University Grants Commission

(Ministry of Human Resource Development, Govt. of India)

Bahadurshah Zafar Marg, New Delhi – 110002

PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

For the Time Period (01st July 2015 – 30th June 2018)

1.	Title of the Project	**GREEN CHEMISTRY ON CONTINUOUS FLOW REACTOR SUPPORTED WITH PALLADIUM AND METAL OXIDE NANOCATALYST**
2.	NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR	**Dr. RENJIS T. TOM,** Assistant Professor, Department of chemistry, St. Joseph's College (Autonomous) Devagiri, Medical College P.O.,Calicut- 673008. Kerala , 8078342721, renjis1@gmail.com
3.	NAME AND ADDRESS OF THE INSTITUTION	THE PRINCIPAL, ST. JOSEPH'S COLLEGE (AUTONOMOUS) DEVAGIRI, MEDICAL COLLEGE P.O.,CALICUT- 673008. KERALA
4.	UGC APPROVAL LETTER NO. AND DATE	**UGC-MRP-MAJOR-CHEM-2013-25352** **(1)Ref: F.No.43-207/2014(SR) Major Research Project, Dated, 22.8.2015** **(2)Ref: F.No.43-207 /2014(SR) Major Research Project, Dated, 28.8.2017** **(3)Ref: F.No.43-207 /2014(SR) Major Research Project, Dated,07.12.18**
5.	DATE OF IMPLEMENTATION	**24th November 2015**

6.	TENURE OF THE PROJECT	**3 years (from 01st July 2015 to 30th June 2018)**
7.	TOTAL GRANT ALLOCATED	**Rs.8,03,000/-**
8.	TOTAL GRANT RECEIVED	**Rs.7,87,000/-**
9.	FINAL EXPENDITURE	**Rs.7,81,575/-** **[Rs. 40,245/- is refunded to UGC on 09/11/2018 as per (3)Ref: F.No.43-207 /2014(SR) Major Research Project, Dated,07.12.18]**
10.	TITLE OF THE PROJECT	**GREEN CHEMISTRY ON CONTINUOUS FLOW REACTOR SUPPORTED WITH PALLADIUM AND METAL OXIDE NANOCATALYST**

SECTION 11 & 12

# OBJECTIVE OF THE PROJECT AND DETAILS OF THE OBJECTIVES ACHIEVED

S. No	Objectives of the proposal during submission	Achieved Yes/No	Reason/Details	Time Expected to Achieve the Target
1	Optimization and Synthesis of Nano catalyst	Yes	(1)12-TPA/SiO$_2$ (2)ZSM-5	Done
2	Characterizations of Catalyst (1)12-TPA/SiO2 (2)ZSM-5	Yes	(1)TEM, XRD (2)SEM, FTIR,XRD	Done
3.	Process Optimization with Nano catalyst (1)12-TPA/SiO$_2$ (2)ZSM-5	Yes	(1)1,4-dihydro pyridines (2)2-aryl-4,5-diphenyl imidazole	Done
4	Design of Flow Reactor	Yes	One PFR/ Two CSTR system with Temperature control System / three Dispensing pump	Done
6	Installation of Flow Reactor Set Up	Yes	PFR (SS,L=13.40 cm, SS, L=30.48 cm, Glass Tube, L= 36 cm, Glass Coil L=72 cm) Two CSTR (2L), 3 Peristaltic pumps, Tubing (Silicon or Viton)	Done

| 7	Process optimization for Non catalytic Reaction
	    (1) Aqueous /thermal
	    (2) Aqueous /sonochemical
	    (3) Organic/thermal
	    (4) Organic/sonochemical
		Yes	Thermal and sonochemical reactions performed for aqueous as well as the organic phase with in a temperature range up to 110 $^{\mathrm{o}}$C, the organic reactions performed with viton tube, while aqueous reactions performed With silicone	

8	Process optimization for Nano- catalytic Reaction	No	Catalytic bed induces an impedance in the flowing of liquid, without back pressure regulator it is difficult to conduct the process. [As per fund sanctioned by UGC we received only one third of the proposed amount. Pumping system with back pressure regulators is unaffordable with current fund]	Hope fully with in a year with support of other funds.
9.	Process optimization with green chemistry	No	Reaction carried out in aqueous/aqueous organic phase. Still reactions carried out in Homogeneous phase. Therefore process is in a full green protocol is not achieved.	31/12/19

10	Reproducibility and Repeatability of process in wide concentration window	No	Lack of time and manpower. The project is not supported with a fellow to carry out the work. The entire work which has been done by Postgraduate Project Students. This creates time delay in executing the project	31/03/20
11	Seminar / Research Paper presented from the project at **Farooq College, (Autonomous), Kozhikode, Kerala**	Yes	Nanocrystalline Heirarchical ZSM-5 Catalyzed Hantzch Dihydropyridine synthesis using sonochemical Reactor Renjis T. Tom, Anjali Jose, Priyanka K. J, Deepa Krishnan Page No. 116, Proceedings International Conference on Emerging Frontiers in Chemical Science, ISBN No.978 -93-5279-617-5	23/09/2017 25/09/2017
12	Invited Talk based on the project at **Christ College (Autonomous) Irinjalakuda, Kerala**	Yes	National Seminar on Design Strategies on Functional materials, Delivered lecture on "Design And Installation of Continuous Flow Reactor For The Synthesis And Scale Up Of Chitosan Graft Copolymers	16/10/2018
13	Publications based on project	Under Processing	Awaiting for more reproducible results	01/07/2019
14	Patents based on project	Under Processing	Awaiting for more reproducible results	31/12/2019

SECTION 13
ACHIEVMENTS OF THE PROJECT
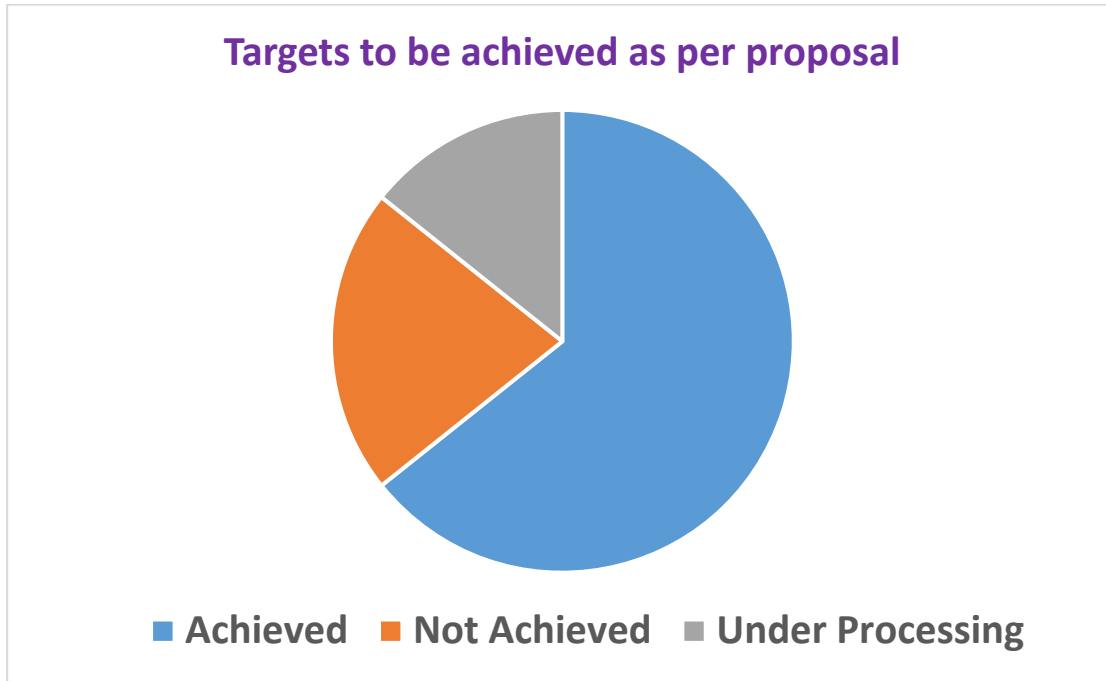
Figure 1: The pie diagram represents percentile of each objective achieved.
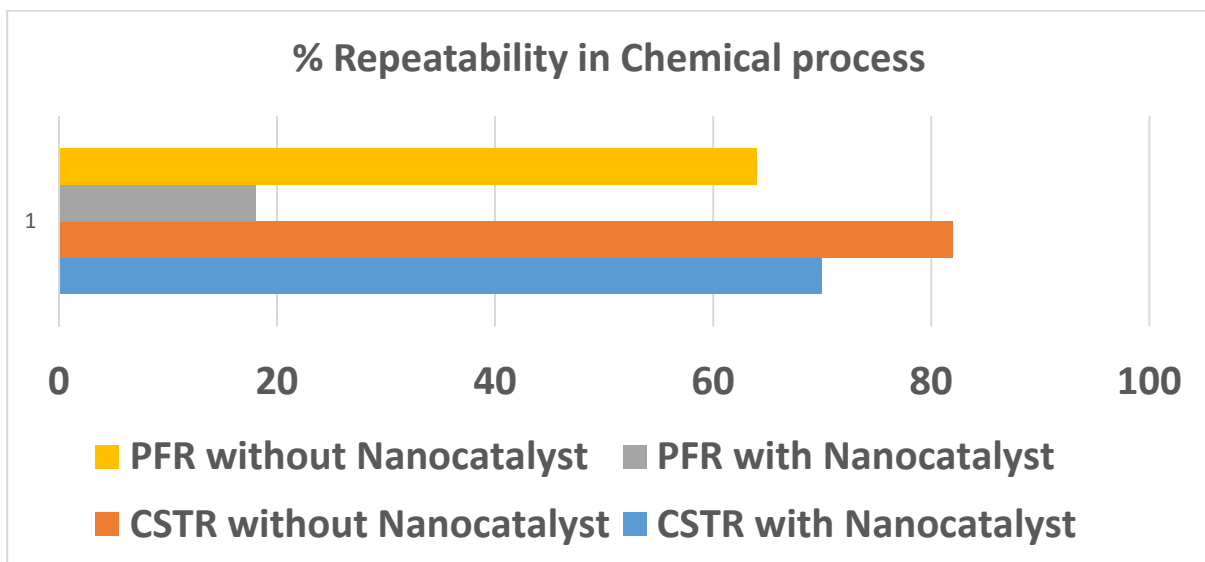
Figure 2: Percentile repeatability of chemical reactions carried out as per project.

As per above bar diagram It is indeed a fact that 80% of the work, which is proposed in the submitted proposal has been accomplished. Still it is a fact that, work has to reach to the level of publication, also the inventions should be patented. The process optimization has been done effectively, with aqueous phase homogeneous phase reaction. The incorporation of 2 CSTRs, 4 PFRs and 3 pumps, which can connected in any design. This flexible design can be altered according to the situations of the reaction. Longer BT300-2J - Medium Flow Rate Peristaltic Pump, The pump provides flow rates from 0.07mL/min to 1140 mL/min. This pump can work in both clockwise and counter-clockwise direction. This enables bidirectional pumping. The pumping system has a capability of mass transfer wide range. Both CSTR and PFR controlled with thermocouple and temperature controller unit. It is indeed that reactor set up has effective control over heat transfer and mass transfer. The thermocouple device enables the measurement input and output temperature and effective calculation of ΔT. With high performance pumping and heating system, along with chemically resistant tubing such as Viton or Silicon the potential of the set-up is marvellous. The incorporation of SONIC ultrasound probe with 20kHz frequency and 750 Watts Power to the flow reactor system is value adding. This enables the possibility of sonochemical flow reaction. Sonochemical flow reactions are more effective than sonochemical batch reaction due to effective heat exchange. Those targets such sonochemical flow reaction using nanocatalyst has to be achieved.

SECTION 14

SUMMARY OF THE FINDINGS

STATITICAL ANALYSIS ON FLOW PROCESS: MASS TRANSFER, HEAT TRANSFER AND COVERSION EFFICIENCY.

So far we have dealt with isothermal chemical reactors and were able, by using only as many species mass balances as there are independent reactions to relate reactor size, inlet and outlet composition. However, even for isothermal reactors we need the energy balance to determine what heat duty is necessary in order to keep the reactor isothermal. For nonisothermal reactors (adiabatic and nonadiabatic) we need the energy balance together with the mass balances in order to arrive at reactor design equations. The energy balance is the principle of conservation of energy or the first law of thermodynamics as applied to our reaction system. The measurement and control of polymerization reactors is very demanding due to the intricacy of the physical mechanisms and chemical kinetics. In these reactors many significant variables, which are linked to end-use material properties, cannot be calculated on-line or can only be restrained at low sampling frequencies. Furthermore, end-use material properties are associated to the whole molecular weight, copolymer composition, sequence length, and branching allocations. This work surveys capably of mass transfer and heat transfer controlling instrumentation, which are of uniquer interest in chemical reactors with prominence on, for instance, measurement of physicochemical features of the reactants and solvent.

The conservation equation requires:

$$(1) \quad \begin{pmatrix} \text{Rate of} \\ \text{input} \end{pmatrix} - \begin{pmatrix} \text{Rate of} \\ \text{output} \end{pmatrix} + \begin{pmatrix} \text{Rate of} \\ \text{generation} \end{pmatrix} = \begin{pmatrix} \text{Rate of} \\ \text{accumulation} \end{pmatrix}$$

Apply it to the energy, the control volume being the <u>total volume</u> of the reaction mixture in the reactor.

The energy per unit mass of the inlet stream may have different forms:

$$\underline{E} = \underline{KE} + \underline{PE} + \underline{u} + \underline{O}$$

$$(2) \quad \begin{pmatrix} \text{Energy} \\ \text{per unit mass} \\ \text{of a stream} \end{pmatrix} = \begin{pmatrix} \text{Kinetic} \\ \text{energy per} \\ \text{unit mass} \end{pmatrix} + \begin{pmatrix} \text{Potential} \\ \text{energy per} \\ \text{unit mass} \end{pmatrix} + \begin{pmatrix} \text{Internal} \\ \text{energy per} \\ \text{unit mass} \end{pmatrix} + \begin{pmatrix} \text{Other} \\ \text{energy per} \\ \text{unit mass} \end{pmatrix}$$

Among other, energy forms may be surface energy (not important in homogeneous flow), magnetic energy, electric energy, etc

$$(3) \quad \begin{pmatrix} \text{Rate of energy} \\ \text{input} \end{pmatrix} = \begin{pmatrix} \text{Rate of energy input by} \\ \text{flow of material streams} \end{pmatrix} + \begin{pmatrix} \text{Rate of heat addition} \\ \text{from the surroundings} \end{pmatrix}$$

$$(4) \quad \begin{pmatrix} \text{Rate of energy input or output by} \\ \text{flow of material streams} \end{pmatrix} = \left(\text{Mass flow rate}\right)\left(\text{Energy per unit mass}\right)$$

For reactions in nonisothermal systems, the thermal time distribution is the analog of the residence time distribution.

$$\frac{dn_i}{dt} = R_{p,i}\,dV_R$$
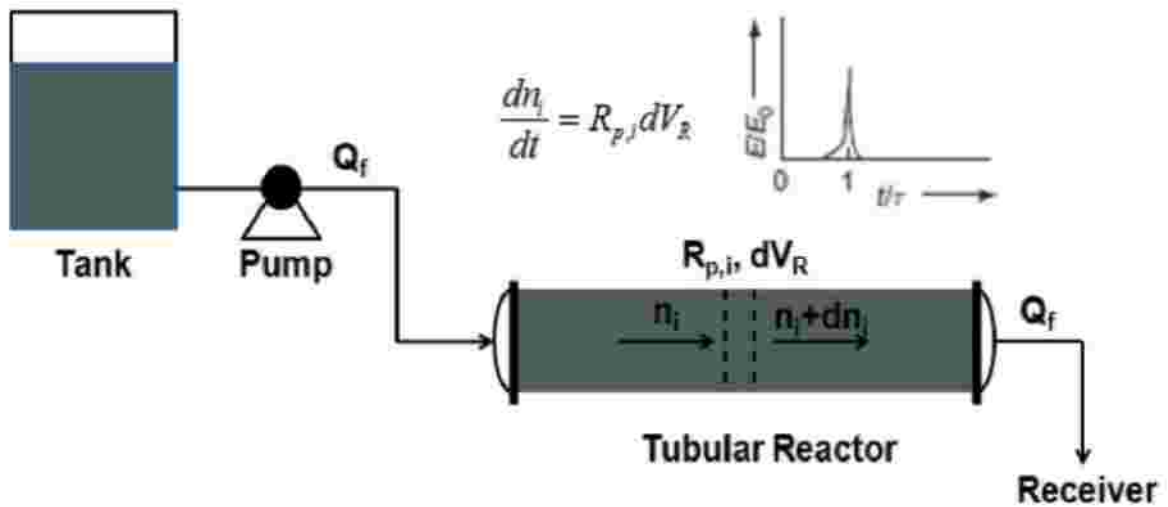
Figure 1. Schematic Representation of Space Time Behaviour of PFR [1]

$$\frac{d(VC_i)}{dt} = Q_f C_{i,f} - QC_i + VR_{p,i}$$
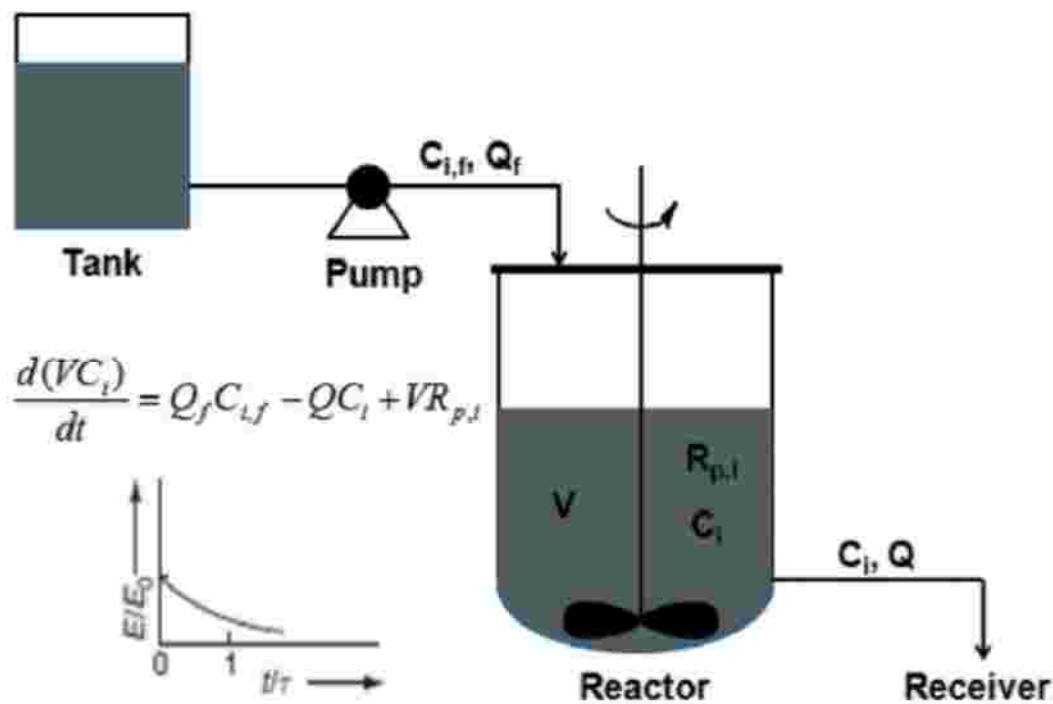
Figure2. Schematic Representation of Space Time Behaviour of CSTR [1]

Residence time distribution (RTD) and concentration profiles of ideal reactors. The symbols t, τ, l, and L represent the reaction time, residence time, location inside the reactor, and total length of the tubular reactor, respectively. E/E0 and [M] represent the fraction of the reaction mixture having residence time between t and (t + dt) and the concentration of a reactant, respectively.

In order to extend raise the throughput and thus the production capacity of the tubular PFR system, either a multiple of the reactor channels in parallel, or an even larger tube diameter than 1 cm ID has to be used, or a combination of both. The first is based on a concept, commonly termed ''numbering-up'' which has been discussed in numerous publications and books,[2-4] and is a very efficient way to scale-up a process without having to redesign the equipment, as all flow characteristics stay constant. In the second case, when increasing the tube diameter of the flow reactor, static mixer inserts can be introduced in order to avoid negative effects from axial dispersion, which were already observed herein, when increasing the tubular id from 1.0 to 2.2mm. We are currently investigating both concepts.

Flow Synthesis of methyl 2- azidoacetate

NaN_3 (1.5 eq) was added to a stirred solution of methyl2-bromoacetate (1.0 eq)in a 150cm^3 acetone /water mixture (1:3). The resulting suspension was stirred at room temperature for 6 hours. It was conducted in flow reactor where one end of the pump is connected to acetone/water mixture and other end of the pump to the reactors i.e. NaN_3 and methyl 2-bromoacetate in Sonicator. There are two peristaltic pumps in a flow set up, one has to be maintained in clockwise direction and the other has to be in anti-clockwise direction. One end of a tube from each peristaltic pump is immersed into first beaker and other end to second beaker.

