

Article

Synthesis and Characterization of a Brand-New Linear Hybrid Co-Polymer (Iso-Butyl Methacrylate -CO- Trimethoxy-silyl propyl methacrylate)

Marwan Talib Joudah

General Directorate of Education in Anbar, Gifted Guardianship Committee, Ministry of Education in
Iraq 40 street, Ramadi-Iraq

E-mail: mrwan_talib@yahoo.com

ABSTRACT

The study aimed to synthesize and precisely identify a linear hybrid co-polymer called (iso-BMA-co-TMSPMA) as a bulky gel polymer. Through the free radical polymerization, an organic monomer (iso-butyl methacrylate/iso-BMA) with an inorganic monomer (Trimethoxysilyl) propyl methacrylate) (TMSPMA) were reacted to yield the product. The manufactured silica is used in a variety of processes that can be combined to create hybrid polymers that can rebuild human bones. A Schlenk flask was used to synthesize the hybrid polymer due to its large surface area for well-distributed heat and stress all over the flask. The hybrid polymer, which contains active groups that serve as the polymer's backbone, was successfully synthesized, as evidenced by the ¹H- NMR and ¹³C-NMR peaks that were obtained. FT-IR for the synthesized gelatinous polymer was obtained as well and showed some signals that identified the molecule as it is shown in the discussion section.

KEYWORDS: Polymer, sol-gel, methacrylate, Free radical, Copolymer, Monomer, NMR spectra, IR spectra.

INTRODUCTION

Polymer is increasingly used in pharmaceutical targeting and controlled release systems. Both natural and synthetic sources can be used to synthesize polymers. It serves as a mechanical support for the sustained release of medications as well as a

solubilizer, flavoring agent, and coloring agent¹. Free radical polymerization has been considered among the most important reactions in synthesizing giant molecules. Techniques that have been significantly developed in recent years including atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer (RAFT) polymerization, nitroxide-mediated polymerization (NMP), and RAFT polymerization. These processes can be used to regulate the chain architecture and molecular weight distribution of polymers. Lewis' acids and polar solvents may be used to direct stereo controlled radical polymerization². Solid dosage forms have been coated with polymeric materials to hide the bitter taste of the medication, protect delicate drug components, regulate the release of drugs, and provide the dosage form a pleasing appearance. Evonik Manufacturing in Germany sells a variety of copolymers based on polymethacrylates under the trade name Eudragit³. A work was reported in 2016 by Sushil and Hari included the synthesis of methacrylated glucose hydrogels using the free radical polymerization⁴. In 2017, R. P. Meena and coworkers reported the synthesis of a polymer using Methoxy ethylmethacrylate through the free radical polymerization. The polymer was successfully synthesized and characterized as well⁵. Hydrogels have recently attracted substantial attention. A three-dimensional move-connected polymer network called a hydrogel can adapt to changes in external variables like pH, temperature, ionic strength, electric field, the existence of enzymes, and numerous other variables by expanding or contracting. They can turn soft and elastic when enlarged, similar to the resident tissue exhibiting excellent biocompatibility. These biomaterials are therefore widely used in the unique fields of pharmaceutical and biomedical engineering⁶. On the other hand, in 2012, Sudhakara R. P. and others proposed a simple and effective method, called template polymerization, to manufacture well-defined core-shell nanoparticles^{19,20,21} by using simultaneous polymerization and self-assemble between the components. It has been demonstrated that during template polymerization, both hydrogen bonds and electrostatic interactions can cause the constituent parts to self-assemble into core-shell nanoparticles⁷.

One crucial method for systematically altering the characteristics of polymers is copolymerization. Copolymers containing reactive or useful monomers are becoming more and more significant. Today, several copolymers containing reactive functional groups are being created, examined, and exploited for both their macromolecular and

functional group features⁸. Copolymer synthesis was proposed by Justin J. Chung. Reversible addition-fragmentation chain transfer (RAFT) and group transfer polymerization (GTP) were used in the synthesis of the copolymers 3(trimethoxysilyl)propyl methacrylate and methacrylate to create a brand-new polymer. A novel polymer that differs from the branching and linear varieties that were previously proposed was also produced, and it possesses special features. Through the sol-gel procedure, those polymers were combined with the hybridized second category. The hybridized molecules have been demonstrated to have greater mechanical qualities than

glass and bioactive hybrids in comparison to earlier investigations. Furthermore, osteogenic cells may attach and grow on hybrids. A star polymer based on n-butyl methacrylate has been researched as an alternative to methyl methacrylate copolymers to increase the flexibility of hybrids. The butyl methacrylate-based hybrid was successful in mimicking the mechanical characteristics of trabecular bone⁹.

