijen IH, Ikhuoria EU, Omorogbe SO and Aigbodion AI 2019b Ordered colloidal crystals fabrication and studies on the properties of poly (styrene-butyl acrylate-acrylic acid) and polystyrene latexes. In: Srivatsan T, Gupta M (Eds) Nanocomposites VI: Nanoscience and Nanotechnology in Advanced Composites (pp. 125-135). Springer, Cham.

Ifijen IH, Maliki M, Ovonramwen OB, Aigbodion AI and Ikhuoria EU 2019c Brilliant coloured monochromatic photonic crystals films generation from poly(styrene-butyl acrylate-acrylic acid) latex. *J. Appl. Sci. Environ. Manage.* 23(9): 1661-1664.

Ifijen IH and Ikhuoria EU 2019 Generation of highly ordered 3D vivid monochromatic coloured photonic crystal films using evaporative induced technique. *Tanz. J. Sci.* 45(3): 439-449.

Ifijen IH, Omorogbe SO, Maliki M, Odiachi IJ, Aigbodion AI and Ikhuoria EU 2020 Stabilizing capability of gum arabic on the synthesis of poly (styrene-methylmethacrylate-acrylic acid) latex for the generation of colloidal crystal films. *Tanz. J. Sci.* 46(2): 345-335.

Ifijen IH and Ikhuoria EU 2020 Monodisperse polystyrene microspheres: studies on the effects of reaction parameters on particle diameter. *Tanz. J. Sci.* 46(1): 19-30.

Ikhuoria EU, Omorogbe SO, Sone BT, Nuru ZY, Khamlich S and Maaza M 2018 Raspberry-like and other hexagonal close packed morphologies of P(St-MMA-AA) particles obtained from different emulsifiers for photonic applications. *J. Mod. Opt.* 65(15): 1817-1826.

Kovtun ID, Lobanova NA, Andreeva AV, Gomzyak VI, Levachev SM, Gusev SA, Chvalun SN and Gritskova IA 2021 Synthesis of monodisperse polymer suspensions with a narrow particle size distribution in the presence of water-insoluble triple block copolymers of polypropylene oxide and polyethylene oxide (pluronics). *Russ. Chem. Bull.* 70: 1784-1790.

Lee KW and Chen H 1984 Coagulation rate of polydisperse particles. *Aerosol Sci. Technol.* 3(3): 327-334.

Omorogbe SO, Ikhuoria SO**,** Ifijen IH, Simo A, Aigbodion AI and Maaza M 2019 Fabrication of monodispersed needle-sized hollow core polystyrene microspheres. In *TMS 2019 148th Annual Meeting & Exhibition Supplemental Proceedings* (pp. 155-164). Springer, Cham.

Perkins-Howard B, Walker AR, Do Q, Senadheera DI, Hazzazi F, Grundhoefer JP, Daniels-Race T and Garno JC 2022 Surface wettability drives the crystalline surface assembly of monodisperse spheres in evaporative colloidal lithography. *J. Phys. Chem.* 126(1): 505-516.

Rong Q, Zhu A and Zhong T 2011 Poly (styrene-n-butyl acrylate-methyl methacrylate)/ silica nanocomposites prepared by emulsion polymerization. *J. Appl. Polym. Sci.* 120(6): 3654-3661.

Sultan MH, Madkhali O and Almoshari Y 2021 Polymeric lipid hybrid nanoparticles (PLNs) as emerging drug delivery platform-a comprehensive review of their properties, preparation methods, and therapeutic applications. *Pharmaceutics* 13(8): 1291.

Wang M, Meng F, Wu H and Wang J 2016 Photonic crystals with an eye pattern similar to peacock tail feathers. *Cryst.* 6(8): 99.

Zhang S, Zhao XW, Xu H, Zhu R and Gu ZZ 2007 Fabrication of photonic crystals with nigrosine-doped poly(MMA-co-DVB-co-MAA) particles. *J. Colloid. Interface Sci.* 316(1): 168-174.