Acetone was removed from the system using rotovaporator. Then DCM was added to the mixture and the organic layer was separated. The aqueous layer was extracted with 3x10 cm^3 aliquots of DCM and the combined organic layer was dried over sodium sulphate. Solvent was removed under reduced pressure and the azide was sufficiently pure to use without further workup. In this reaction, 2-bromo methyl acetate (1.82131g) is reacted with sodium

azide (7.582g) in acetone/ water mixture (1:3). This reaction is carried out for 6 hours in flow reactor at room temperature Sodium azide is a good nucleophile, so it displaces bromide and gives the corresponding organoazide. The azide group is characterized by the asymmetric stretching frequency at 2100cm^{-1}. The band at 1710 is due to the C=O stretching vibration. The C-O stretch occurs in two or more bands, stronger and broader than other, occur at 1010 and 1210 respectively. The C-H stretching frequency (usually occurs in the range 2800-3200cm^{-1}) is shown by the peaks at 2990. The peak at 1430cm^{-1} indicates C-N stretching vibration. The reaction repeated 32 times. The mean yield observed is 68.25%, with a standard deviation 5.28%.(Supporting Information)
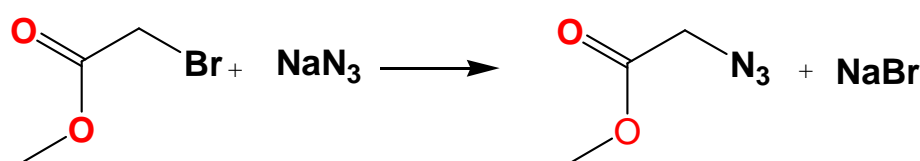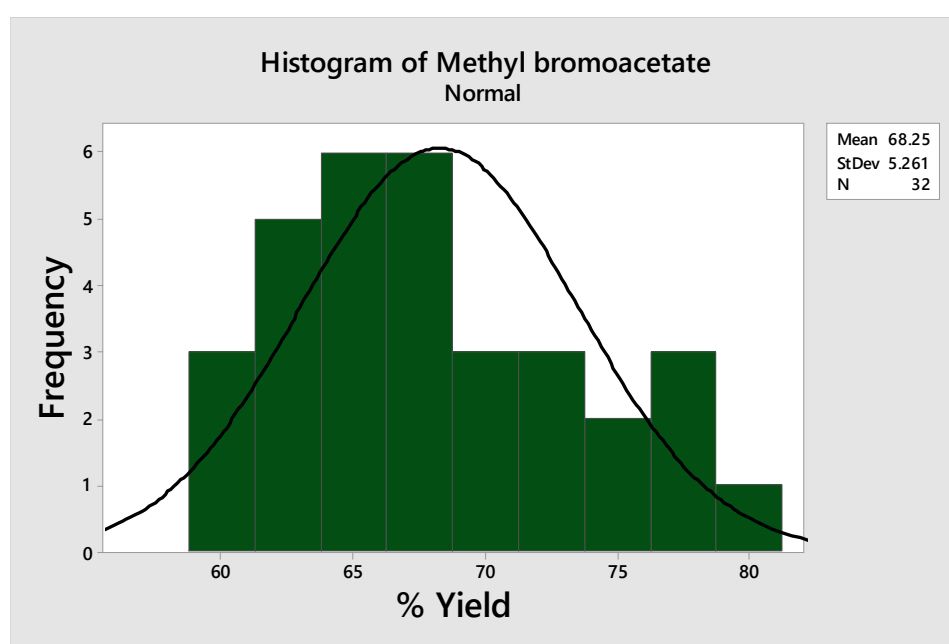
Figure 3. The Histogram me represents the conversion efficiency of continuous flow reactor.

Reaction between 1-bromohexane and sodium azide using C-TAB as a surfactant

The reaction was conducted between 1-bromohexane (1.8213 ml), sodium azide (7.582g) and cetal trimethyl ammonium bromide (C-TAB) in tetrahydrofuran (THF)/ water mixture (1:3). It is stirred for 6 hours in flow reactor at room temperature. After the reaction, DCM was added to the mixture and the organic layer was separated. The organic layers were dried over sodium sulphate. Solvent was removed under reduced pressure in rotovaporator, and the

product 1-azidohexane was obtained as colourless liquid. The product obtained was identified by comparing its infrared spectrum with those in literature data. The flow reaction monitored 32 times and calculated the yield of hexyl azide. The mean yield observed is 69.09%, whith a standard deviation of 5.32%.

Histogram of Bromohexane
Normal

Mean	69.09
StDev	5.532
N	32

$$C_5H_{11}\!-\!Br + NaN_3 \longrightarrow C_5H_{11}\!-\!N_3 + NaBr$$

Histogram of Bromooctane
Normal

Mean	63.50
StDev	4.992
N	32

$$C_7H_{15}\!-\!Br + NaN_3 \longrightarrow C_7H_{15}\!-\!N_3 + NaBr$$
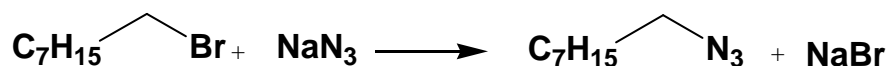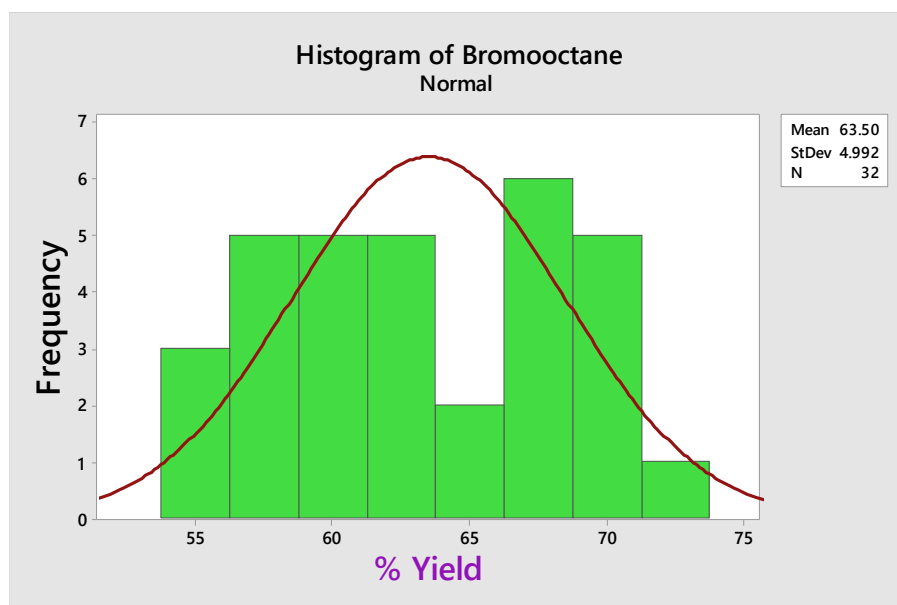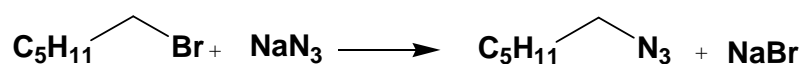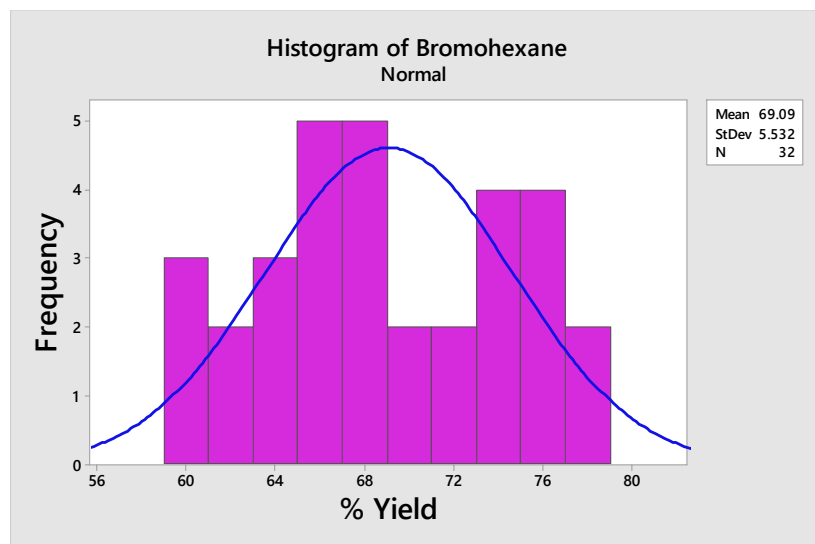
Figure 4: Histograms depicts the conversion efficiency of flow reactor at various 32 time intervals. The variation in yield observed due to the difference in conversion efficiency of improvised flow reactor at various time intervals.

The band at 2010cm^{-1} is due to asymmetric stretching of the azide group. The symmetric stretching is characterized by the peak at 1270cm^{-1}. The C-H stretching frequency is shown by the peaks at 2920, 2850cm^{-1}. The C-N stretching vibration occurs at 1470cm^{-1}. The C-C stretch occurs as less intense peaks below 1200cm^{-1}.Similar methodology applied for synthesys of azido octane.After the reaction, DCM was added to the mixture and the organic layer was separated. The organic layers were dried over sodium sulphate. Solvent was removed under reduced pressure , and the product 1-azidooctane was obtained as a colour less liquid in good yield. The product obtained was identified by comparing its infra-red spectrum with those in literature data The azide group is characterized by the asymmetric stretching frequency at 2095.66cm^{-1}, the symmetric stretching frequency at 1260.03. The C-H stretching frequency (usually occurs in the range 2800 – 3200cm^{-1}) is shown by the peaks at 2961.53, 2928.49, 2856.98cm^{-1}. The peak at 1465.47 indicates C-N stretching vibration. The C-C stretch occurs as weak peaks in the range 1200-800cm^{-1}. (Supporting Information)

Residence Time Distribution (RTD)

Longer BT300-2J - Medium Flow Rate Peristaltic Pump, The pump provides flow rates from 0.07mL/min to 1140 mL/min. A tubular plug flow reactor is achieved by attaching the Viton or silicon tube to SS or Glass PFR, reactants are fed continuously into the reactor via peristaltic pump from CSTR, while the products and unreacted reactants are removed continuously from the reactor automatically and drained into settling tank. The product in the clarified settling tank kept for precipitation. The RTD of an ideal tubular reactor is a function of space time(τ). One of the biggest advantage of a PFR is the excellent heat transfer due to its large heat exchange surface area-to fluid volume ratio.

Space time τ = Total length of cylindrical pipe (L cm) /Fluid velocity (ν cm/s)

= L/ν seconds

ν = Flow rate/ cross sectional area = F cm^3/s /πD^2/4 cm2 = 4F/πD^2 cm/s

τ = L / { 4F/πD^2} = πD^{2}L/4F s
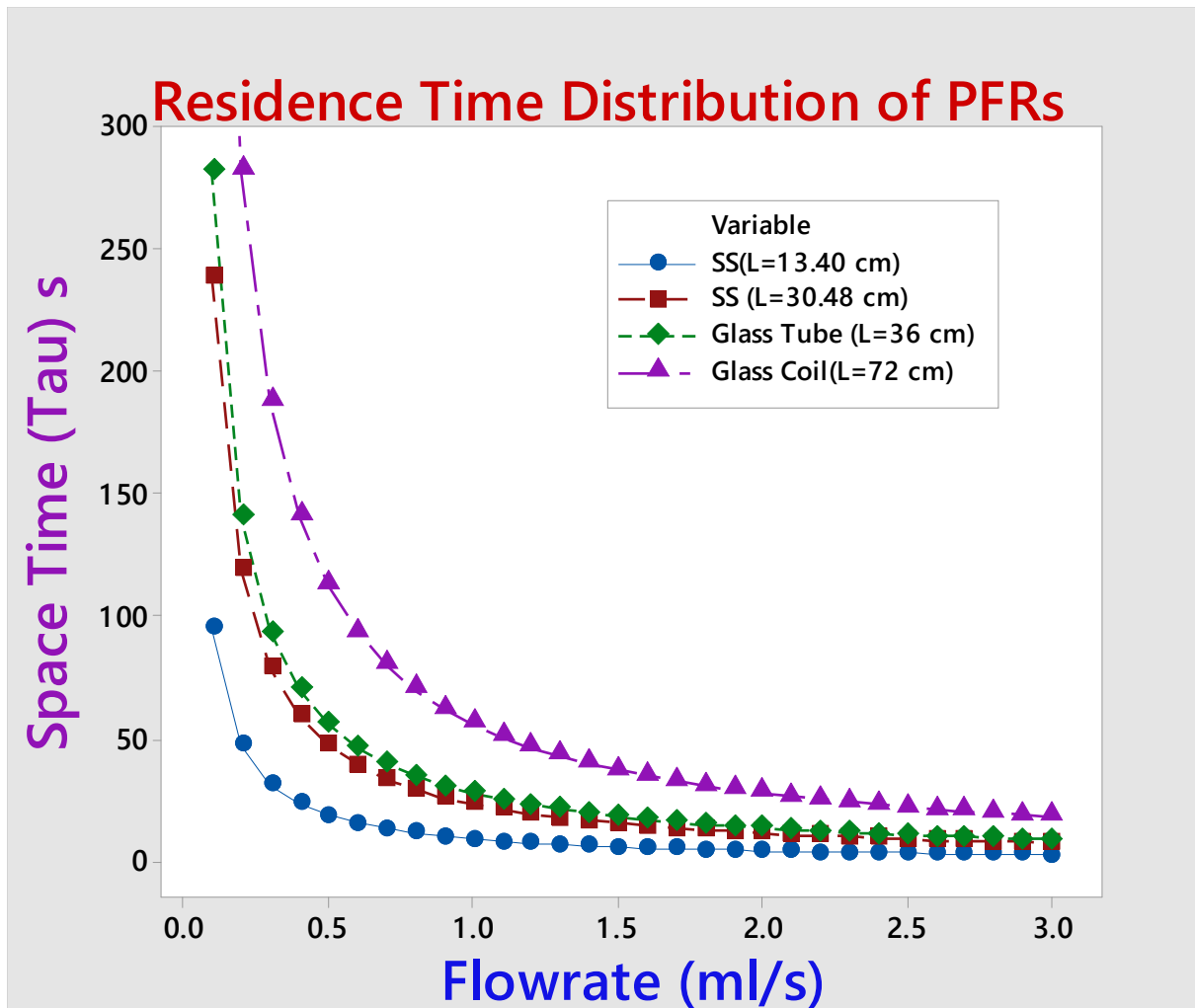
Figure 5: Schematic representation of the behaviour of space time (τ) vs flow rate in various PFRs such as (SS, L=13.40 cm, SS, L=30.48 cm, Glass Tube, L= 36 cm, Glass Coil L=72 cm). The cure shows that flow rate less than 1ml s is the optimum RTD condition for all the reactors mentioned above.
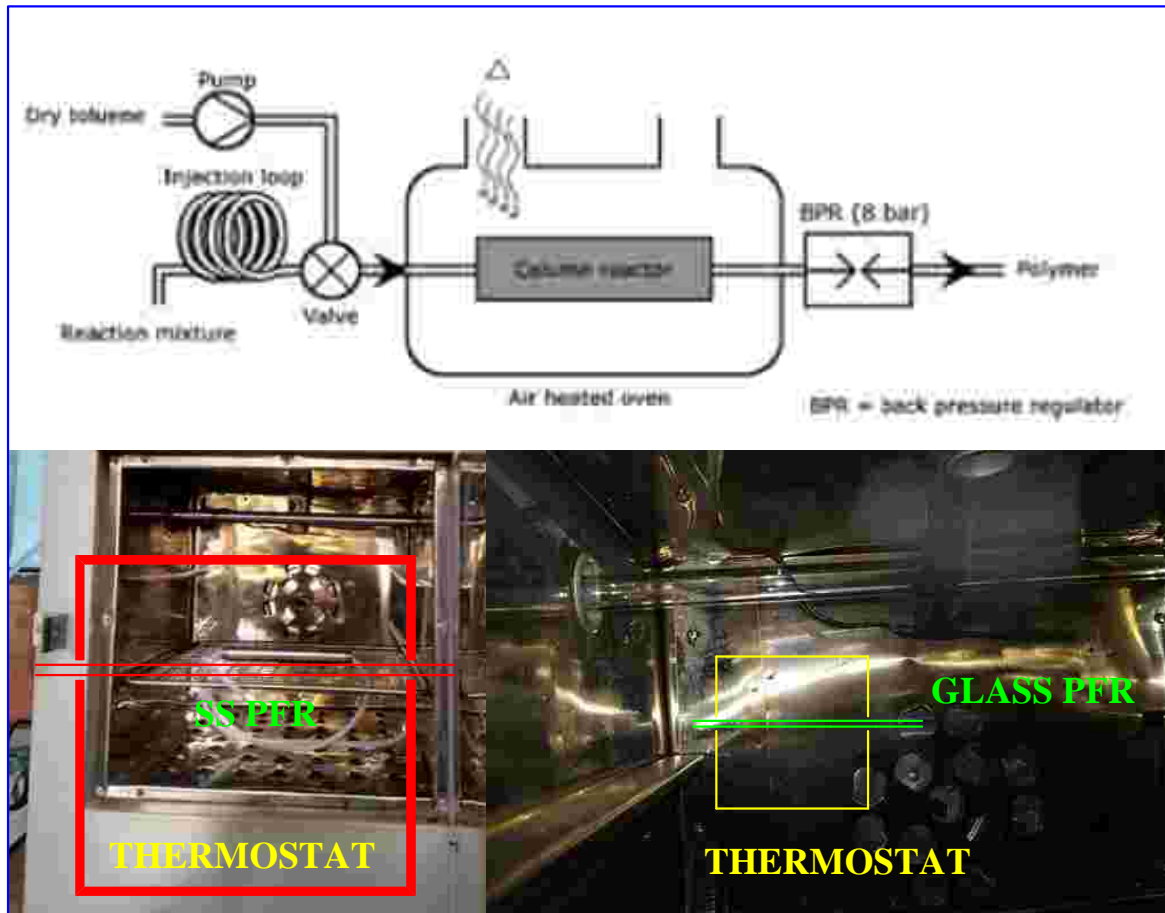
Figure 6: Our design of keeping the PFR inside the thermostat is based on work by François Grenier et al [5]. SS PFR and Glass Tube PFR is shown in the image.

Q = Flow rate X Cp of Water X (Tw-To)

= F ml/s X Cp X ΔT K   = Fρ g/s X 4.186 joule/gram K^{-1} X , ρ is density   = 4.186 F ρ ΔT J /s

Q $_{total}$ = 4.186 F ρ ΔT   J /s X $\pi D^2 L/4F$ =4.186 /4 $\pi D^2 L \rho$ ΔT   J /s =1.0465$\pi D^2 L \rho \Delta T$ J

As D=1, ρ =1, the equation will transform to **Q $_{total}$ = 1.0465$\pi L \Delta T$ J =3.286 LΔT J**

Internal contact area of SS cylinder =πDL cm^2

Total heat transfer per unit area per time = Qτ/Aτ =Q/A J/s cm2 = Q/A W/ cm2

=(4.186 F ρ ΔT   W) / (πDL cm^2) = 4.186 F ρ ΔT/ πDL W/cm^2

Heat flux for cylindrical SS reactor per m^2 surface area is ϕ_1 W/m^2

$$\phi_1 = 4.186 \text{ X } 10^4 \text{ F } \rho \text{ } \Delta T / \pi DL \text{ W/m}^2$$

Heat flux or thermal flux, sometimes also referred to as heat flux density or heat flow rate intensity is a flow of energy per unit of area per unit of time. In SI its units are watts per square metre ($W \cdot m^{-2}$)
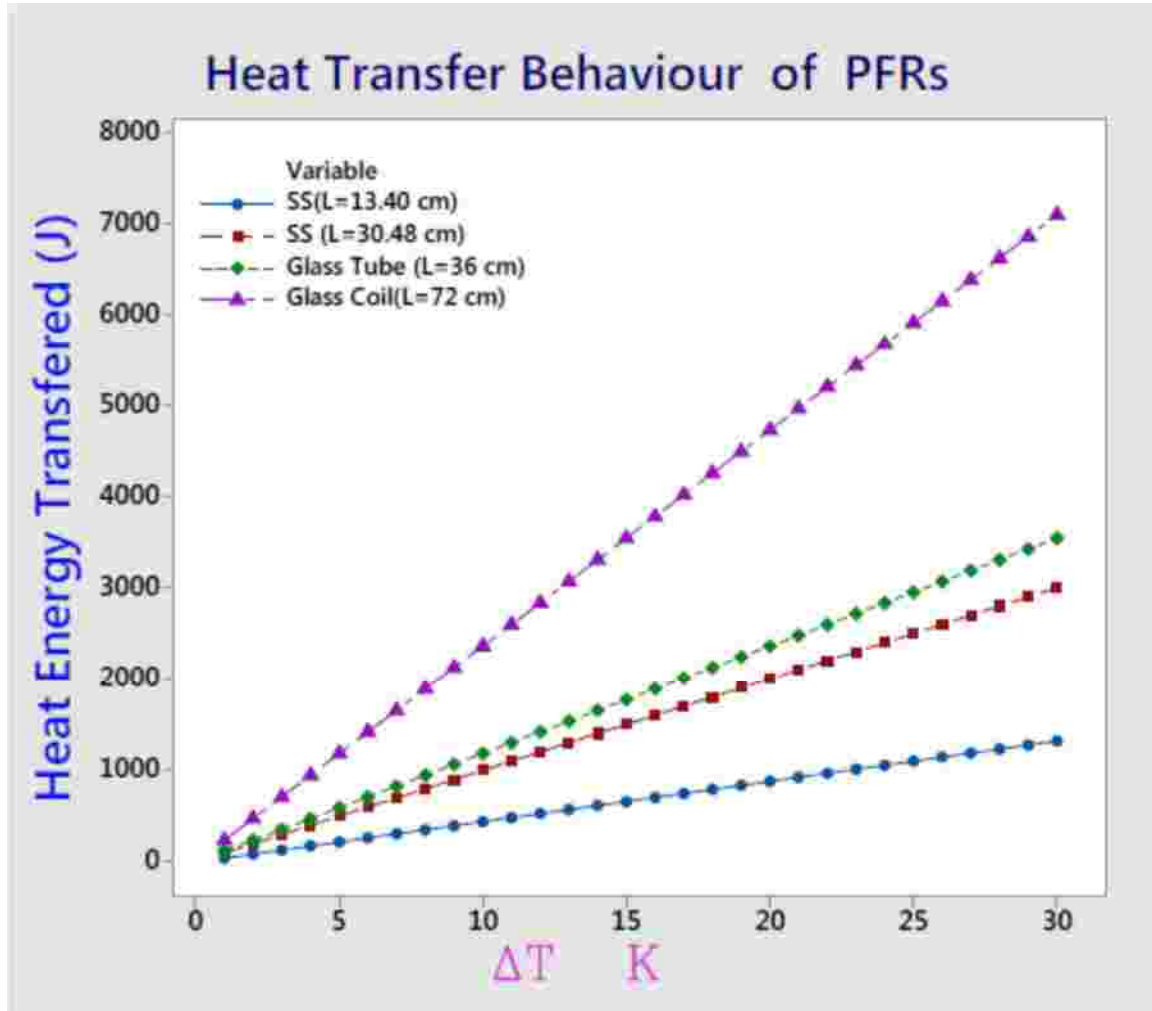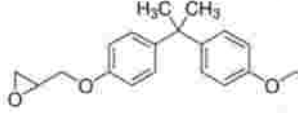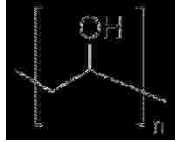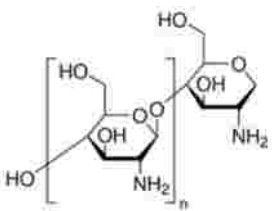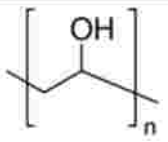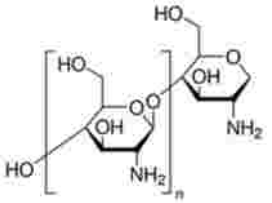
Figure 7: Heat Energy Transferred to the 1ml of water flowing through the reactors of having length L=13.40 cm, 30.48 cm, 36 cm and 72 cm (Q=3.26 L ΔT Joules)