Because they provide the body with its structural support, guard the soft tissues and inner organs, manufacture white blood cells, and maintain the equilibrium of ionic metals, bones are regarded as the most important tissue in physiology. It is thought that anano molecule of collagen's fiber and (hydroxy apatite HA) based on $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ are responsible for the mechanical properties of bones. The macropore architecture may be used to accomplish the mechanical qualities because the compressive strength of HA metal and the tensile hardness of collagen form a link¹⁰. In 2022, Chiquita Prahasanti and co-workers proposed the use of Methacrylate (PMMA) along with Hydroxyapatite in dentistry. The paper discusses the prospect for using PMMA/HA compound as a biomaterial candidate for the creation of porous trabecular dental implant fixtures¹¹. Tetraethoxysilane (TEOS) and dimethyldiethoxysilane (DMDES) were used to synthesize (PMMA / SiO_2 - CaO) nano compounds in 2009 by Rhee and Kyu-Hyeon (DMDES). Siloxane bonds can develop in two and four dimensions following the sol- gel process. The source of silica was dimethyldithoxysilane. Although fracture toughness, hardness, and the capacity to produce forming ability in simulated bodily fluid all somewhat decreased, it was discovered that there is a noticeable development in fracture hardness (SBF). The reduction in the number of siloxane bonds and the addition of alkyl groups to the silica structure are credited with improving the fracture toughness of sample D while maintaining its capacity to form apatite. The siloxane linkages provide a harsh and

brittle fracture behavior in the nanocomposite. On the other hand, alkyl groups contribute to the crystalline structure of silica¹².

The main object behind conducting this study is to synthesize a linear hybridized co- polymer. Gel polymers are a combination of liquid electrolytes and solid polymers which could be created to maintain the liquid electrolyte's ionic conductivity while obtaining the mechanical qualities of the solid polymer. The bulky gel polymer (iso-BMA-co-TMSPMA) was synthesized using an organic monomer (iso-butyl methacrylate (iso-BMA) with an inorganic monomer (Trimethoxysilyl)propyl methacrylate) (TMSPMA) through the free radical polymerization¹³.

MATERIALS AND METHODS

The polymerization was conducted using a (250 ml) Schlenk flask that provided a wide surface area for a well distributed heat and stress all over the flask. It also possesses a 24/40 mm neck to allow inert gases during the reaction. The linear hybridized co- polymer was synthesized using an organic monomer (iso-butyl methacrylate (iso-BMA) with an inorganic monomer (Trimethoxysilyl)propyl methacrylate) (TMSPMA) in a one pot polymerization technique. In the Schlenk flask, (0.0715 mol, 10.17 mL) of iso-BMA and (0.006 mol, 1.60 mL) of TMSPMA were mixed up followed by the addition of 20 ml of ethanol. The flask was sealed properly, and then (0.5 mL) of benzoyl peroxide was injected under nitrogen gas. Afterward, the flask was placed in an oven for (3hr) at 70 °C to initiate the polymerization. Then, the resulting hybrid polymer was dried out for (14 days) at room temperature to end up with a bulky gel. Figure 1 shows the general equation for the synthesis of the hybridized linear polymer (iso-BMA-co-TMSPMA), while Figure 2 shows the bulky gel polymer (iso-BMA-co-TMSPMA)¹³.