MASS TRANSFER PROPERTIES

The plot of mass flux vs flow rate of each component is studied to understand the conversion efficiency of each component [6-9]

chemical	MOLECULAR STRUCTURE	Weight per ml in water g/ml	Mass flux g/m²s	Space Time τ sec.	Heat Flux ϕ_q W/m²
SYSTEM A					
BPDGE		0.016571	16.57143	239.268	935.1091
PVA		0.047619	47.61905	239.268	935.1091
CHITOSAN		0.004762	4.761905	239.268	935.1091
	TOTAL SOLUTE	0.068952	68.95238	239.268	935.1091
SYSTEM B					
GLUTERAL		0.005048	5.047619	239.268	925.0135
PVA		0.047619	47.61905	239.268	925.0135
CHITOSAN		0.004762	4.761905	239.268	925.0135
	TOTAL SOLUTE	0.057429	57.42857	239.268	925.0135

Table 1. The parameters of blending done in a cylindrical flow reactor ID=1 cm, L=30.48 cm, Flow rate is 0.1 ml/s, Tw =100ºC, T i=80ºC,ΔT = 20K, solvent deionized .water
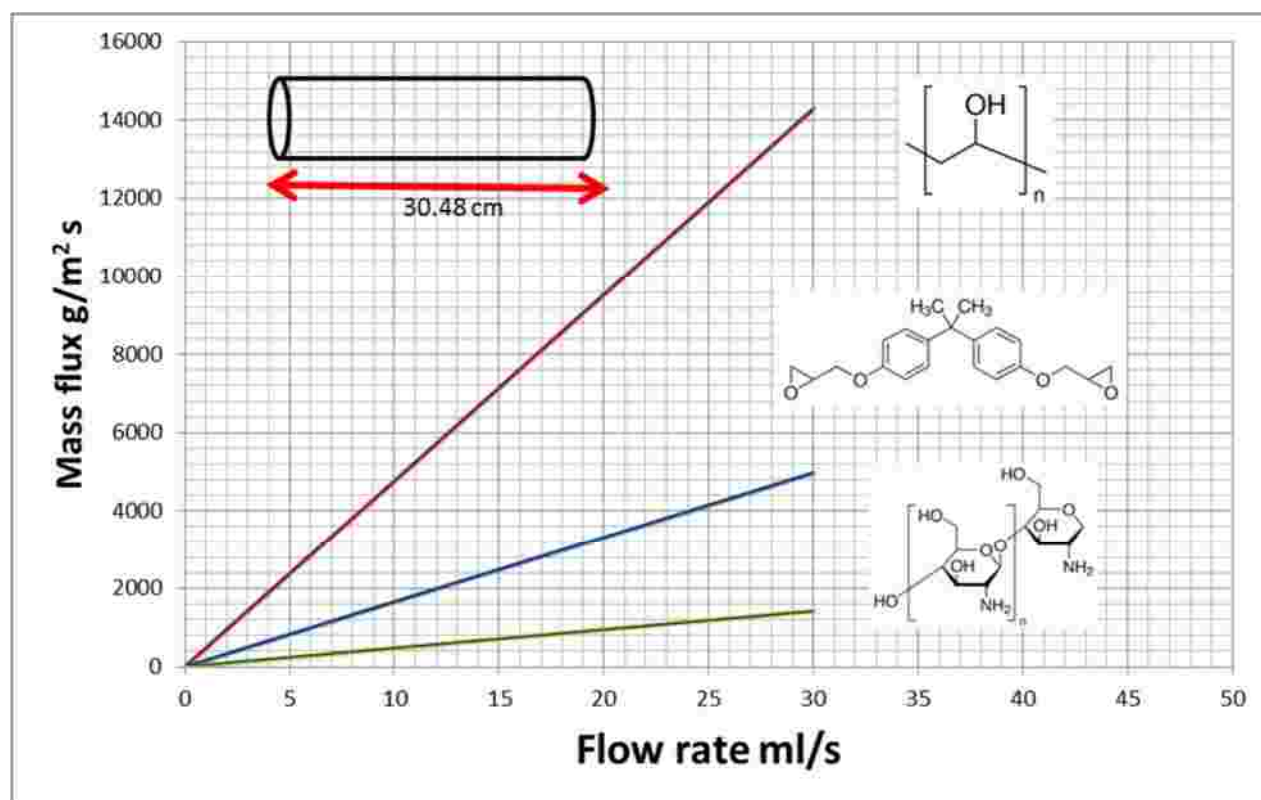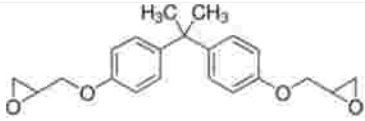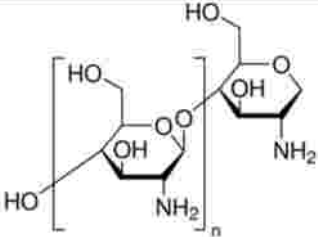
Figure 8: Mass transfer properties vs flow rate

After the flow process the blend poured into glass tray and casted in a Vacuum Oven. The casted films showed very effective texture in the microscopic image. FTIR spectra of the film is taken in ATR mode. (Supporting Information)
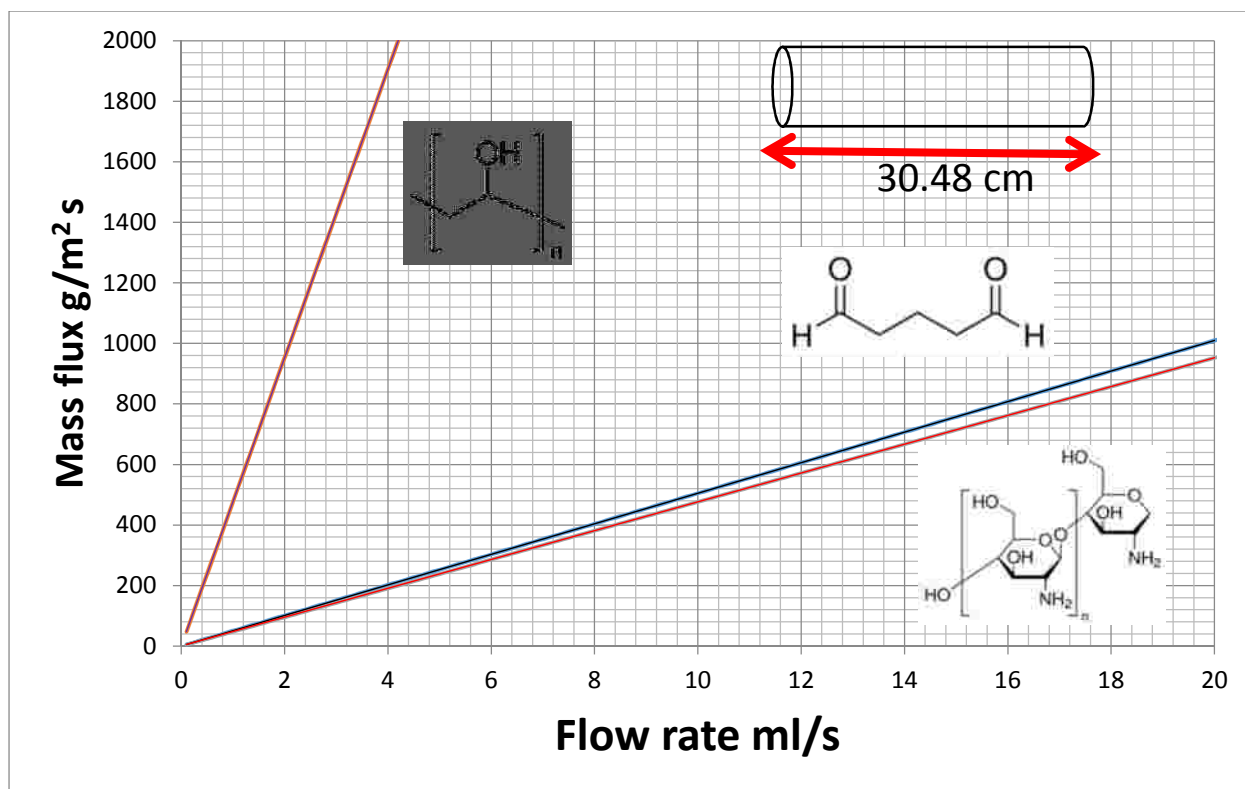
Figure 9: Mass transfer properties vs flow rate

After the flow process the blend poured into glass tray and casted in a Vacuum Oven. The casted films showed very effective texture in the microscopic image. FTIR spectra of the film is taken in ATR mode. (Supporting Information)

chemical	MOLECULAR STRUCTURE	Weight per ml in water g/ml	Mass flux g/m^{2}s	Space Time τ sec.	Heat Flux ϕ_q W/m^2
BPDGE		0.005577	5.576923	239.268	1402.6637
CHITOS AN		0.004808	4.807692	239.268	1402.6637
ACETIC ACID	**CH₃CO₂H**	0.005043	5.043269	239.268	1402.6637
ACETO NE	**CH₃COCH₃**	0.037716	37.71635	239.268	1402.6637
	TOTAL SOLUTE	0.053144	53.14423	239.268	1402.6637

Table 2: The reaction conditions are given above. The parameters of blending done in a cylindrical flow reactor ID=1 cm, L=30.48 cm, Flow rate is 0.1 ml/s, T_w =110ºC, T i=80ºC, $\Delta T = 30K$, solvent deionized .water
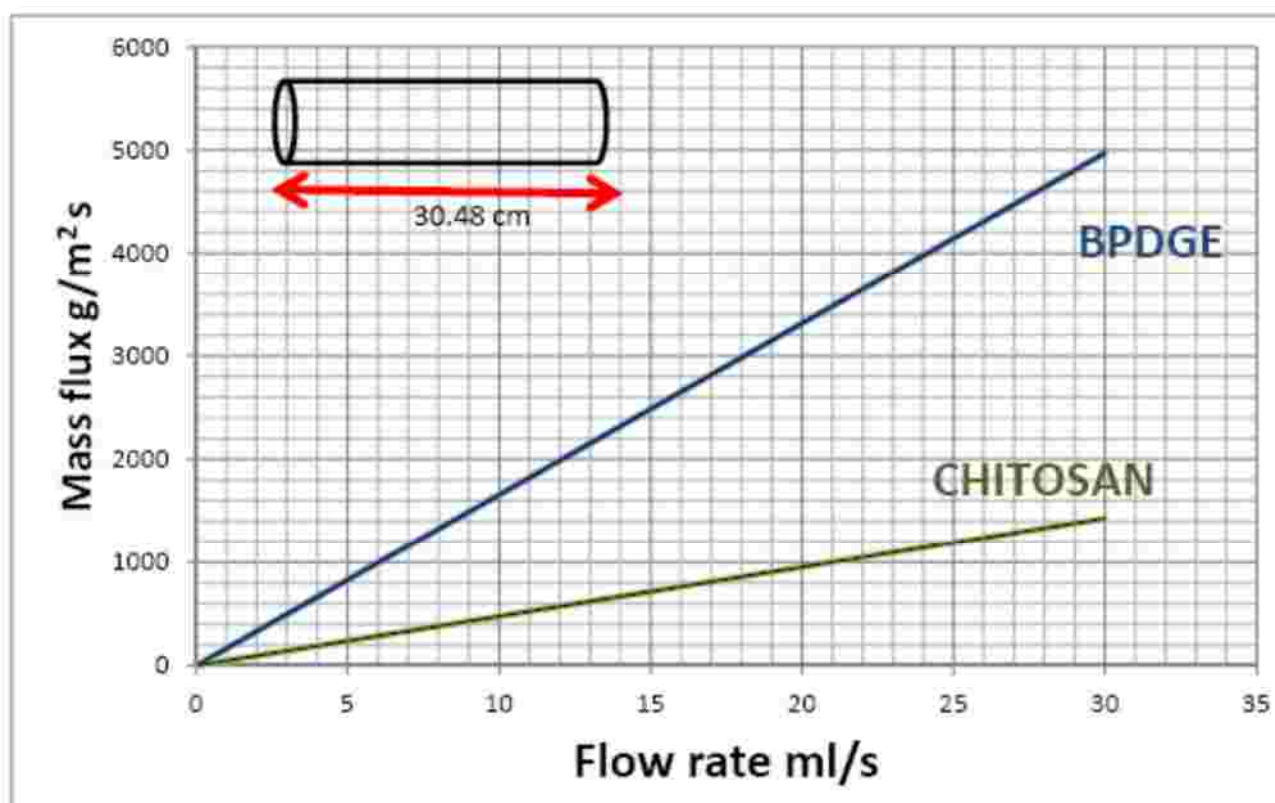
Figure 10: Mass transfer properties vs flow rate

After the flow process the blend poured into glass tray and casted in a Vacuum Oven. The casted films showed very effective texture in the microscopic image. FTIR spectra of the film is taken in ATR mode. (Supporting Information)

THERMAL AND SONOCHEMICAL SYNTHESIS OF 1, 4-DIHYDROPYRIDINES CATALYZED BY HIERARCHICAL ZSM-5

Recent developments in 1,4-dihydropyridine chemistry and interest in the developments of efficient and environmentally friendly procedures for the synthesis of heterocyclic compounds, prompted the study of conversion of ethyl acetoacetate into fused 1,4-dihydropyridines in the presence of hierarchical ZSM-5 (Si/Al:100). The raeation was carried out at room temperature under ultrasonic irradiation of SONIC ultrasound probe with 20kHz frequency and 750 Watts Power. The reaction of ethyl acetoacetate (2eq) with 1equivalent of each of various aryl aldehydes and NH_4OAc inEtOH in the presence of ZSM-5 furnished the desired fused 1,4-dihydropyridine derivatives(scheme 1-3) in reasonable reaction times (nearly 3 hours) and high yields(87-90%). Moreover, the catalyst was easily recovered. The acoustic waves crated in the medium activate the catalytic site. And also the

yield of 1,4-dihydropyridine products   by the reaction using nano reaction with nano particle ZSM-5 without NR macrotemplate (85-90%).
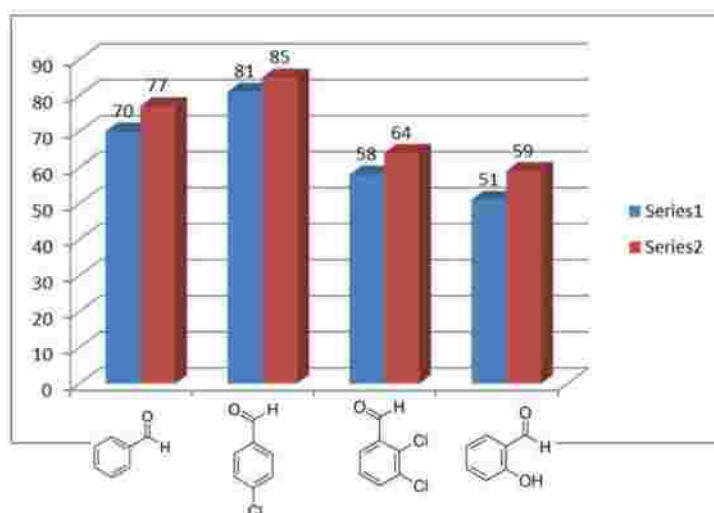
Figure 11: The Bar diagram comparing the yields of thermal batch reactions (1) and sonochemical batch reactions (2) in the Synthesis of Diethyl 1,4-dihydro-2,6-dimethyl-4-aryl pyridine-3,5-dicarboxylate from various aromatic aldehydes as shown above with hierarchical ZSM-5 catalyst.
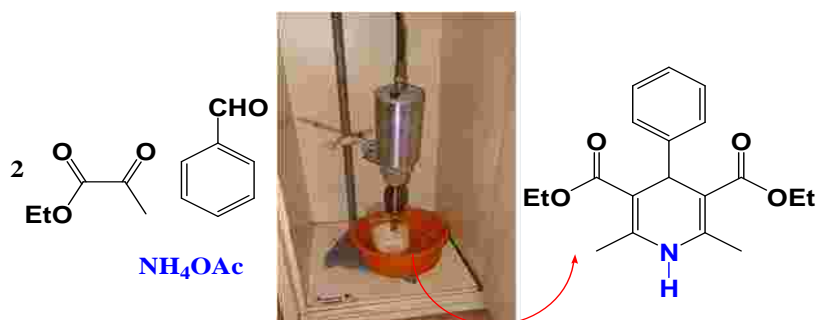
Figure 12: Sonochemical synthesis 1,4 dihydropyridines using ZSM-5 catalyst

PREPARATION OF 12-TUNGSTOPHOSPHORIC ACID INCLUDED ON SILICA NANO PARTICLE & EFFICIENT GREEN SONOCHEMICAL SYNTHESIS OF 2-ARYL-4,5-DIPHENYLIMIDAZOLE

a) Synthesis of 2 Aryl,4,5-Diphenyl-1H-imidazole:

A 250 ml round-bottomed flask was charged with a mixture of benzil (2.1 g), benzaldehyde (10 m.mol), ammonium acetate (5ml), glacial acetic acid (5ml), DMSO (50 ml) and the catalyst (3g). The mixture was heated at 145°C in PFR for 200 minutes. The sonochemical reaction carried out at 70° C with ultrasonic irradiation 20kHz with 750 Watts power. The reaction was followed by TLC. After completion of the reaction, the reaction mixture was poured into ice (100cc) taken in a 250 ml beaker. The precipitated white solid, 2,4,5-Triphenyl-1H-imidazole was filtered at suction using Buckner funnel and dried at pump.
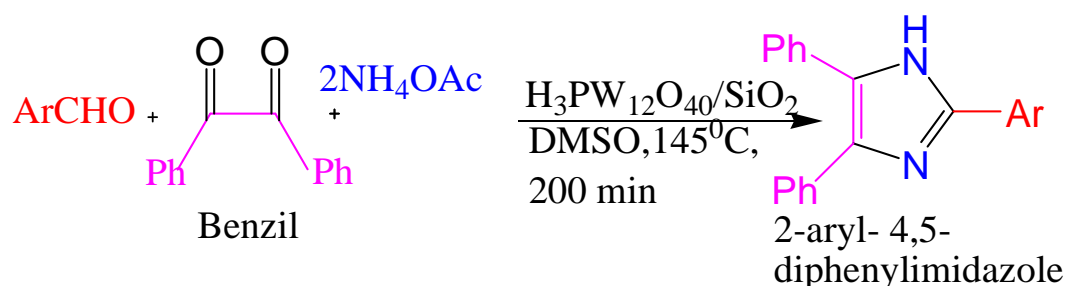
FTIR 2,4,5-Triphenyl-1H-imidazole

The yield obtained is 89% and Rf value is 0.648.

The molecular structure shows the presence N-H stretching vibrations at $3417cm^{-1}$. The aliphatic C-H stretching vibrations found at 2963, 2928 and $2926 cm^{-1}$. The aromatic C-H strectching vibration appears at $3023cm^{-1}$. The C=C stretching vibrations in the range of $1650-1723cm^{-1}$. The identification of C-N stretching frequency is a very difficult task, since the mixing of bands is possible in this region. Hence, the FTIR bands at 1487, 1446, 1461 and $1393 cm^{-1}$ in imidazole have been designated to C-N stretching modes of vibrations. The C-H out-of-plane bending vibrations occurs as peaks below $900 cm^{-1}$.(Supporting Information)

FTIR of 2-(4-Chloro-phenyl)-4,5-diphenyl-1H-imidazole

The yield obtained is 81% and Rf value is 0.7435.

The molecular structure shows the presence N-H stretching vibrations at 3417cm⁻¹.The aliphatic C-H stretching vibrations found at 2923, 2961and 2851cm⁻¹. The aromatic C-H stretching vibrations found at 3023cm-1. The C=C stretching vibrations in the range of 1599-1650cm⁻¹.The identification of C-N stretching frequency is a very difficult task, since the mixing of bands is possible in this region. Hence, the FTIR bands at 1486, 1448, 1434 and 1325 cm-1 in imidazole have been designated to C-N stretching modes of vibrations. The C-H out-of-plane bending vibrations of chlorosubsituted aromatic ring occur at 829cm⁻¹. The peak at 774cm-1 indicates C-Cl stretching vibration. (Supporting Information)

FTIR of 2-(2,3-Dichloro-phenyl)-4,5-diphenyl-1H-imidazole

The yield obtained is 84% and Rf value is 0.3152. The molecular structure shows the presence N-H stretching vibrations at 3493cm⁻¹.The aromatic and aliphatic C-H stretching vibrations found at 3061, 2919cm⁻¹ respectively. The C=C stretching vibrations is found as broad peak 1610cm⁻¹.The identification of C-N stretching frequency is a very difficult task, since the mixing of bands is possible in this region. Hence, the FTIR bands at 1489, 1448 cm-1 in imidazole have been designated to C-N stretching modes of vibrations. The C-H out-of-plane bending vibrations of dichlorosubstituted aromatic ring occurs at below 900cm⁻¹. The peak at 695cm-1 indicates C-Cl (chlorine at position 2 of the disubstituted benzene ring)stretching vibration and the sharp peak at 764cm-1 indicates the C-Cl (chlorine at position 3 of the disubstituted benzene ring) stretching vibration. (Supporting Information)

FTIR of 2-(2-Hydroxy-phenyl)-4,5-diphenyl-1H-imidazole

The yield obtained is 82% and Rf value is 0.4523.

The broad peak at 3418cm⁻¹ is due to the presence of O-H stretching vibration. The
 C-H stretching vibrations is engulfed inside the broad peak of O-H. The C=C stretching vibrations is found as a peak 1644cm⁻¹.The identification of C-N stretching frequency is a very difficult task, since the mixing of bands is possible in this region. Hence, the FTIR bands at 1488, 1434cm-1 in imidazole have been designated to c-n stretching modes of vibrations. the C-H out-of-plane bending vibrations of   aromatic ring occur at below 900cm⁻¹. (Supporting information)

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[5]Electroactive and Photoactive Poly[Isoindigo-alt-EDOT] Synthesized Using Direct (Hetero)Arylation Polymerization in Batch and in Continuous Flow, François Grenier,Badrou Réda Aïch,,Yu-Ying Lai, Maxime Guérette, Andrew B. Holmes, Ye Tao, Wallace W. H. Wong, and Mario Leclerc,Chem. Mater. 2015, 27, 2137–2143

[6]Controlled Polymerization in Flow Microreactor Systems, Nagaki, Aiichiro; Yoshida, Jun-ichi, Advances in Polymer Science (2012), 259: 1-50

[7]Measurement and control of polymerization reactors, John R. Richards, John P. Congalidis, *Computers and Chemical Engineering 30 (2006) 1447–1463*

[8] Effect of channel size on mass transfer during liquid–liquid plug flow in small scale extractors, Chemical Engineering Journal, Volume 262, 15 February 2015, Pages 785-793

[9] Scalability of mass transfer in liquid–liquid flow, Chemical Engineering Science, Volume 116, 6 September 2014, Pages 1-8
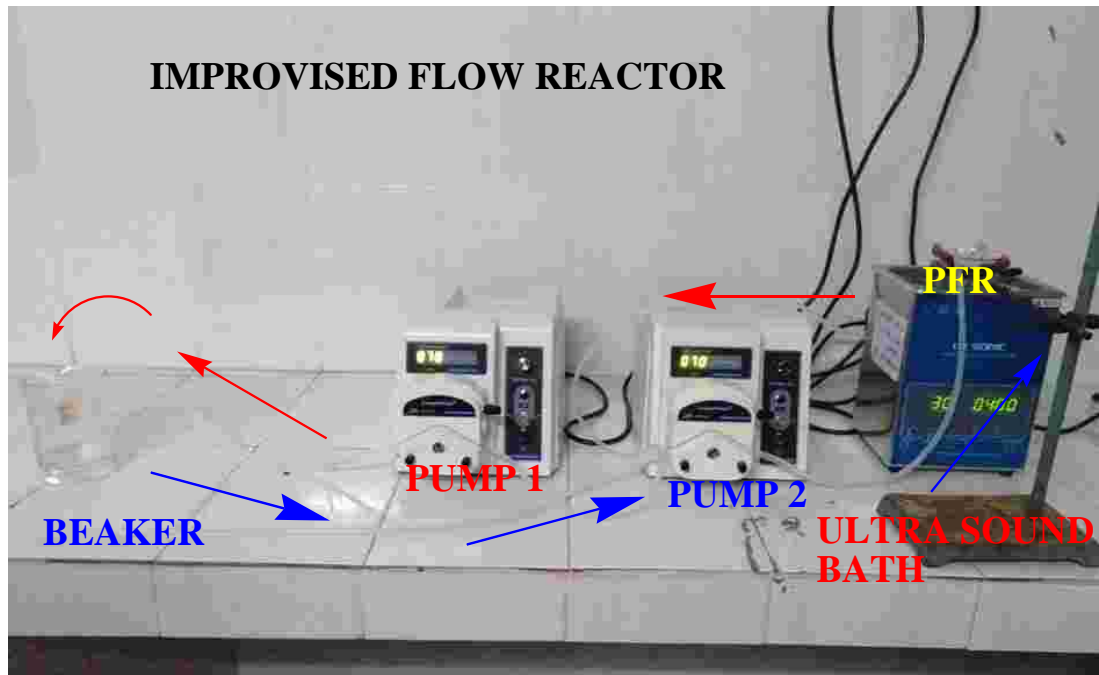
Figure 13: Improvised Plug Flow Reactor (PFR)

Figure 14: Components of flow reactor.
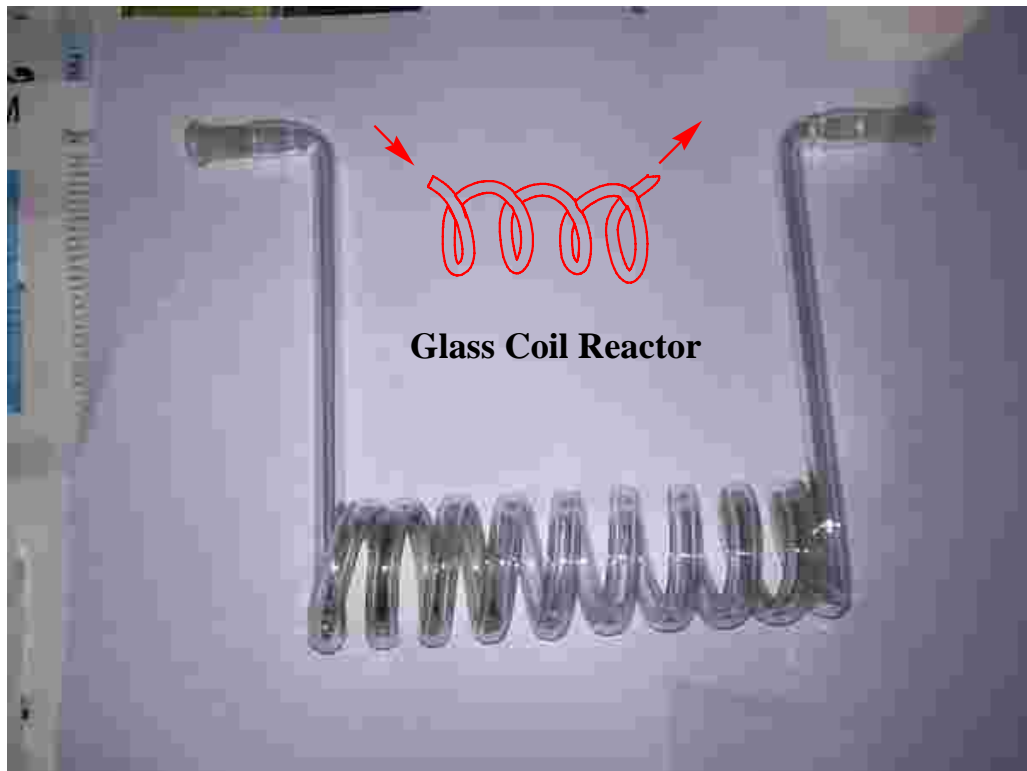
Figure 15: Glass Coil PFR inside the thermostat.
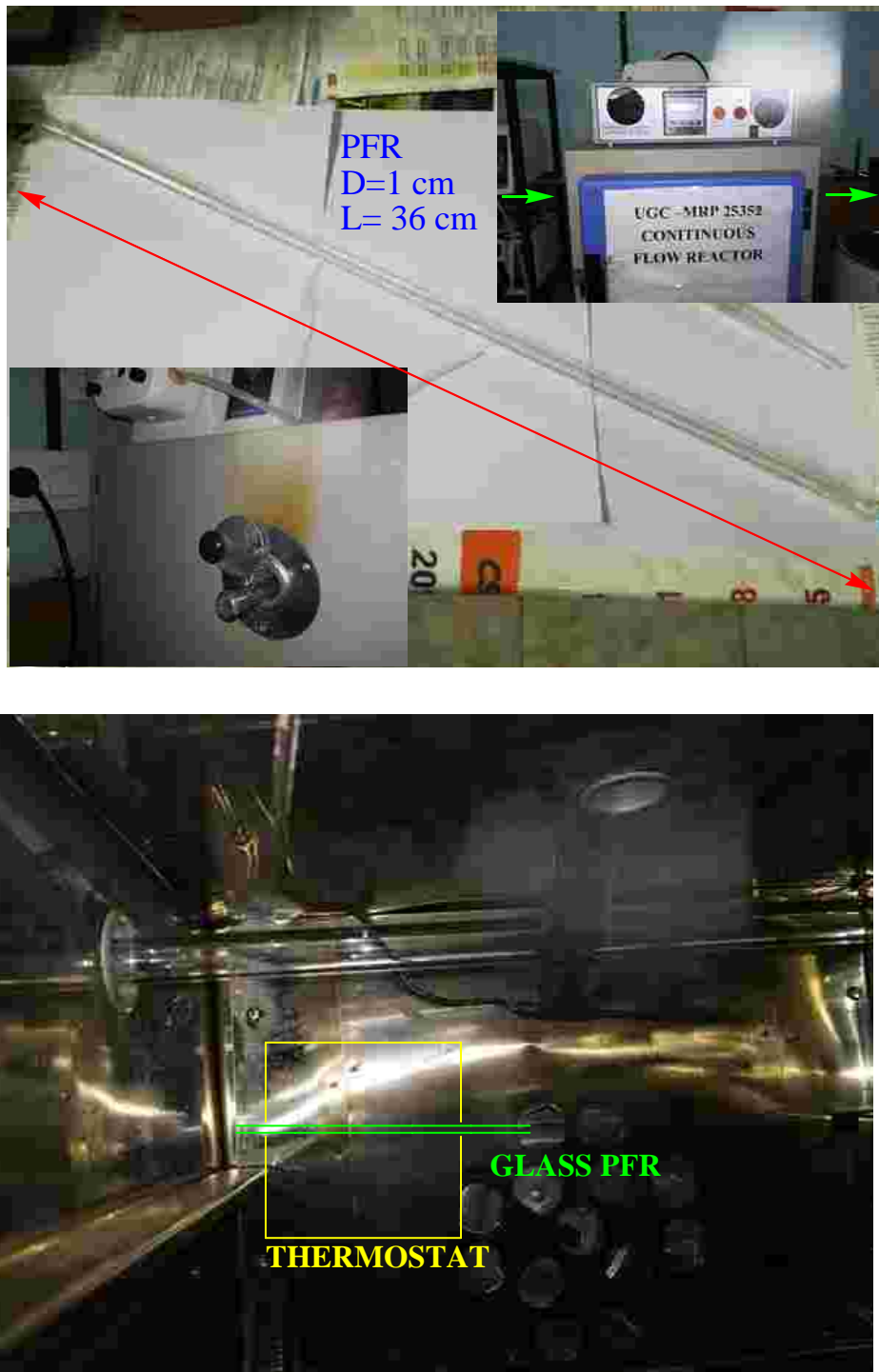
Figure 16: Glass Tube PFR inside the thermostat

Figure17. The flow reactor set up for the synthesis of chitosan methacrylate/siloxane graft.
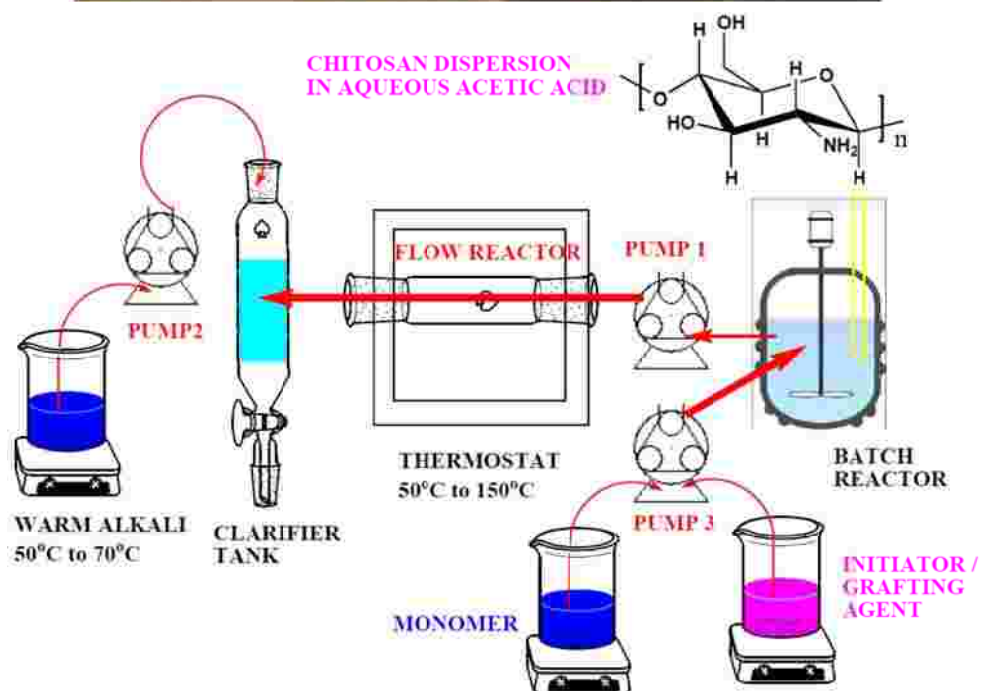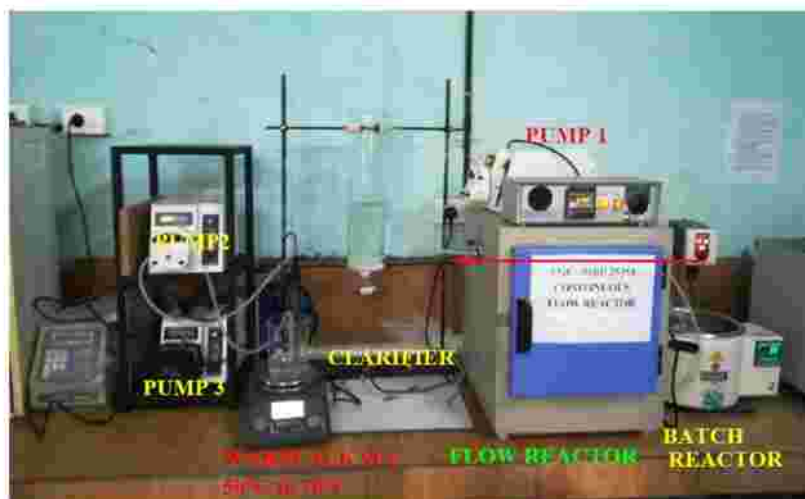
Figure 18. The PFR design for the chitosan Graft.

Figure 19. The Flow reactor set up for the Chitosan modification using BPDGE.
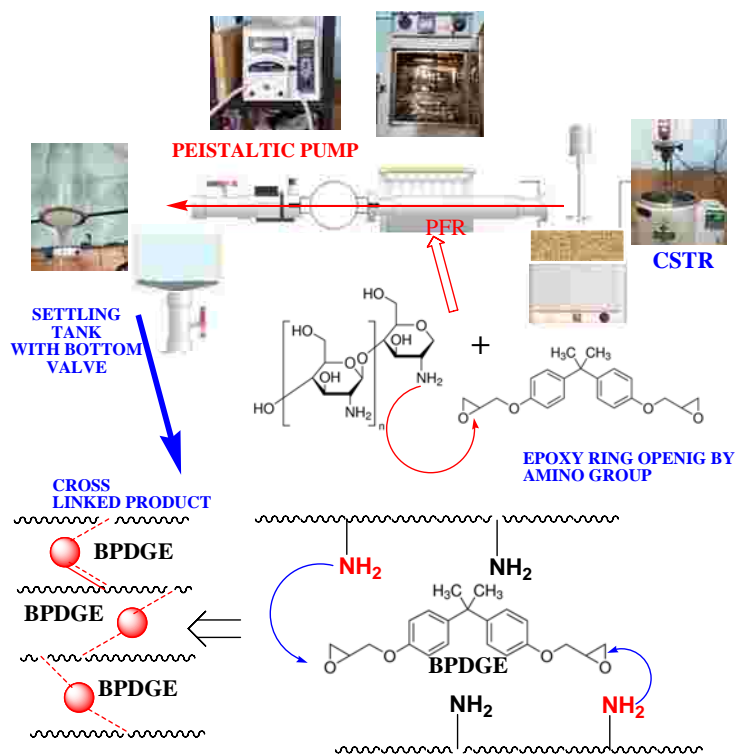
Figure 20. The scheme demonstrate flow reactor set up used for the synthesis of chitosan medication using **BPDGE**

Figure 21: (A) CSTR with EQUITRON oil bath   **(B)**Chitosan solution prepared in aqueous acetic acid using 750 Watts, 20kHz probe sonicator (2g of Chitosan in 392 ml deionized water and 2ml Acetic acid mixture)
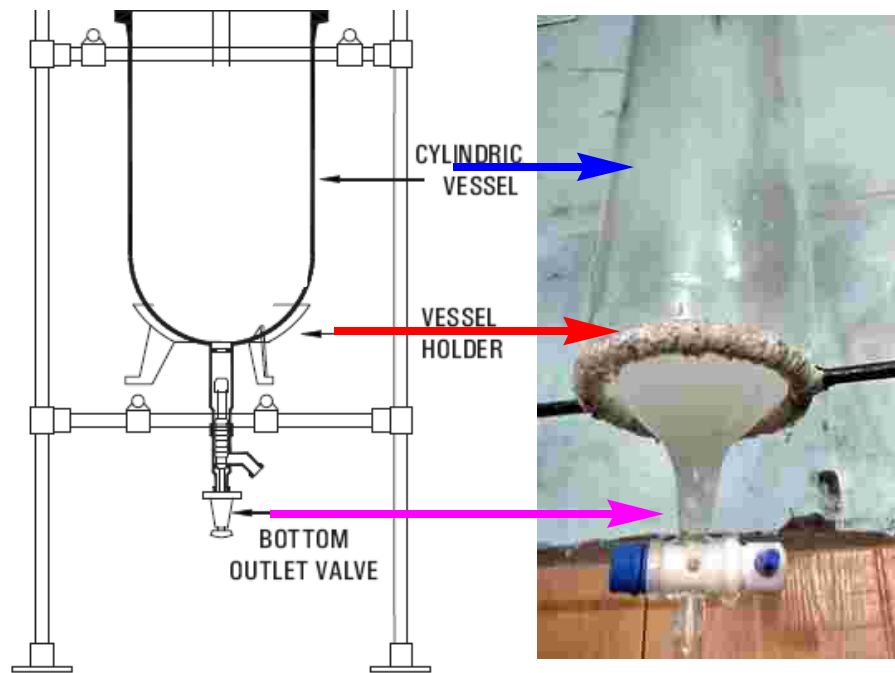
Figure22: The Clarifier set up with PTFE bottom valve, with 10 mm bore size