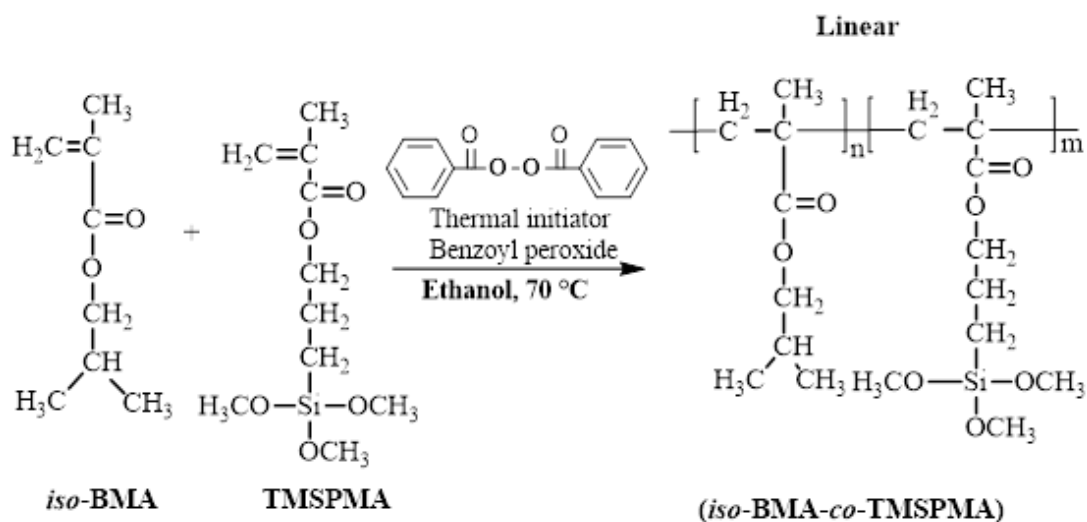


Figure 1: The hybrid linear polymer (*iso*-BMA-co-TMSPMA)

RESULTS AND DISCUSSION

^1H NMR spectroscopy is one the most common and effective methods to use for molecule identification in the field of organic and pharmaceutical molecules. It is also used in the identification of antimicrobial activities of Flavones and Schiff Base'. ^{14}H NMR و ^{13}C NMR for the iso-BMA-co-TMSPMA polymer were ran for (iso-BMA-co-TMSPMA) polymer. The various spectroscopy signals were well assigned, however, ^{29}Si spectra could not be performed through ^{29}Si MAS NMR technique to determine the scaffolds silica nets. All the obtained peaks were corresponded to some primarily studies as well as the order of carbon's atoms. Below are the ^1H و ^{13}C chemical shifts for the hybridized linear polymer (iso-BMA-co-TMSPMA):

Poly(iso-BMA-TMSPMA): ^1H NMR (300 MHz, DMSO, δ , ppm): 6.03-5.67 (H_* , $\text{CH}_2=\text{C}$), 3.90-3.88 (4H_b), 3.31 (9H_c), 1.89 (6H_d), 1.06 (12H_a), 0.93(2H_e).

Poly(iso-BMA-TMSPMA): ^{13}C NMR (300 MHz, DMSO, δ , ppm): 166.46 (3C), 135.97 (2C), 125.41(2C), 69.99 (2C), 55.98 (3C), 27.25(2C), 18.80(4C).

Figure (3) shows the distinguished peaks located close to ($\delta = 6.03, 5.97$ ppm) which refers to the peaks of $\text{C}=\text{C}$ bond protons. It is believed that obtaining these two peaks is due to the existence of moieties of the non-polymerized TMSPMA, which was stated in numerous primely studies ^{15,16}. The chemical shifts ($\delta = 3.90\text{-}3.88$ ppm) is attributed to the (protons of $-\text{OCH}_2-$ group, peak b), while the ($-\text{Si}-(\text{OCH}_3)_3$ peaks -C) were recorded at ($\delta = 3.31$ ppm). Protons of $-\text{CH}_2$ -groups, peak were recorded at $\delta = 1.89$ -d). A peak around ($\delta = 1.06$ ppm- e) was shown for the protons of $-\text{SiCH}_2$ -groups.

The obtained ^1H -NMR peaks showed a success in synthesizing the hybrid-copolymer that contains the active groups which represent the backbone of the polymer as it is

shown in figure (3). While figure (4) shows the ^{13}C -NMR peaks for the same synthesized linear hybridized co-polymer. The (-COO group) shows a peak at ($\delta=166.46$ ppm), and it also shows -SiCH₂- (peak a and b). Along with the ^1H -NMA spectra of the olefins groups, the ^{13}C -NMR peaks $\text{C}=\text{CH}_2$ for the same group at $\text{C}=\text{CH}_2$ for the non-crystallized TMSPMA monomer at (peak 1 $\delta=135.97$ - 125.41 ppm). The chemical shifts for -OCH₂- (peak c) that is located at ($\delta=69.66$ ppm) followed (Si-OCH₃-trimethoxy silane) at ($\delta=55.98$ ppm peak c). As the observed peaks in fig 3, it was revealed that the polymerization initiated from $\text{C}=\text{C}$, and the Si-OCH₃ peaks stayed unchanged.