SUPPORTING INFORMATION

SECTION 4
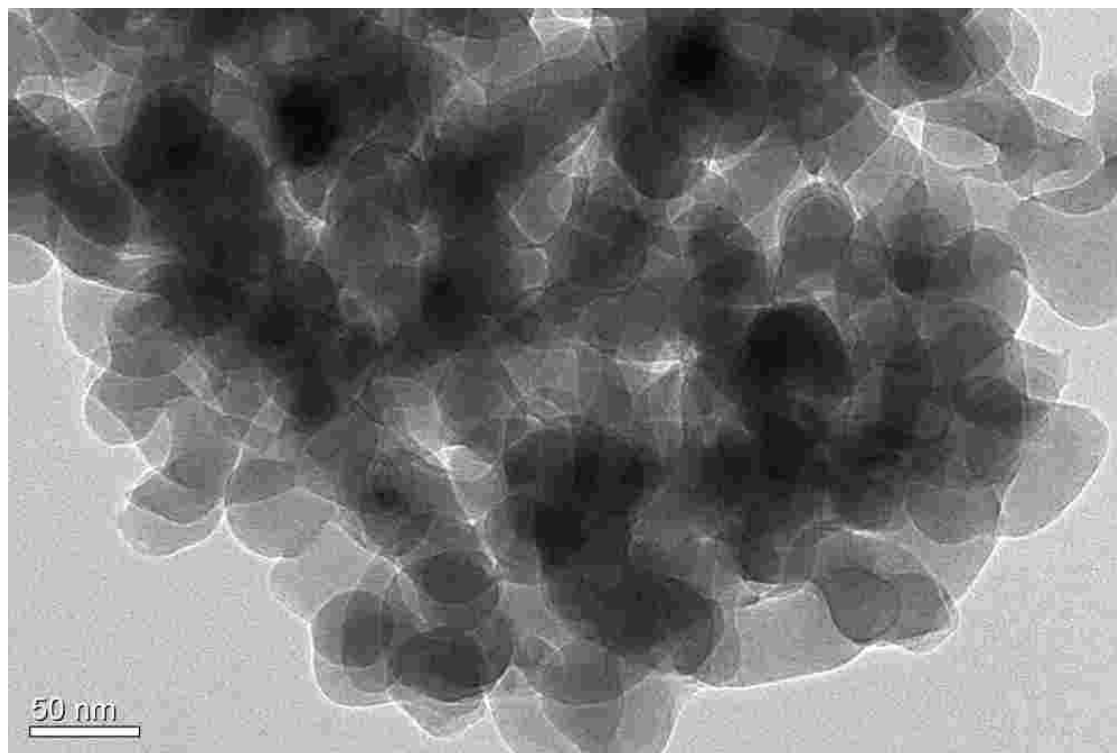
(1)TEM images of 12-tungstophosphoric acid included on silica nanoparticles catalyst (25 wt% DTP/SiO$_2$)
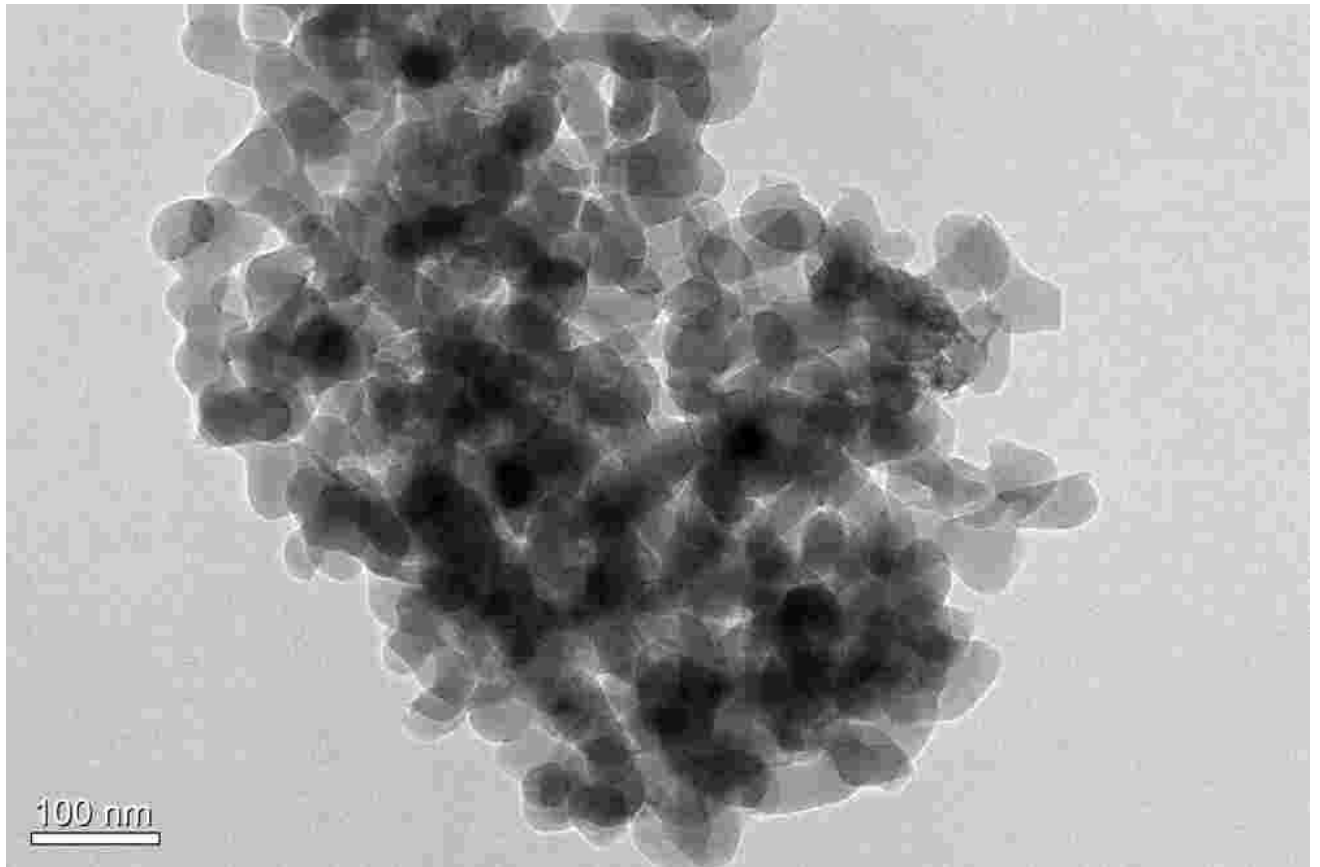
(2)TEM images of 12-tungstophosphoric acid included on silica nanoparticles catalyst (25 wt% DTP/SiO$_2$)
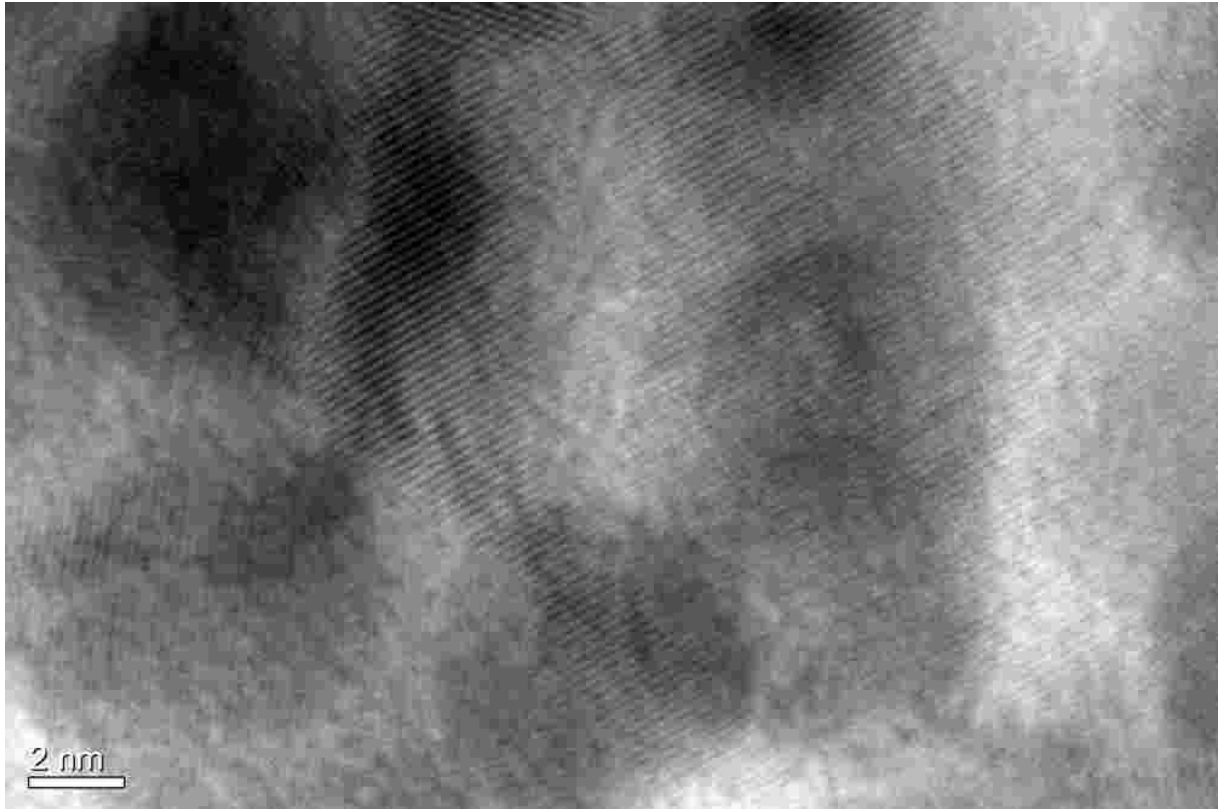
(3)TEM images of 12-tungstophosphoric acid included on silica nanoparticles catalyst (25 wt% DTP/SiO₂)
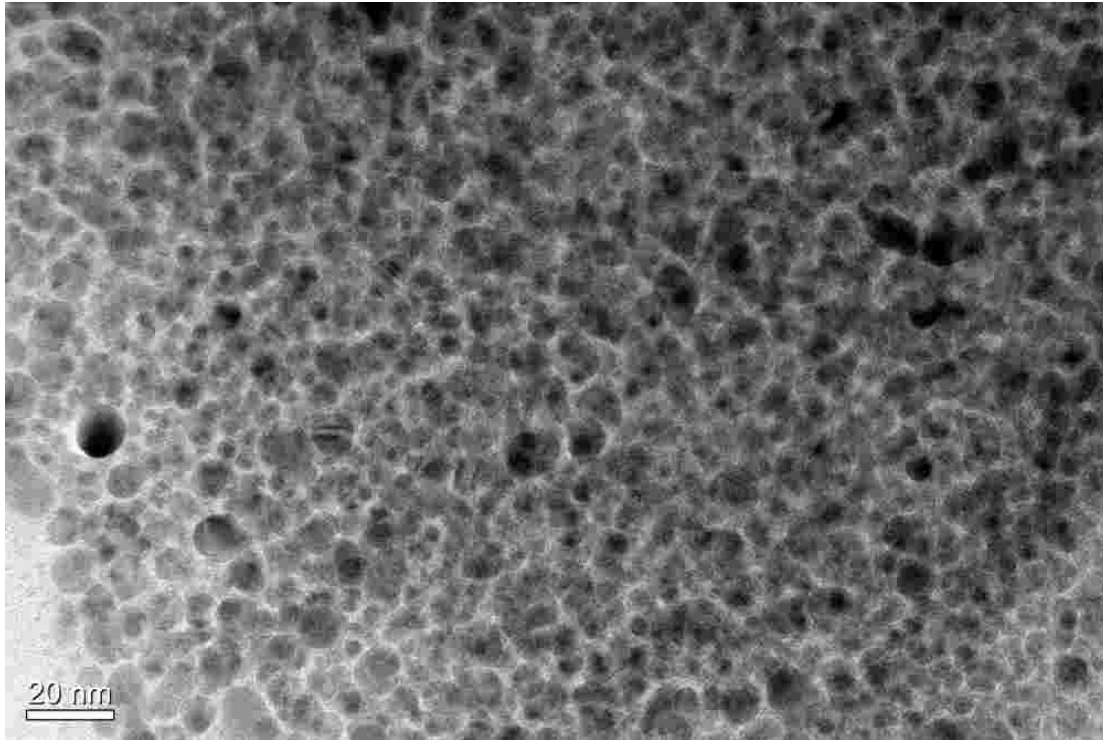
(4)TEM images of 12-tungstophosphoric acid included on silica nanoparticles catalyst (25 wt% DTP/SiO$_2$)
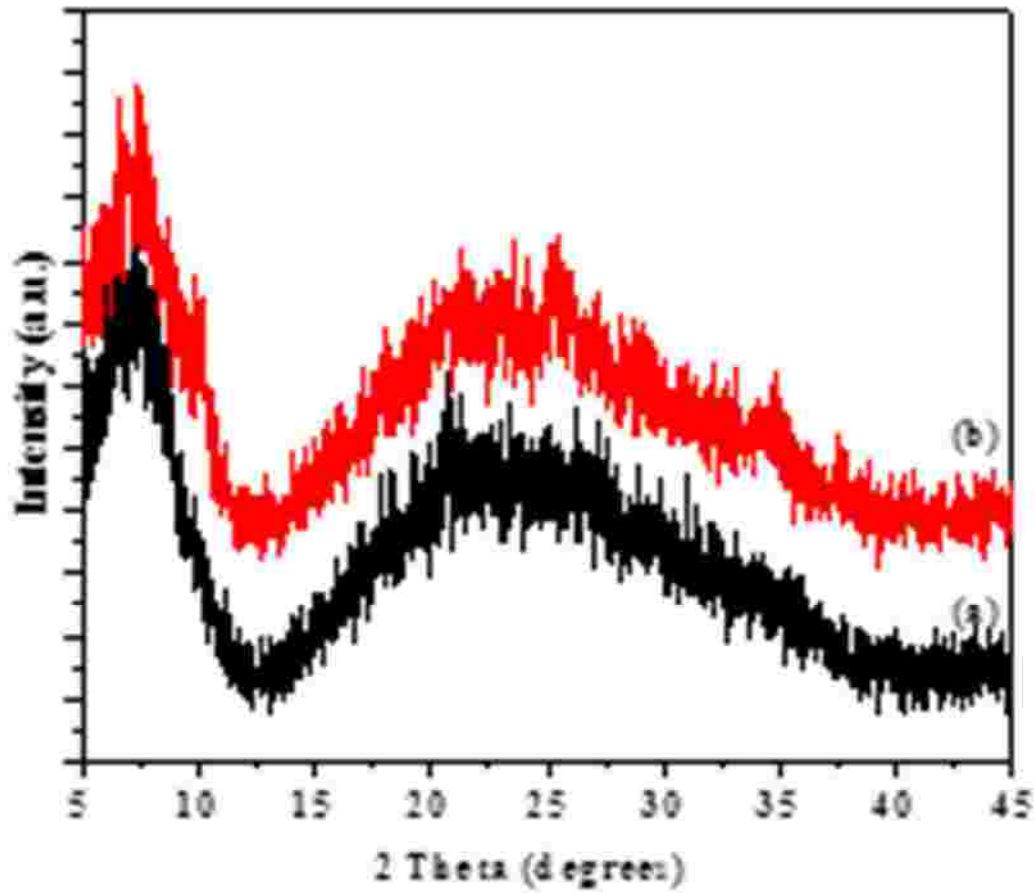
(5)X-Ray Diffraction Analysis (XRD) a) TPA steamed b) TPA before steaming
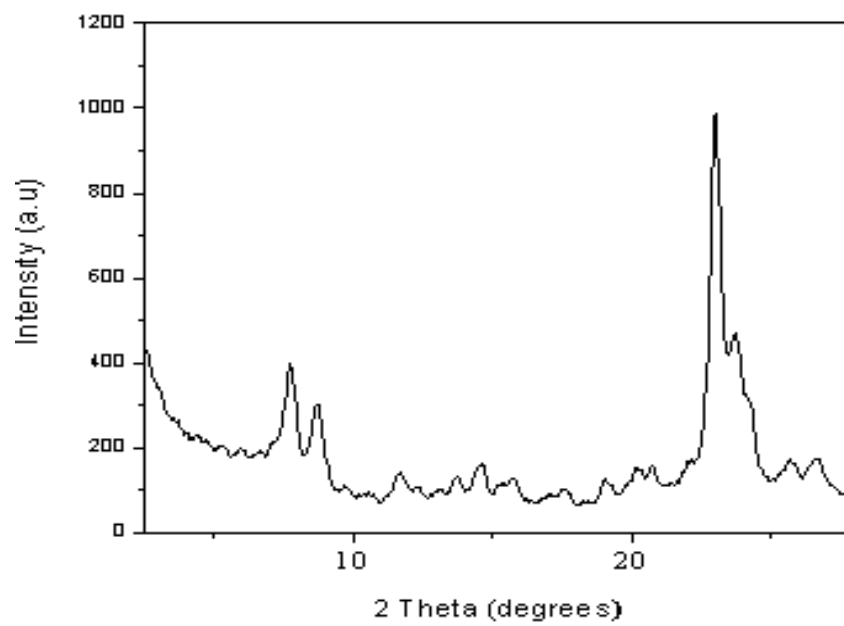
(6) XRD patterns of hierarchical nanozeolite

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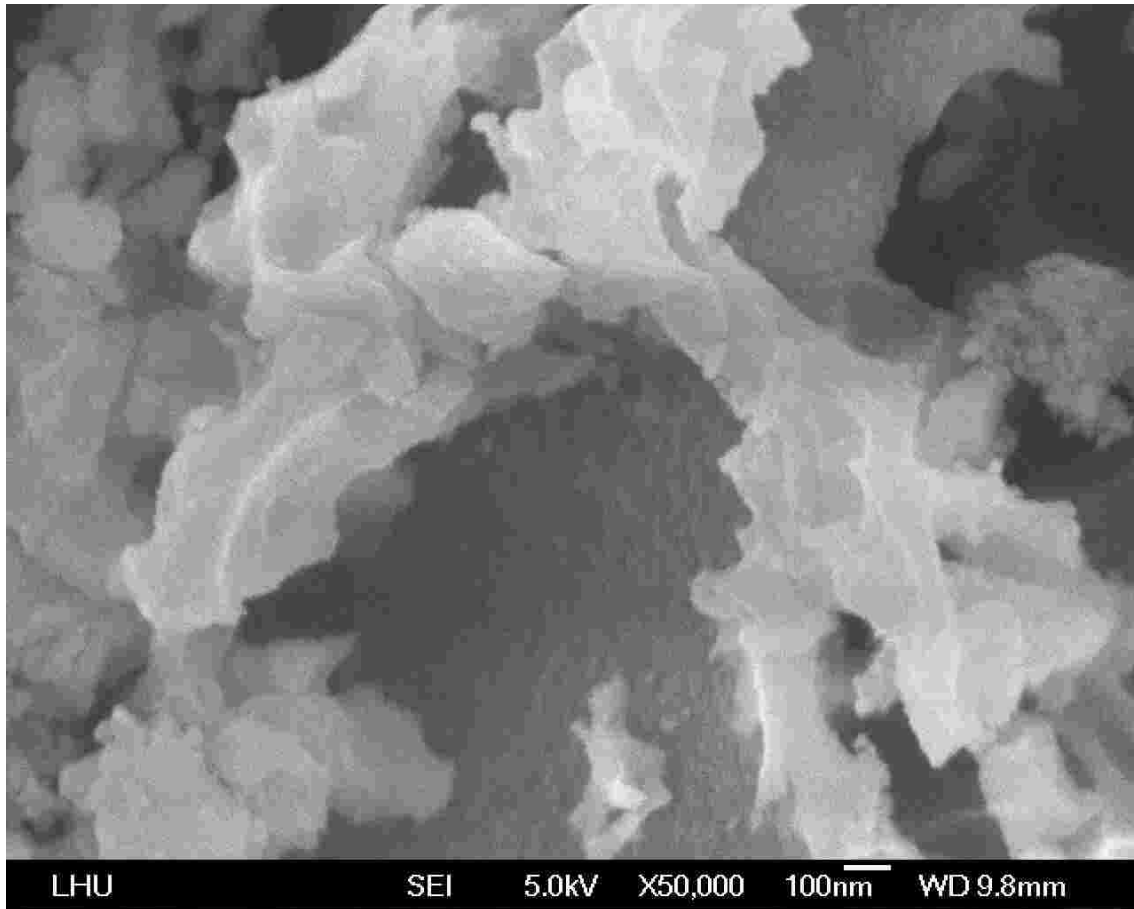
(7) SEM images of ZSM-5 heirarchichally porous nanocatalyst
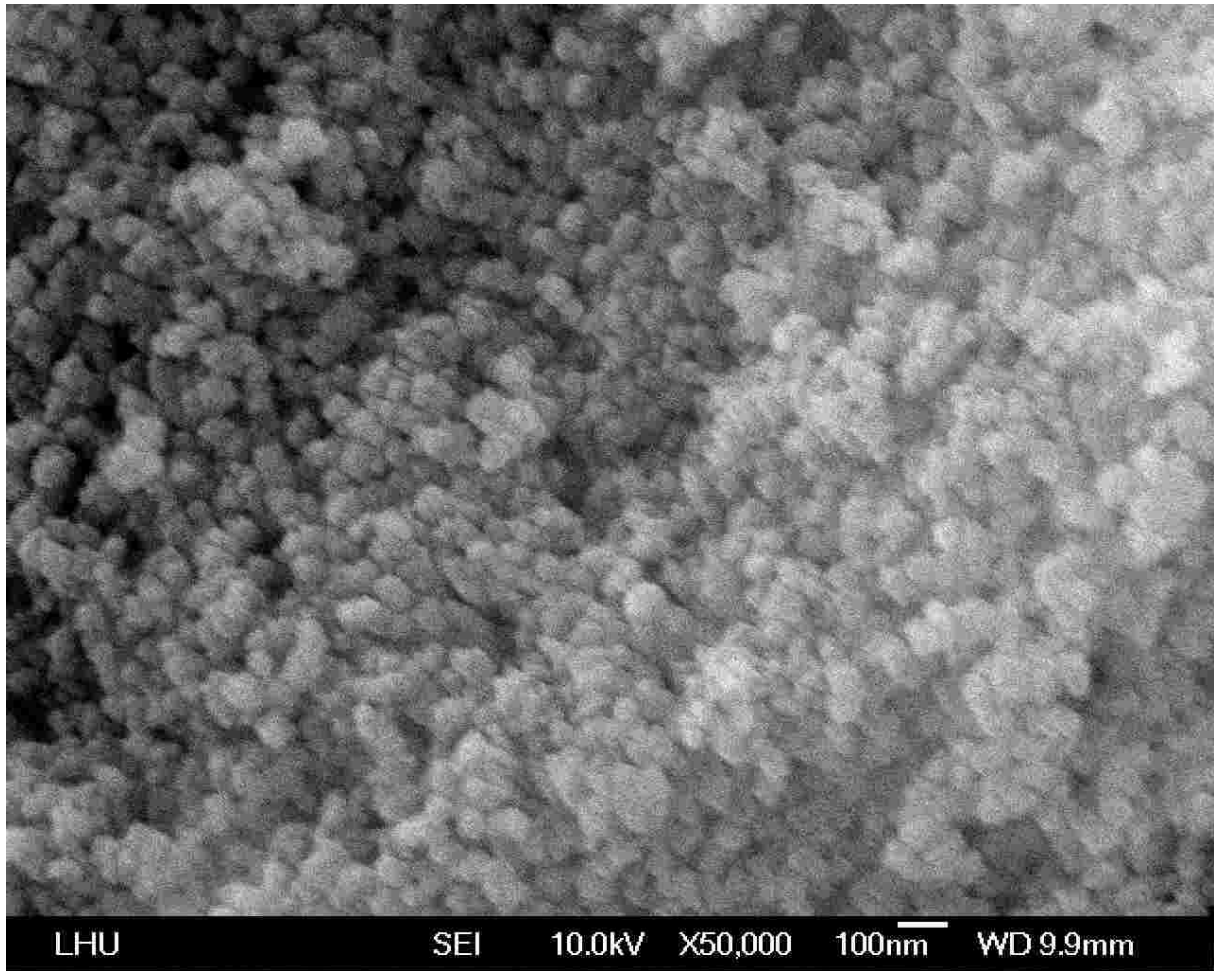
(8) SEM images of ZSM-5 heirarchichally porous nanocatalyst

(9) SEM images of ZSM-5 heirarchichally porous nanocatalyst

LHU   SEI   5.0kV   X25,000   1 μm   WD 9.9mm
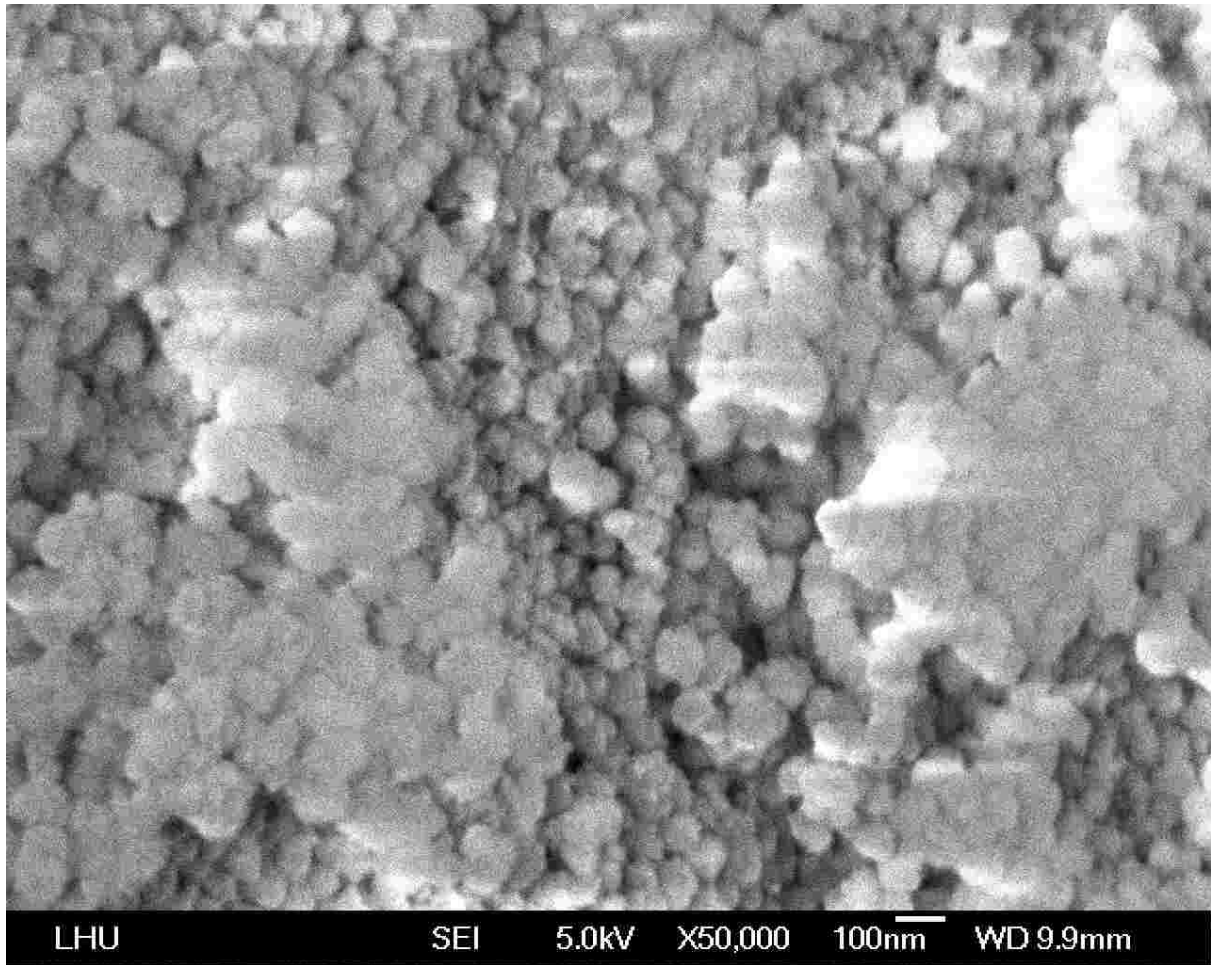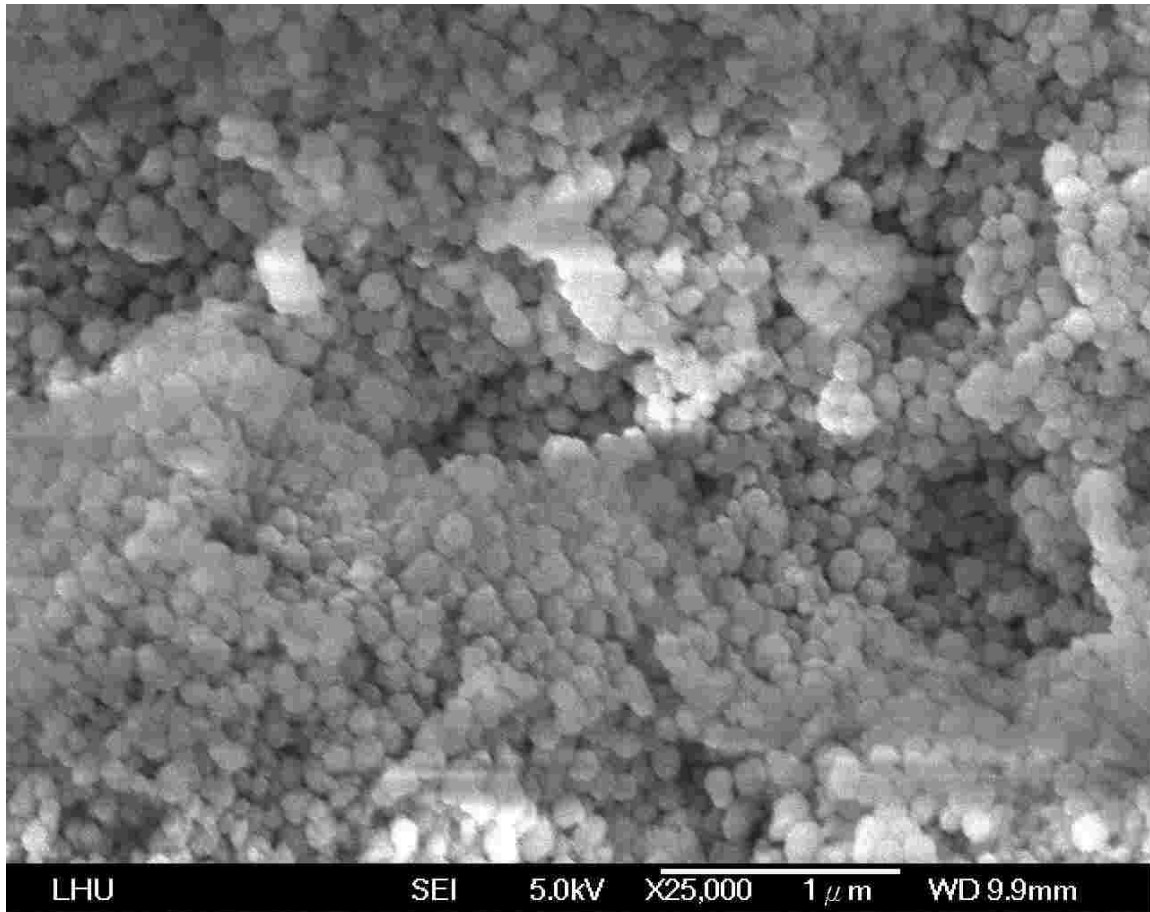
(10)SEM images of ZSM-5 heirarchichally porous nanocatalyst