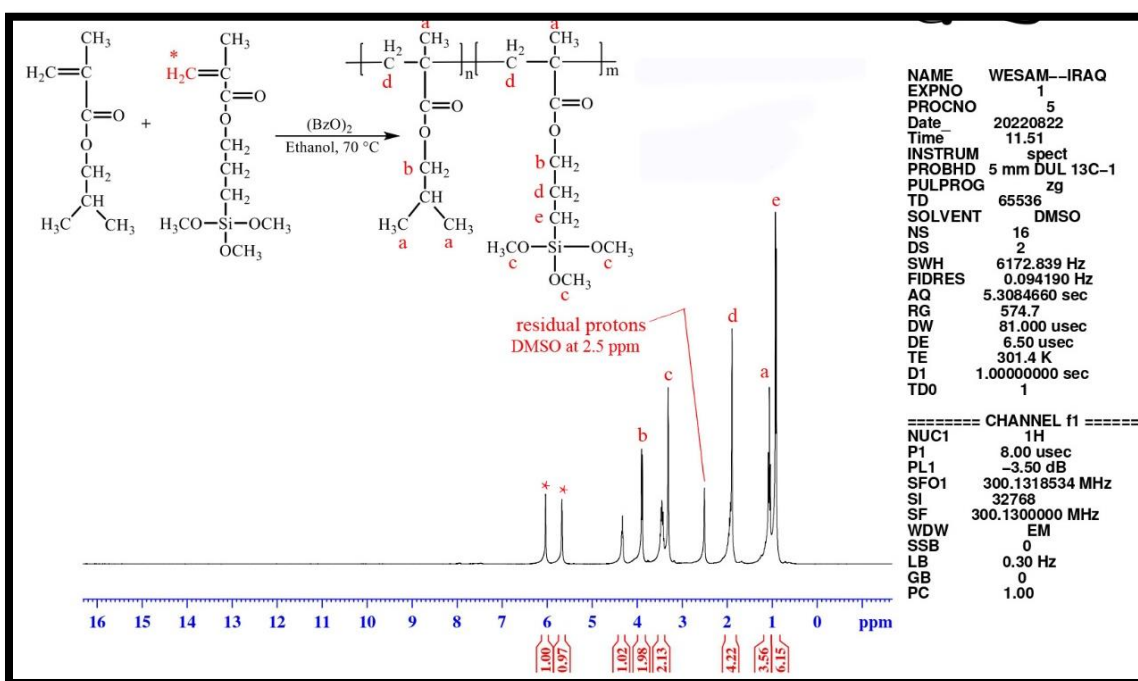


Figure 3: ^1H NMR for (iso-BMA-co-TMSPMA) ¹³

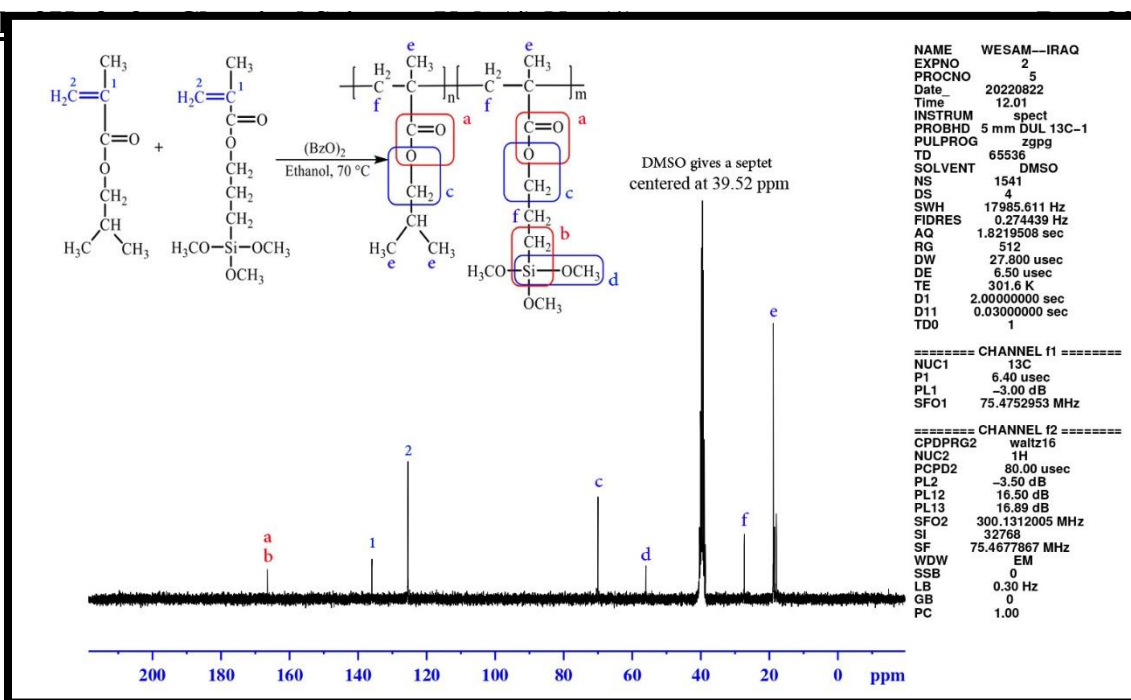


Figure 4: FTIR spectra of the synthesized hybrid copolymers¹³

FT-IR was utilized to identify the *iso*-BMA-*co*-TMSPMA. Even though the discovery of the copolymers is sometimes tough after the polymerization, therefore separating the polymer into two monomers before the polymerization process. Figure 5 shows the FT-IR for the synthesized gelatinous polymer. While table 1 demonstrates the vibration transmissions in the range of the free silanol Si-OH (3849 cm^{-1}) and (3741 cm^{-1}). The first one is for sedimented silanol groups unlike the silanol groups that the signals disappear at. Whereas the second peak refers to the range of the free terminal silanol groups. The FT-IR shows a strong wide (OH- signal) at (3419 cm^{-1}). That signal indicates the existence of high concentrations alcohol in the gelatinous polymer which remained there even with low polymerization temperature¹³.

A weak signal was shown at (2920 cm^{-1}) for the (C-H) of ($\text{CH}_2 - \text{CH}_2 - \text{Si}$). (Si-H) was easily identified that shows at ($2329\text{--}2359\text{ cm}^{-1}$). The weak carbonyl groups signal is shown at (1832 cm^{-1}) which is similar to the spectroscopy of carbonyl groups in anhydrides that contains two carbonyl groups. It was believed that obtaining this signal is due to the presence of numerous carbonyls groups in the polymer that possesses an organic and inorganic monomer. (C=C) signal is shown as a sharp signal which is attributed to the non-crystallized TMSPMA concentrations. The most common signals that show in hard and gelatinous polymers is the scissors-bending of water (H-O-H), which is accompanied to the (O-H starched signal). Most liquids possess a property of light transmission except water because they exhibit intense wide ranges over the

infrared, however, in the under-investigation hybrid polymer, it was shown two weak signals at (554-1516 cm^{-1}). It was obviously noted (CH_3 and CH_2) bent signals at (1424-1454 cm^{-1}) in the hybrid copolymer. The most significant spectral regain is between (1000-1100 cm^{-1}), that shows the appearance of a stretch pattern of (Si-OCH_3) in a single signal at (1043 cm^{-1}) along with the silano group at (3741-3849 cm^{-1}), which indicates that the polymer was successfully synthesized. While the other signals correspond to the bent vibrations of (Si-O and Si-C) at (570-601 cm^{-1}) and (464 cm^{-1}) respectively.