(11) FT-IR Spectrum of ZSM-5 with NR macrotemplate
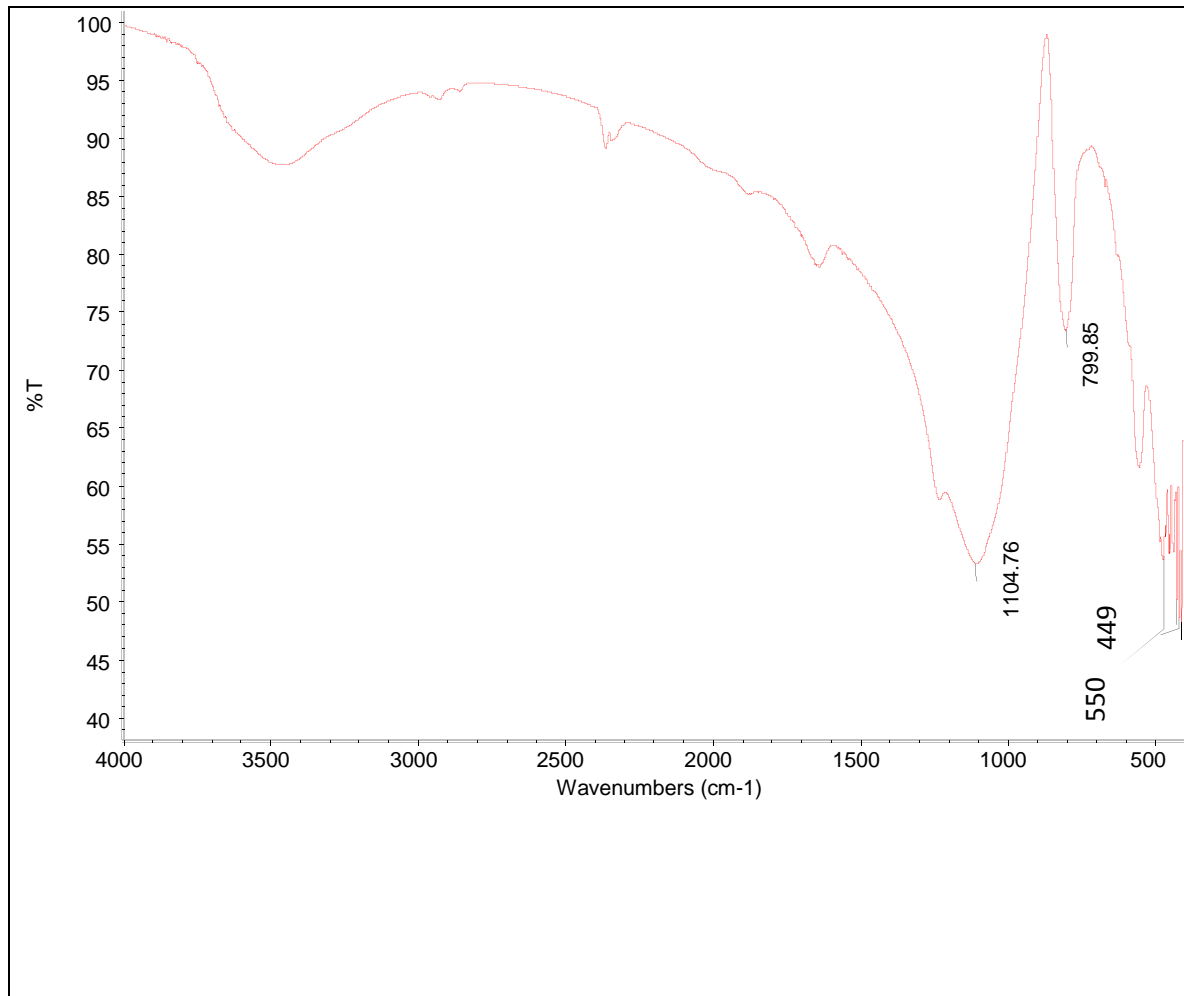
(11) FT-IR Spectrum of ZSM-5 with NR macrotemplate
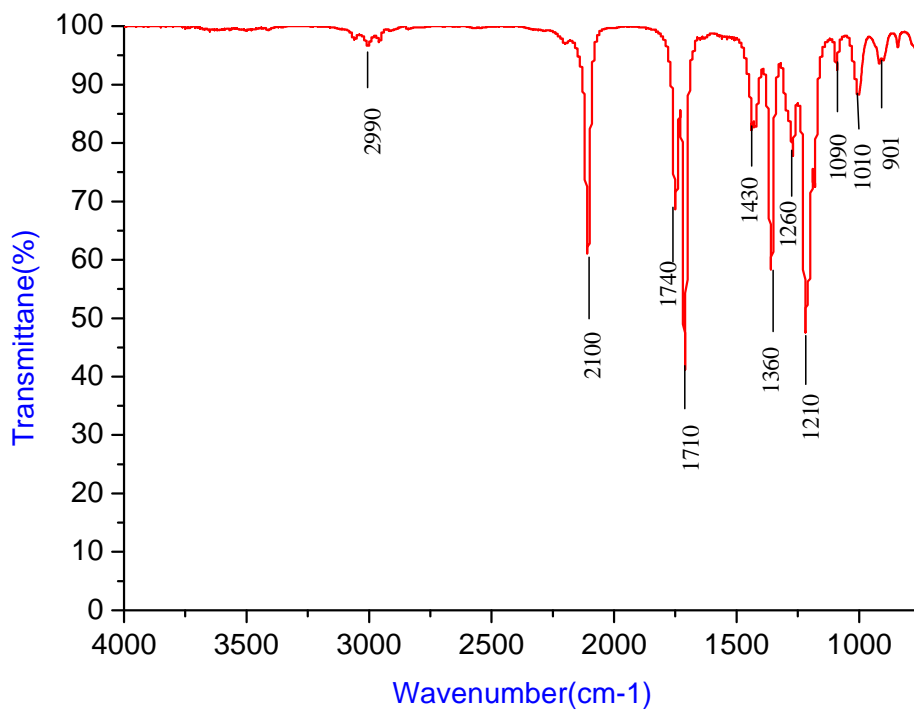
(12) FTIR spectrum of methyl azidoacetate
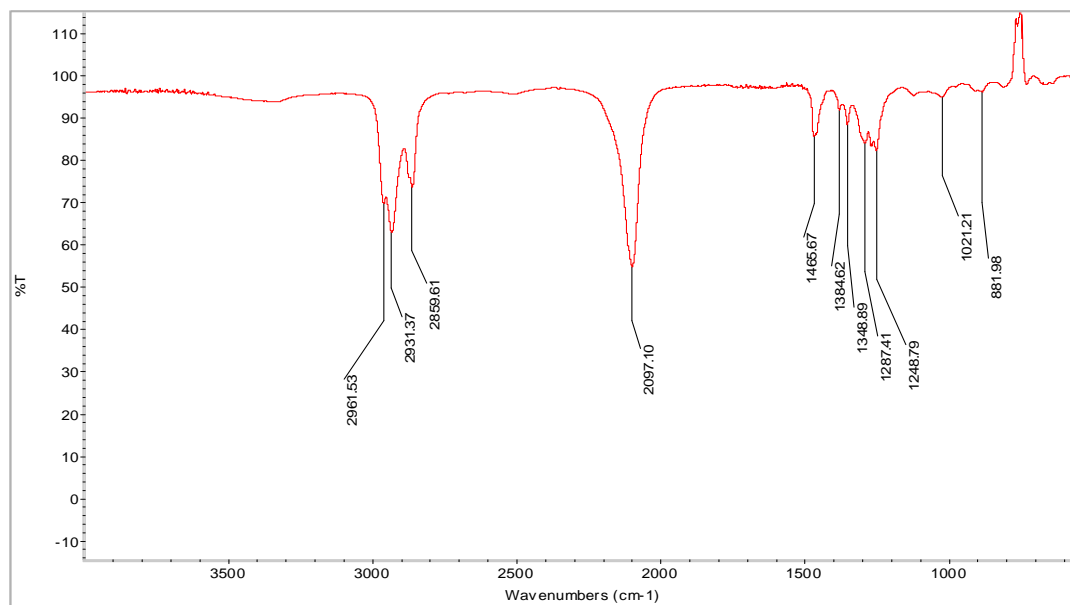
(13)FT-IR spectrum of 1-azidohexane
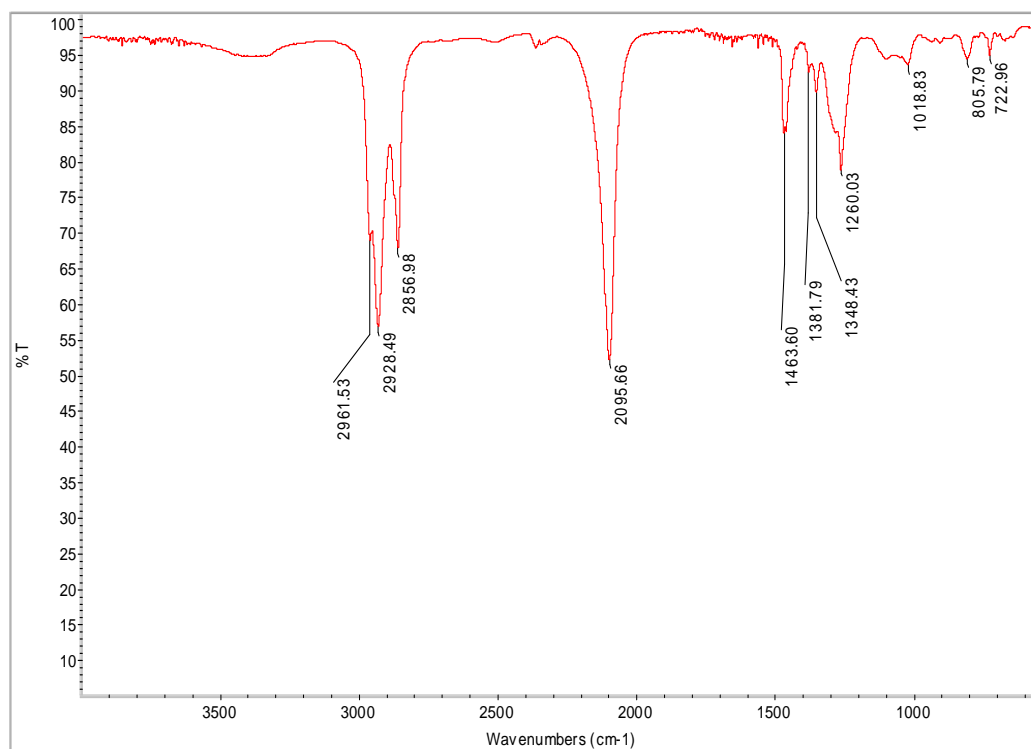
(14) FT-IR spectrum of 1-azidooctane
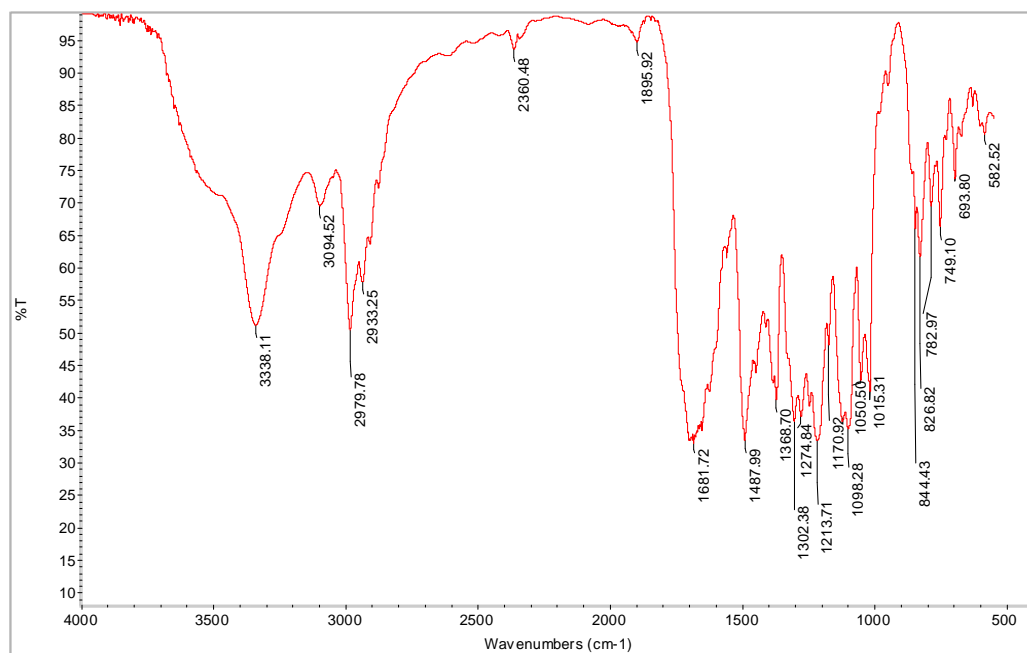
(15)FT-IR Spectrum of diethyl 4-(4-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate
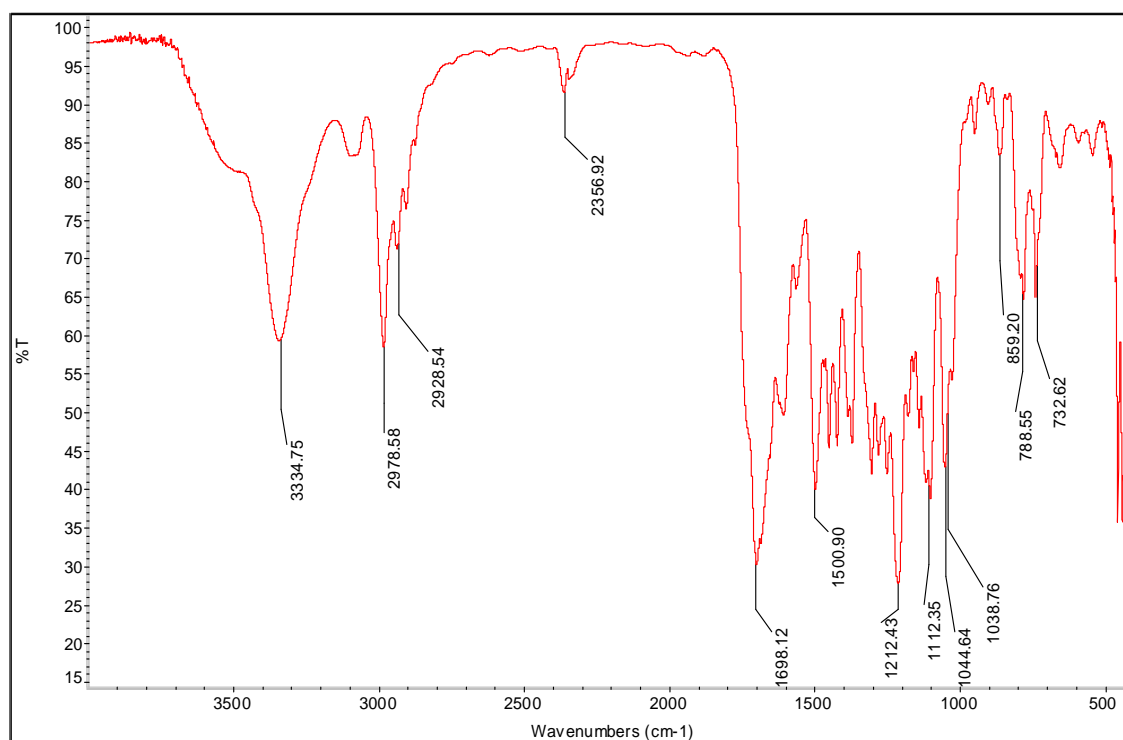
(16)FT-IR Spectrum of Diethyl 4-(3,4-dichlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate
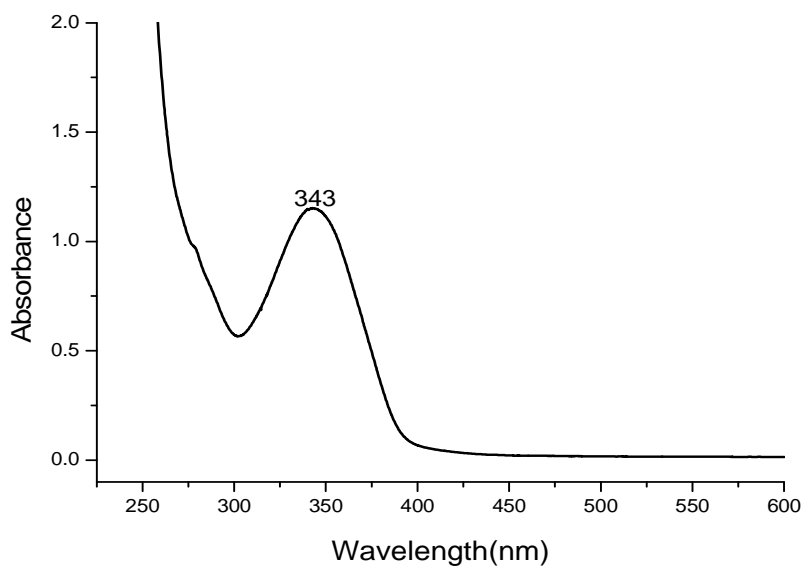
(17)UV-Visible Spectrum of Diethyl 4-(4-Chlorophenyl)-1,4-Dihydro-2,6-Dimethylpyridine-3,5-Dicarboxylate
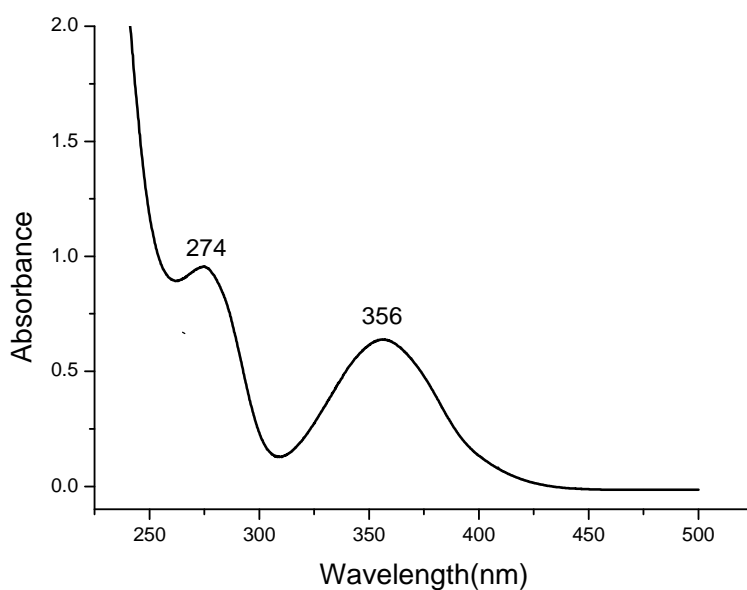
(18)UV-Visible Spectrum of Diethyl 4-(3, 4-Dichlorophenyl)-1,4-Dihydro-2,6-Dimethylpyridine-3,5-Dicarboxylate. It shows a λ_{max} at 274 and 356nm. It is due to aryl and DHP chromophores in the compound..
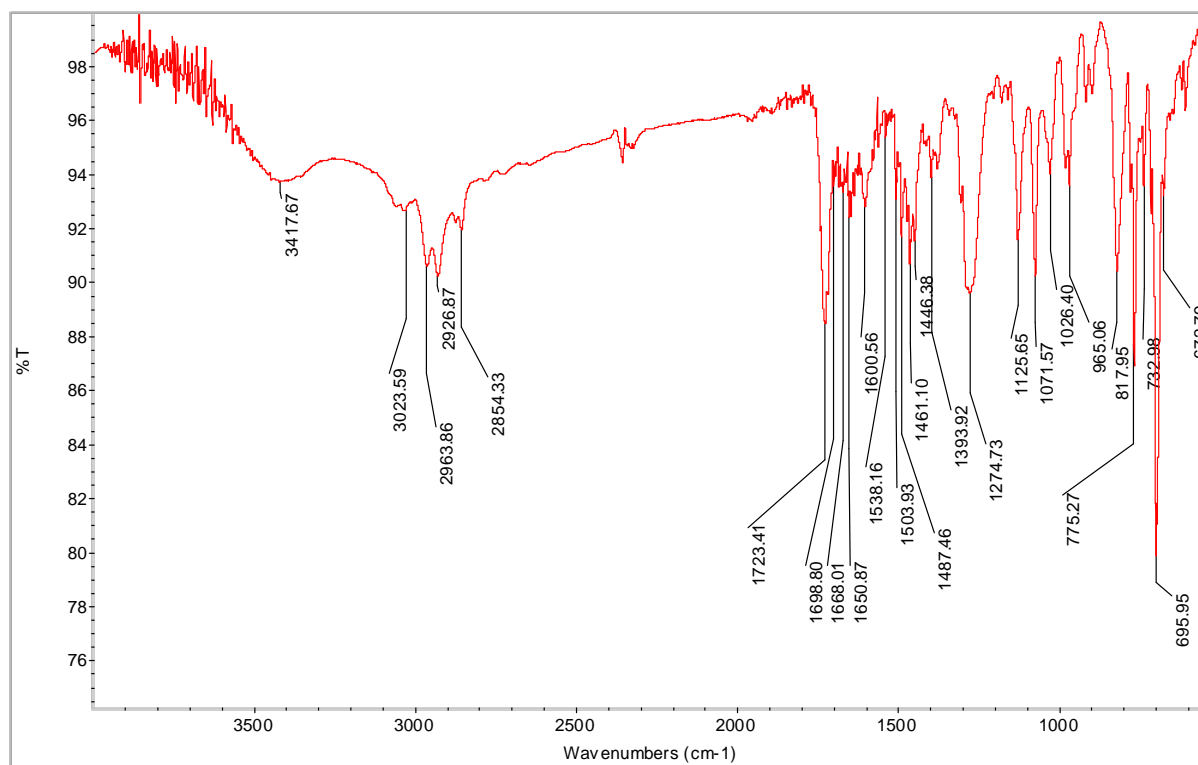
(19)FT-IR spectrum of 2,4,5-Triphenyl-1H-imidazole
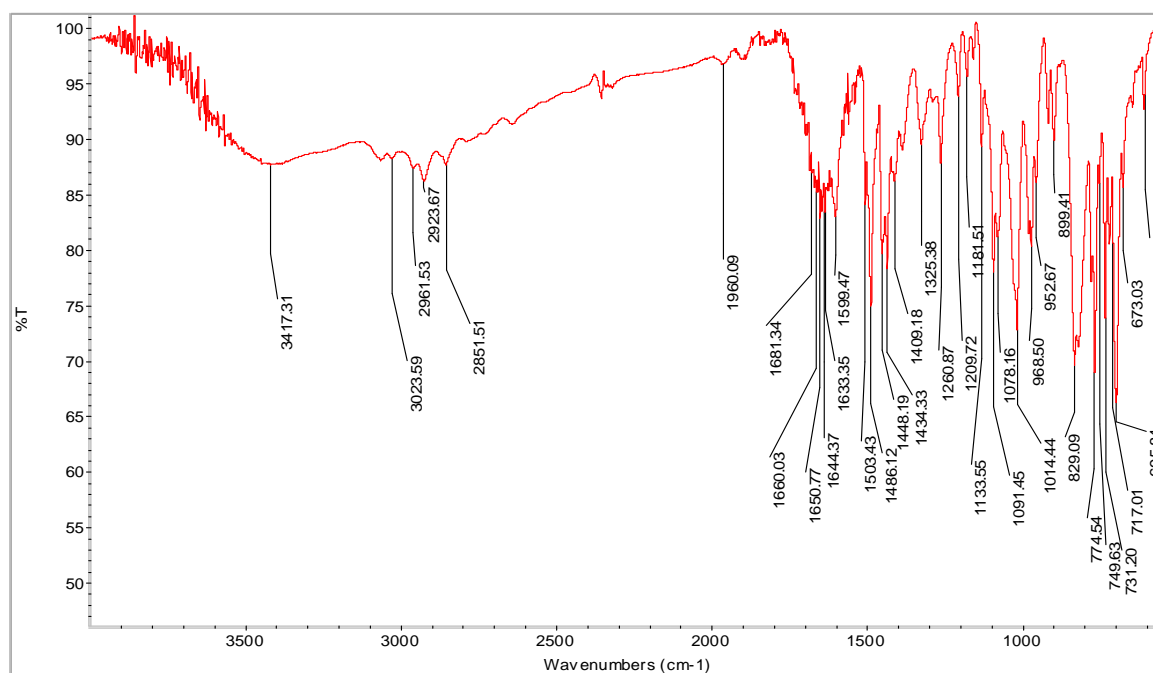
(20)FT-IR spectrum of 2-(4-Chloro-phenyl)-4,5-diphenyl-1H-imidazole
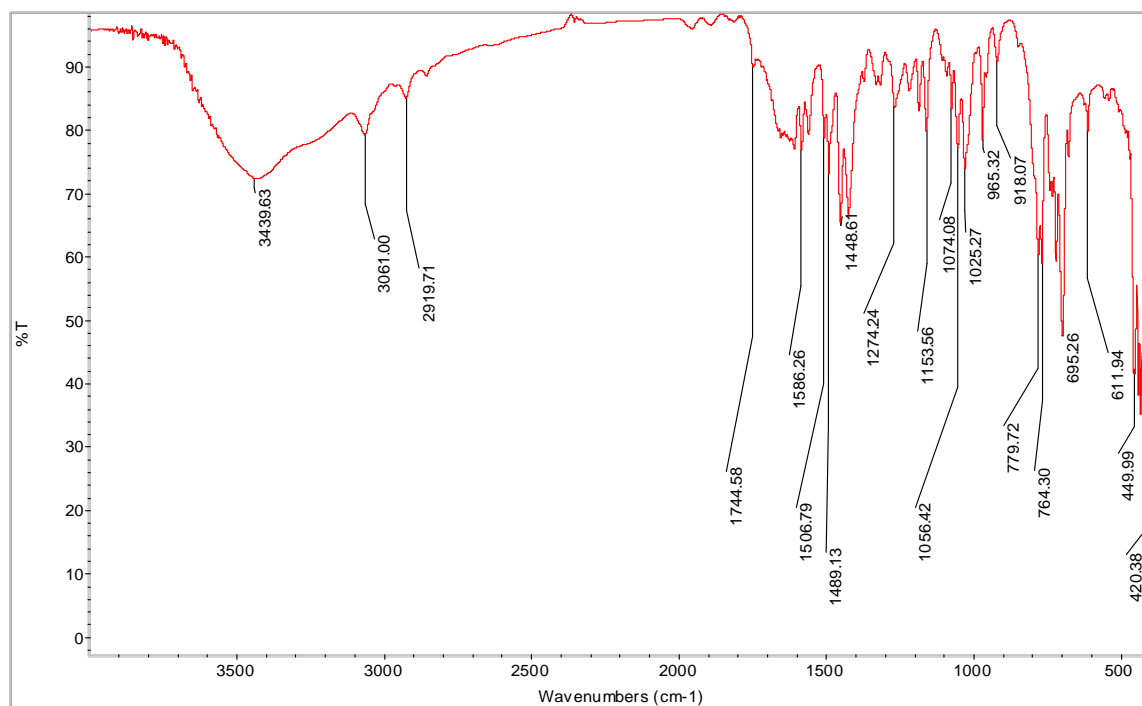
(21)FT-IR spectrum of 2-(2,3-Dichloro-phenyl)-4,5-diphenyl-1H-imidazole
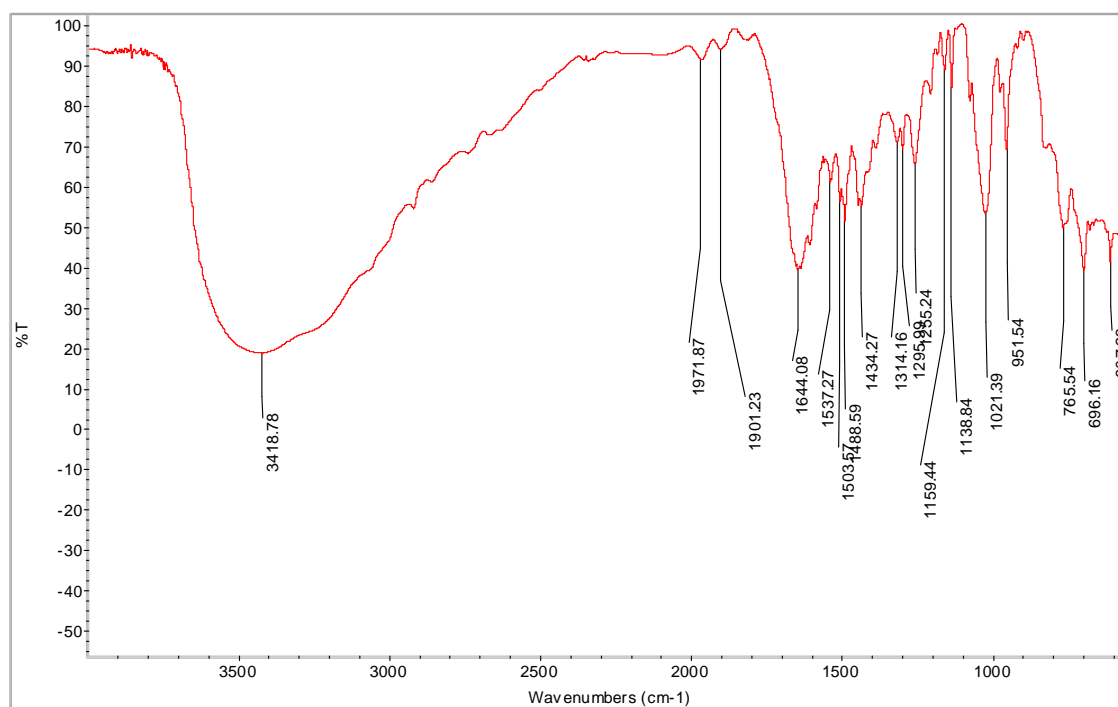
(22)FT-IR spectrum of 2-(2-Hydroxy-phenyl)-4,5-diphenyl-1H-imidazole
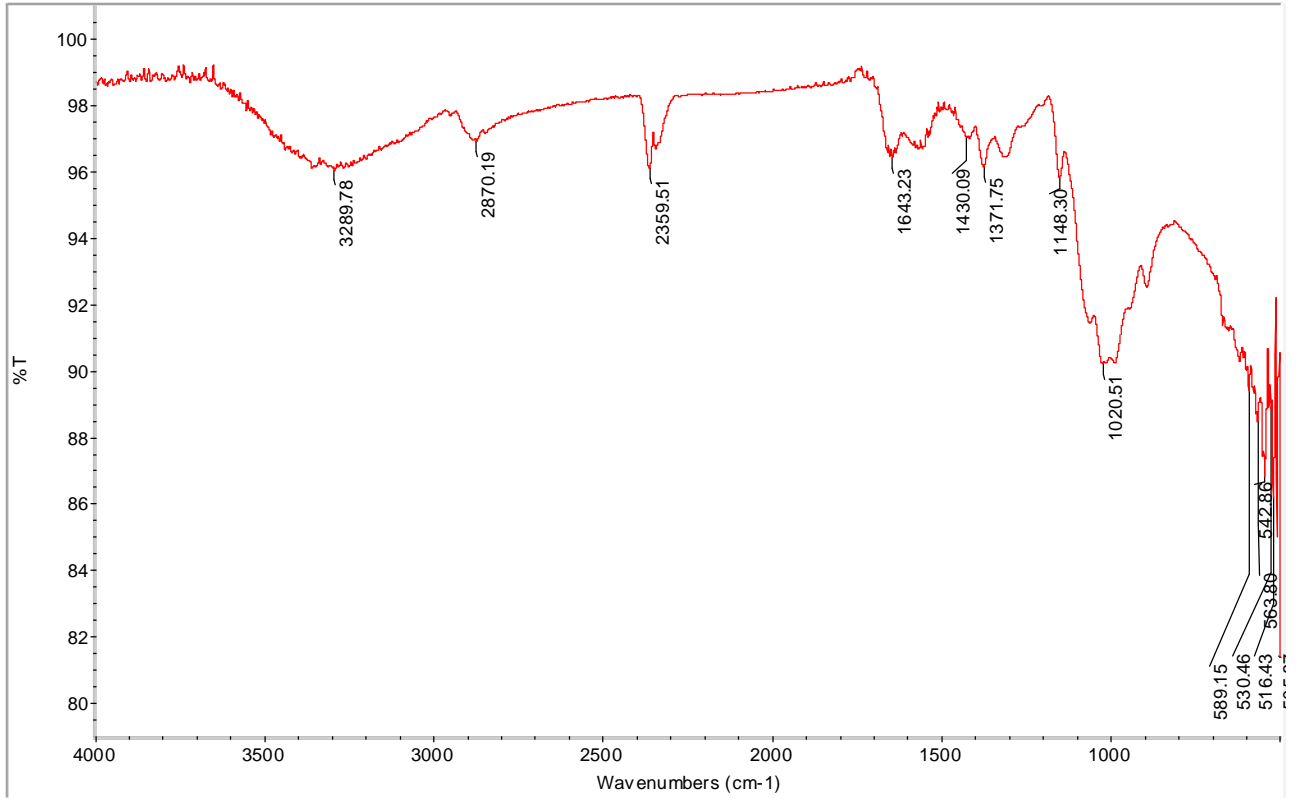
(23) FTIR Spectrum of Chitosan
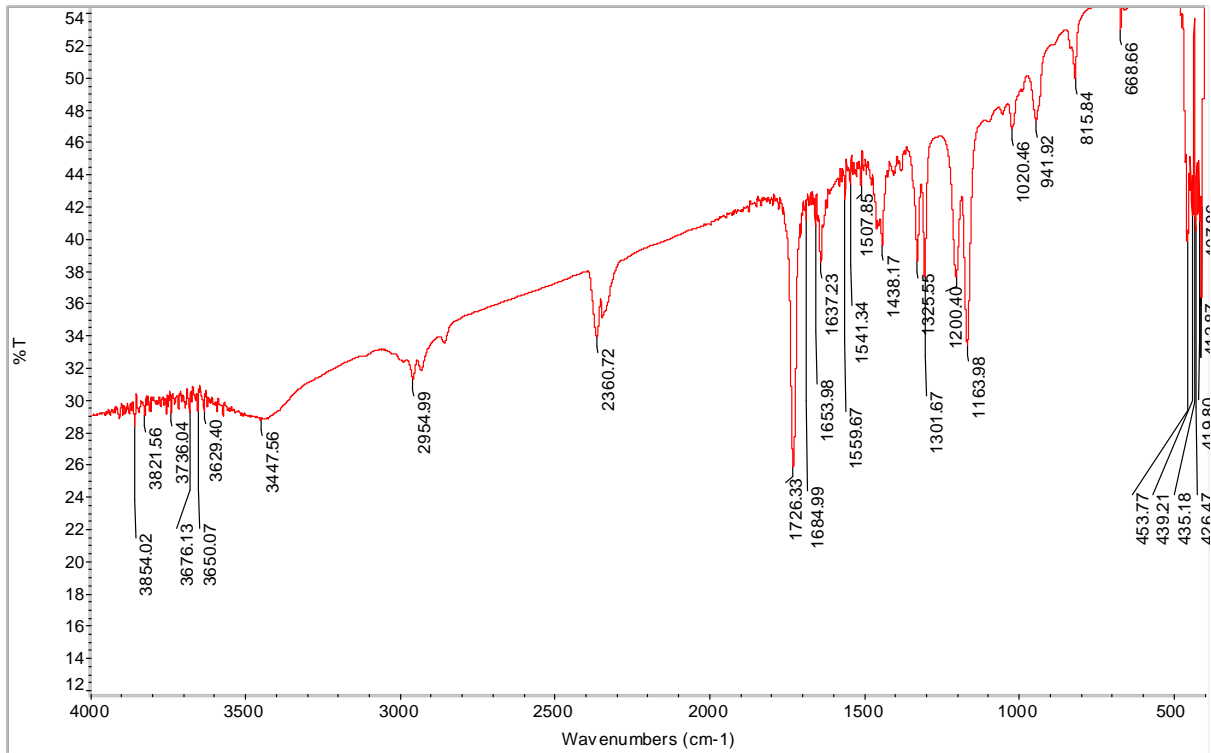
(24) FTIR Spectrum of MMA
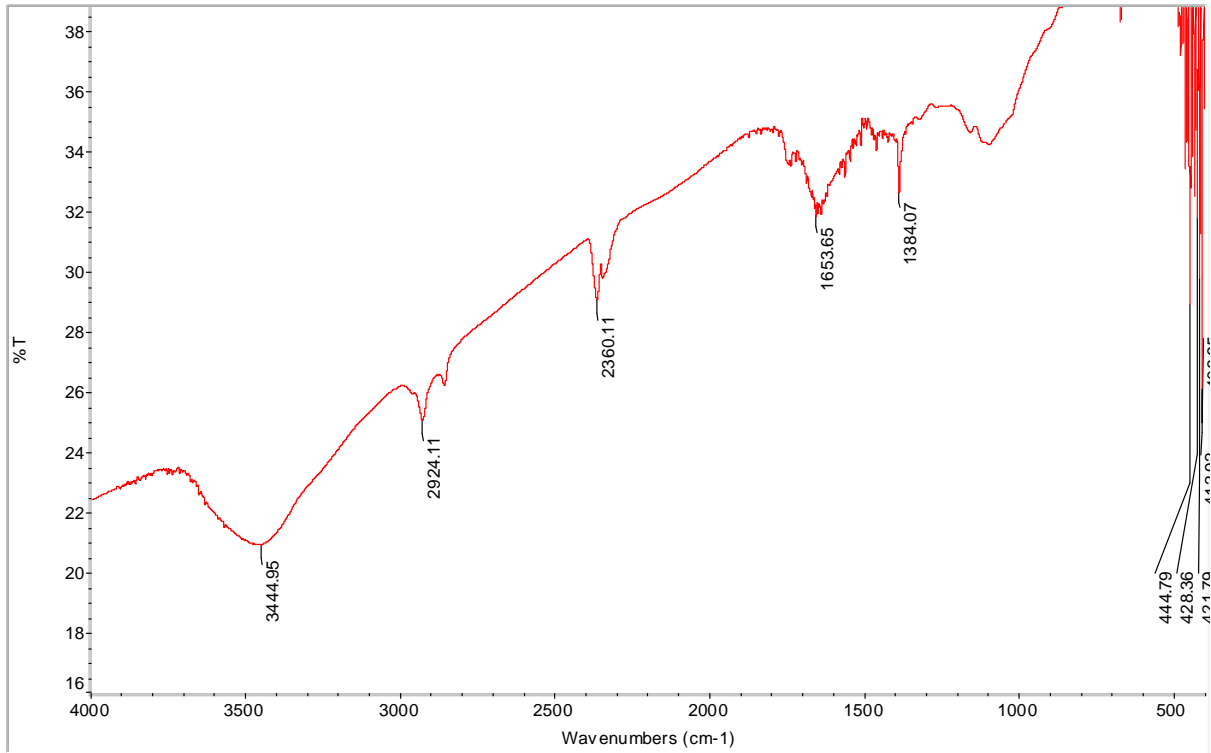
(25) FTIR Spectrum of Chitosan-PMMA graft
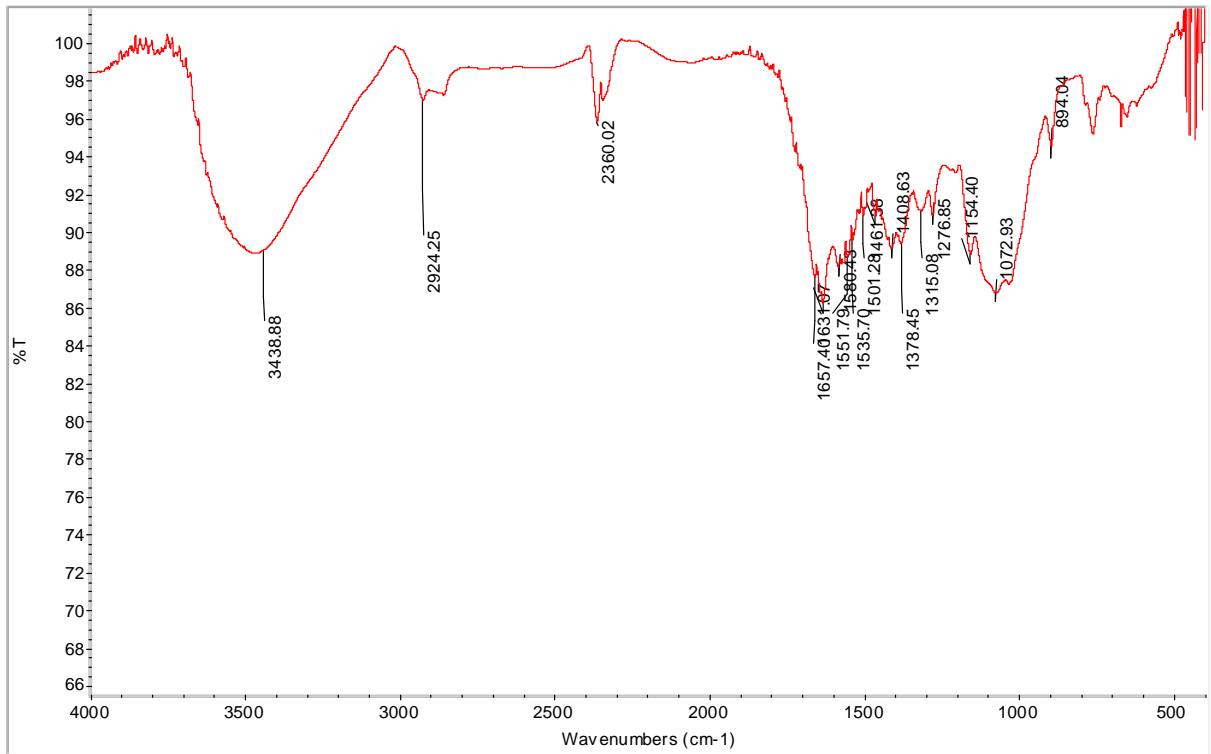
(26) FTIR Spectrum of Chitosan-Gluteraldehyde Schiff Base
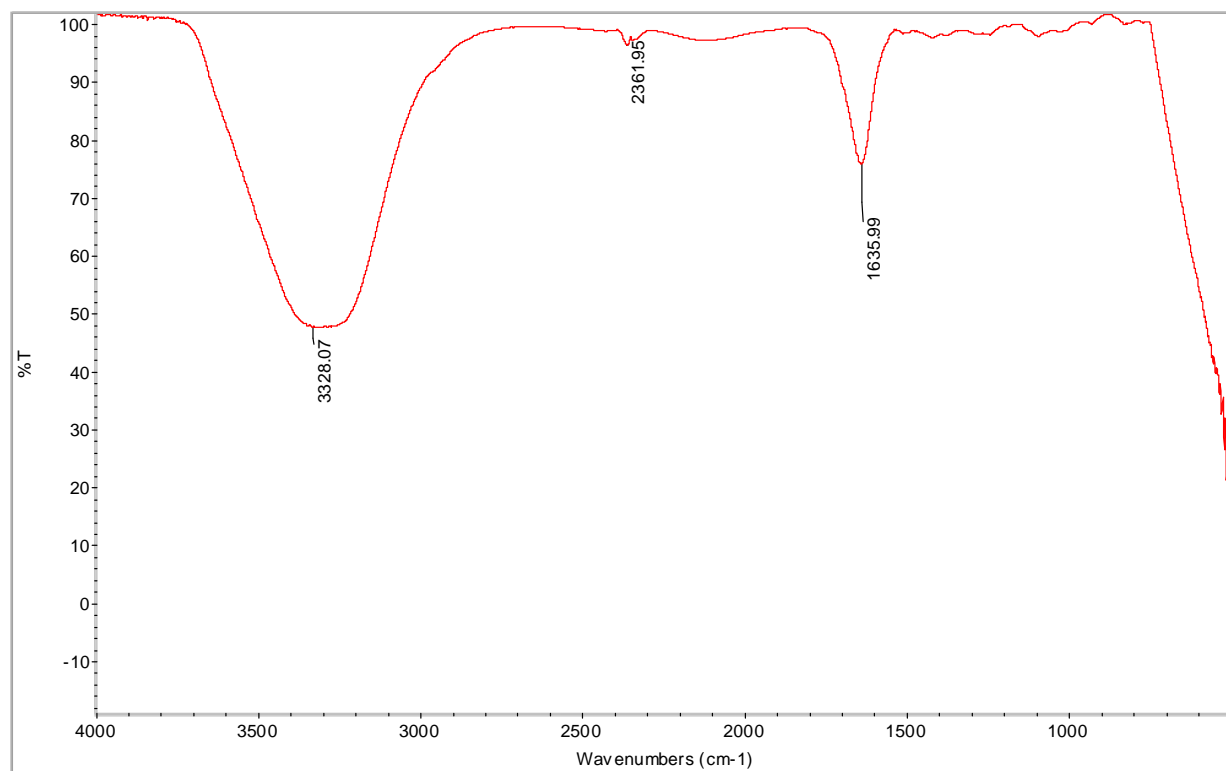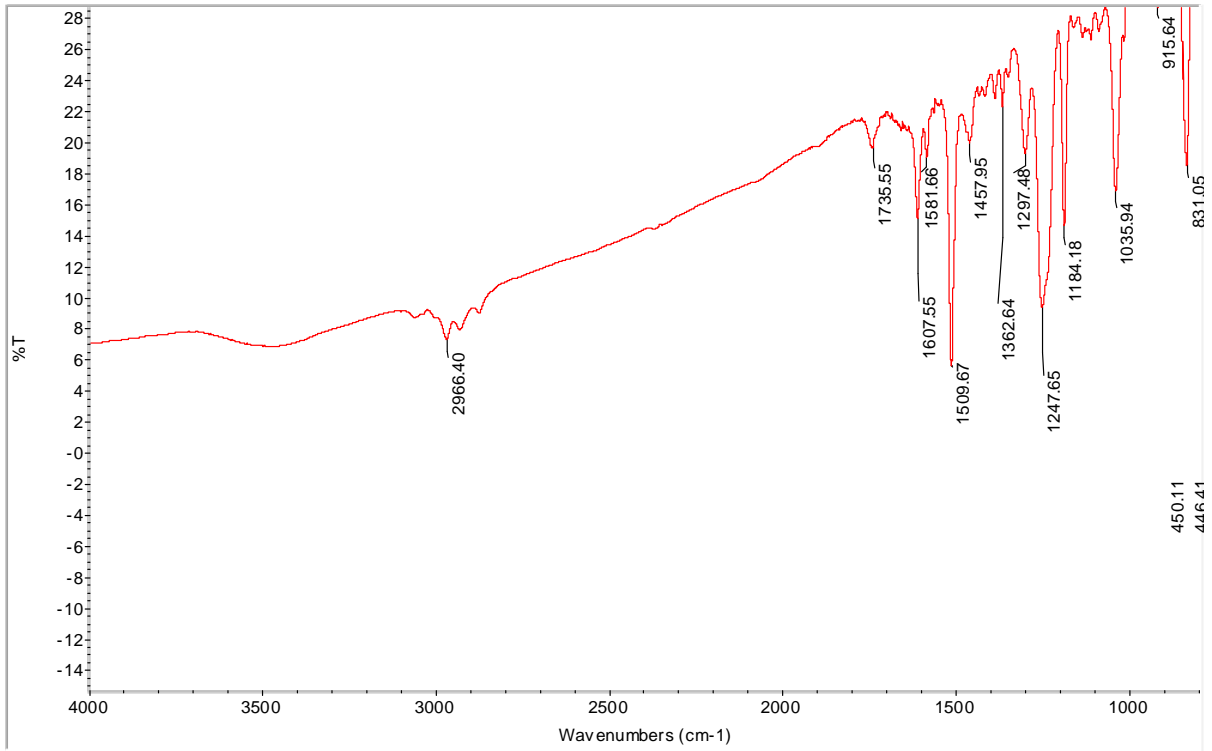
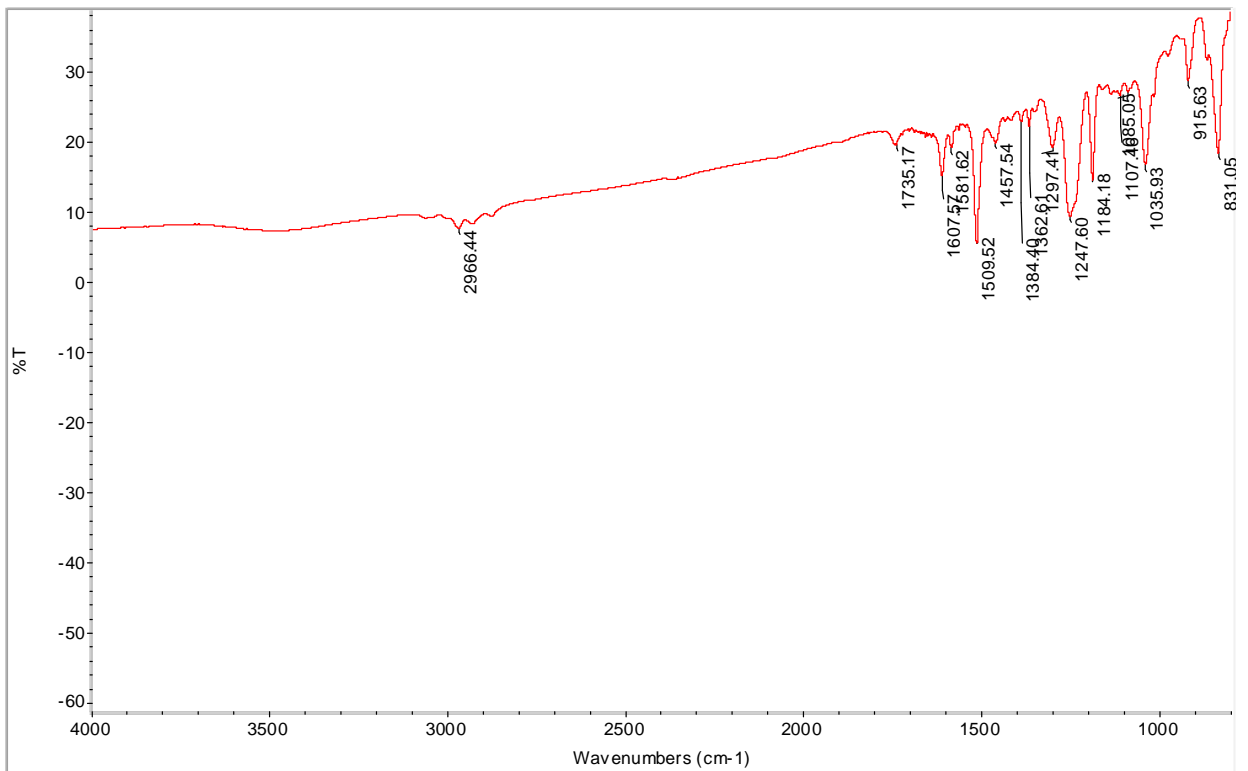(27) FTIR Spectrum of Chitosan-BPDGA-PVA film (ATR mode)
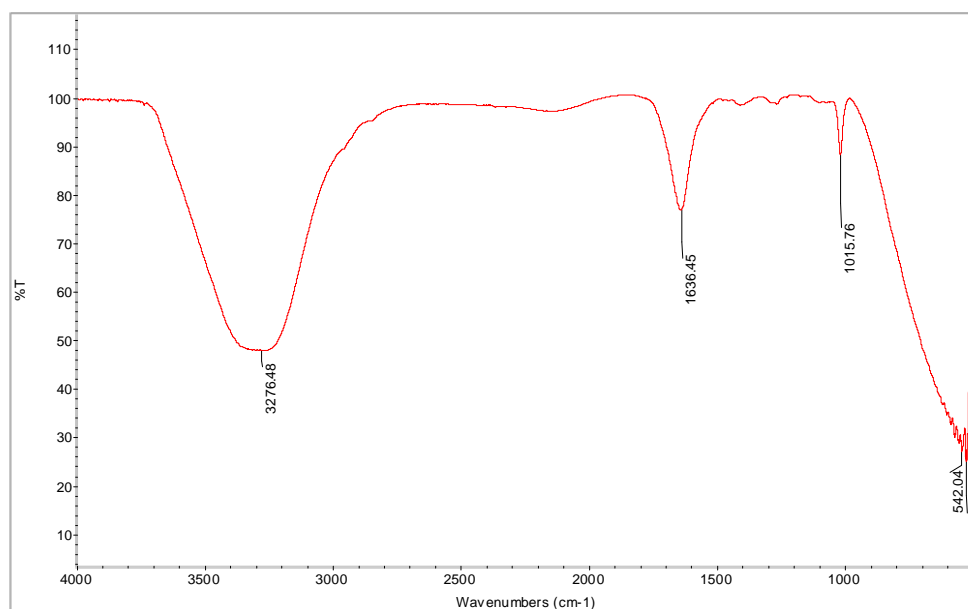
(28) FTIR Spectrum of Chitosan-Gluteraldehyde-PVA film (ATR mode)
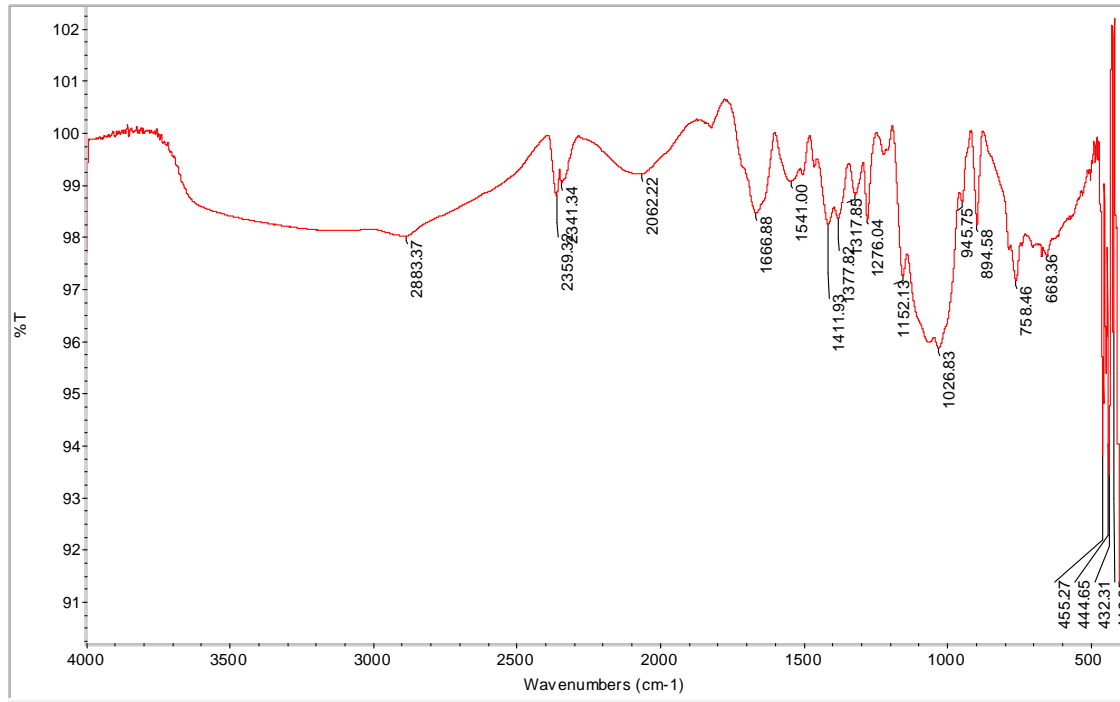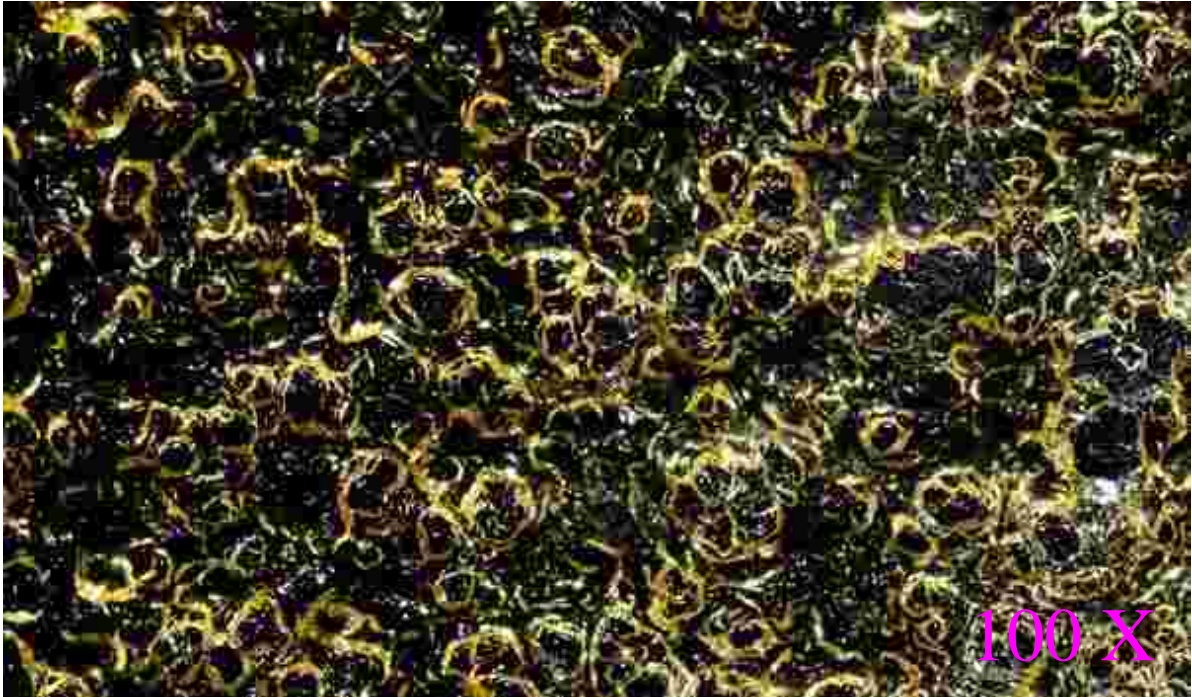
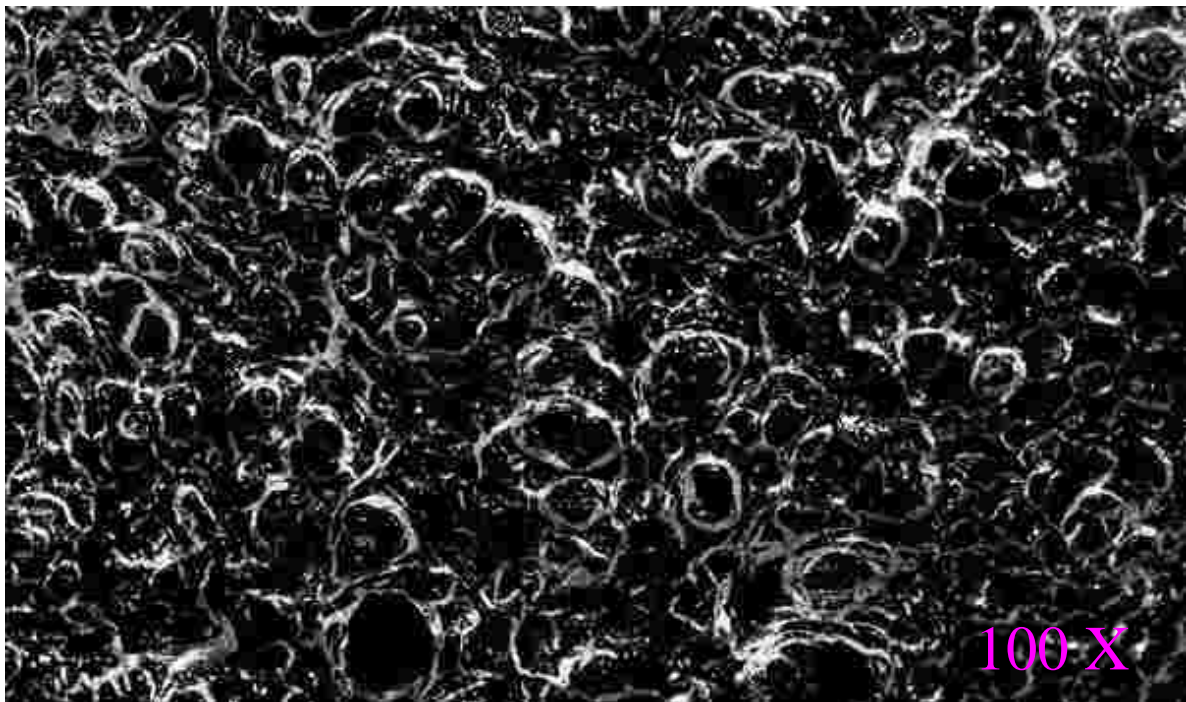(29) FTIR Spectrum of Chitosan-Gluteraldehyde film (ATR mode)