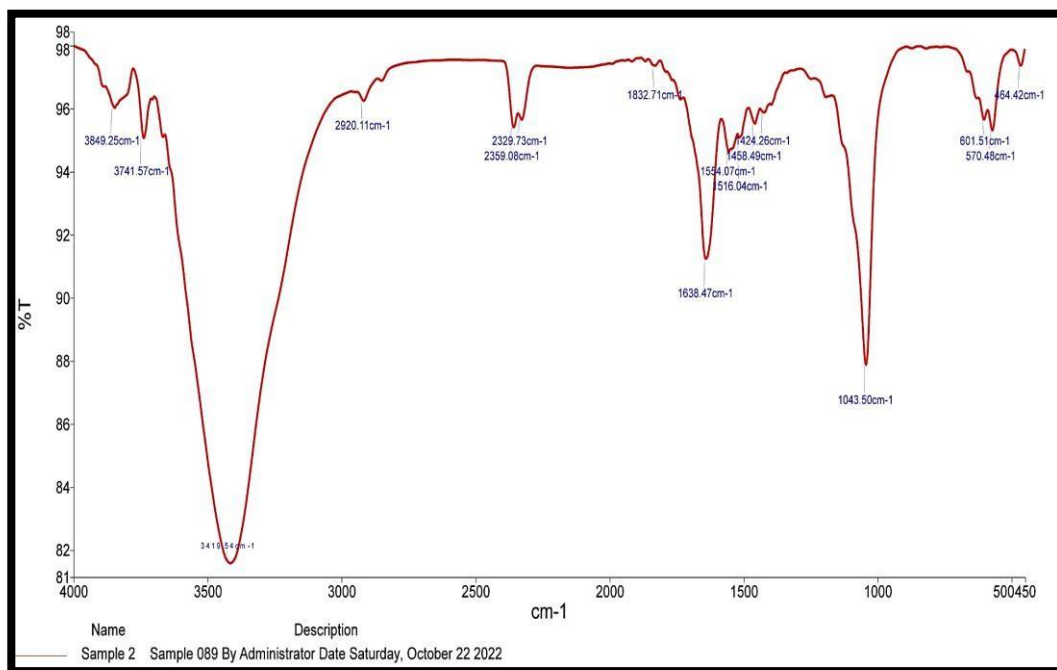


Figure 5: FTIR of (*iso*-BMA-co-TMSPMA) ¹³

Table 1: The vibration transmissions for (iso-BMA-co-TMSPMA)

Description		Wavenumber(cm^{-1})		
		Pure	T%	
			I	II
<i>iso</i> -BMA-co-TMSPMA	ν Si-OH precipitated		3849	
	ν Si-OH terminal	3742	3741	3741
	OH-stretching, strong, broad	3550-3230	3419	3419
	ν CH ₂ (CH....OSi)		2920	2920
	ν Si-H	2100-2360	2329	2359
	ν C=O as anhydride	1800-1840	1832	1832
	ν C=C monosubstituted	1640-1680	1638	1638
	H ₂ O	1365-1545	1516	1554
	CH ₂ bend	1400-1450	1424	1454
	ν Si-OCH ₃	1070	1043	1043
	Si-C	626	601	570
	Si-O	455	464	464

CONCLUSION

(Iso-BMA-co-TMSPMA) as a bulky gel polymer was successfully synthesized and characterized through free radical polymerization. NMR spectra, FTIR spectra and (SEM) images were obtained for the synthesized polymers. Synthetic silica is employed in numerous procedures that can be coupled to produce hybrid polymers that can repair human bones.

CONFLICT OF INTEREST:

The author has no conflicts of interest regarding this investigation.

ACKNOWLEDGMENTS:

I would like to thank everyone who has contributed differently to get this work done successfully. Likewise, a huge thanks to the scientific laboratories in the university of Anbar to allow me to use its laboratories through the work.

REFERENCES

- [1] Nishita Singh, Arun Tiwari, Roohi Kesharwani, Dilip K. Patel. Pharmaceutical Polymer in Drug Delivery[2016] : A Review. Research J. Pharm. and Tech. 9(7):982-994. doi: 10.5958/0974-360X.2016.00188.8
- [2] George W. Handbook of Solvent (2019): Properties 3rd Edition Volume (1), ChemTec Publishing (cP), Toronto.
- [3] Aditi Yadav, Ritesh Kumar Tiwari, Lalit Singh [2023]: Significance of Hydrophobic Polymer in Novel Drug Delivery System. Research Journal of Pharmacy and Technology. 16(1):73-8. doi: 10.52711/0974-360X.2023.00013.
- [4] Sushil Kumar Pandey, Hari Om Pandey [2016]: A novel sugar bis-methacrylate as cross linker: Synthesis and application. Asian J. Research Chem. 9(7): 343-349. doi: 10.5958/0974-4150.2016.00052.
- [5] R. P. Meena, K. Abdul Wasi, K. Anver Basha [2017]: Microbial Screening of Thermally stable N-Vinyl Carbazole-co-Methoxyethyl methacrylate Copolymers: Synthesis and Characterization. Asian J. Research Chem. 10(6):725-731. doi: 10.5958/0974-4150.2017.00123.7
- [6] Ayushmaan Roy. Anjali Wahane, Siddharth Karankal, Prachi Sharma, Daves Khutel, Onkarnath Singh, Vinay Shardul, Pitamber, Nausheen Sabha, Jyoti Dewangan, Ajay Dewangan, Akash Jangde, Chaya Rani, Tekeshwar Sahu, D. K. Tripathi, Mukta Agrawal, Ajazuddin, Gyanesh Sahu, Amit Alexander [2018]: Pharmaceutical Aspects on the Formulations of Hydrogel: An Update. Res. J. Pharma. Dosage Forms and Tech. 10(2): 79-84. doi: 10.5958/0975-4377.2018.00012.5.
- [7] Sudhakara Reddy Pondugula, Nataraj Narra, Sunil J., Srinivas B [2012]: Stable and pH-Responsive Core-Shell Nanoparticles Based on HEC and PMAA Networks via Template Copolymerization. Asian J. Research Chem. 5(1): January.108-115.

- [8]Jyoti Chaudhary, Swati Purohit, Radha Chaudhary [2017]: Studies on Reactivity Ratio and Thermal Studies of Copolymers of N-Substituted Maleimide with Vinyl Pyridine [VP]/2-Hydroxy ethylmethacrylate [OHEMA]. Asian J. Research Chem. 10(3):297-300. doi: 10.5958/0974-4150.2017.00048.7
- [9]Chung, Justin.[2016]: Polymethacrylate based hybrids for bone regeneration through controlled polymerisation (Doctoral dissertation) Department of Materials, Imperial College London.
- [10]Eastoe JE, Eastoe B.[1954]: The organic constituents of mammalian compact bone. J. Biochemical 57(3): 453-459. DOI: 10.1042/bj0570453
- [11]Chiquita Prahasanti, Darmawan Setijanto, Diah Savitri Ernawati, Rini Devijanti Ridwan, David Buntoro, Kamadjaja, Anita Yuliati, Asti Meizarini, Nike Hendrijantini, Agung Krismariono, Shafira Kurnia Supandi, Tania Saskianti, Ratri Maya Sitalaksmi, Djoko Kuswanto, Tansza Setiana Putri, Nastiti Faradilla Ramadhani, Muhammad Dimas Adiya Ari, Alexander Patera Nugraha. [2022]: Utilization of Polymethyl Methacrylate and Hydroxyapatite Composite as Biomaterial Candidate for Porous Trabecular Dental Implant Fixture Development: A Narrative Review. Research Journal of Pharmacy and Technology. 15(4):1863-9. doi: 10.52711/0974-360X.2022.00312
- [12]Lee KH, Rhee SH. [2009]: The mechanical properties and bioactivity of poly(methyl methacrylate)/SiO(2)-CaO nanocomposite. Biomaterials. Jul;30(20):3444-9. doi: 10.1016/j.biomaterials.2009.03.002. Epub 2009 Mar 21. PMID: 19304322.
- [13]Ali ,Sarah Radhi Mohaisen , Thesis Submitted to the Council of the College of Education for Pure Sciences, University of Anbar,2022.
- [14]Anita, Priyanka Ghanghas, Kavita Poonia. [2022]: Synthesis, Characterization, UTI and Antibacterial Activity of Schiff Base, (E)-2-(decan-2-ylidene) hydrazine-
- [15]-carboxamide Co²⁺, Mn²⁺ and Fe³⁺Metal Complexes. Asian Journal of Research

in Chemistry. 15(2):145-0. doi: 10.52711/0974-4150.2022.00023

[16]

[17]Hench LL, Jones JR [2005]: Biomaterials artificial organs and tissue engineering.

a. CRC press, Woodhead, Boca Raton, Cambridge.

[18]Mahony O, Jones JR. [2008] : Porous bioactive nanostructured scaffolds for bone regeneration: a sol-gel solution. Nanomedicine(Lond). 3(2) : 233-245. doi: 10.2217/17435889.3.2.233.

[19]Suresh Dhanaraj, P. Bharathiraja, R. Dhandapani , R. Subbaiya, A. K. Kathiresha. [2018] :Biosynthesis and Characterization of Silver Nanoparticles from *Aspergillus niger* and its Antibacterial Activity. Research J. Pharm. and Tech. 11(12): 5282-5286. doi: 10.5958/0974-360X.2018.00962.9

[20] N'diaye M, Pascaretti-Grizon F, Massin P, Basle MF, Chappard D. [2012]: Water Absorption of Poly(methyl methacrylate) Measured by Vertical Interference Microscopy. Langmuir 28(31); 11609-11614.