(30) FTIR Spectrum of Chitosan-BPDGE film (ATR mode)

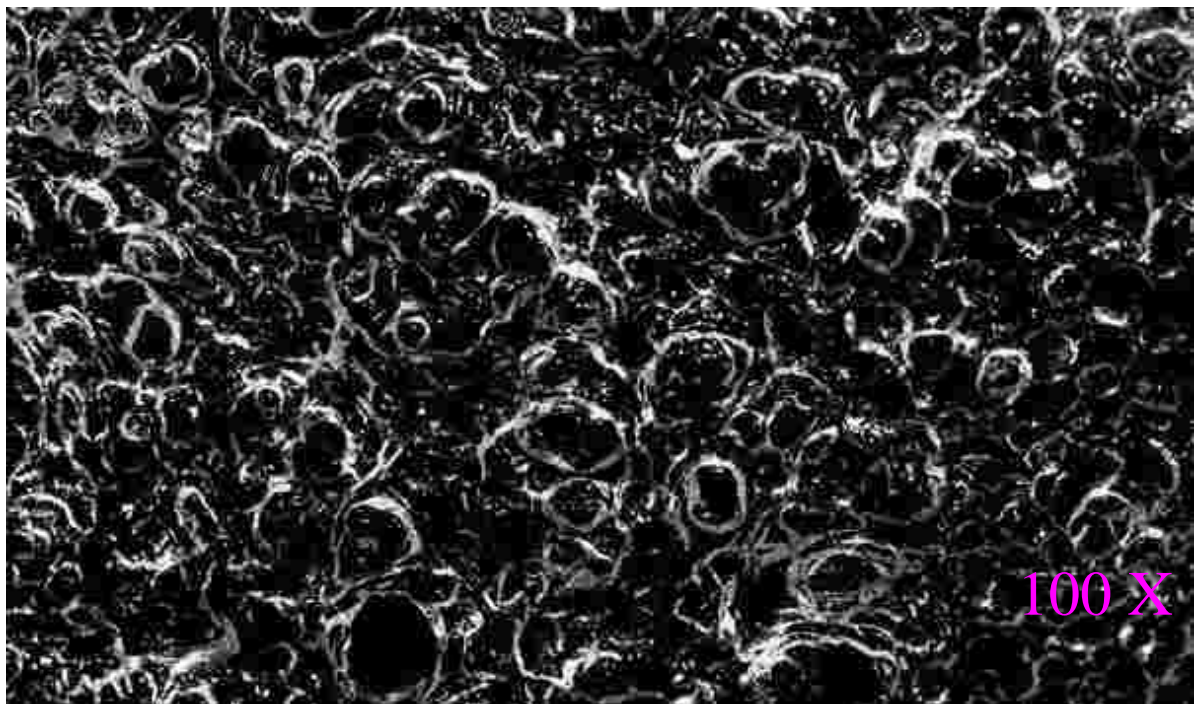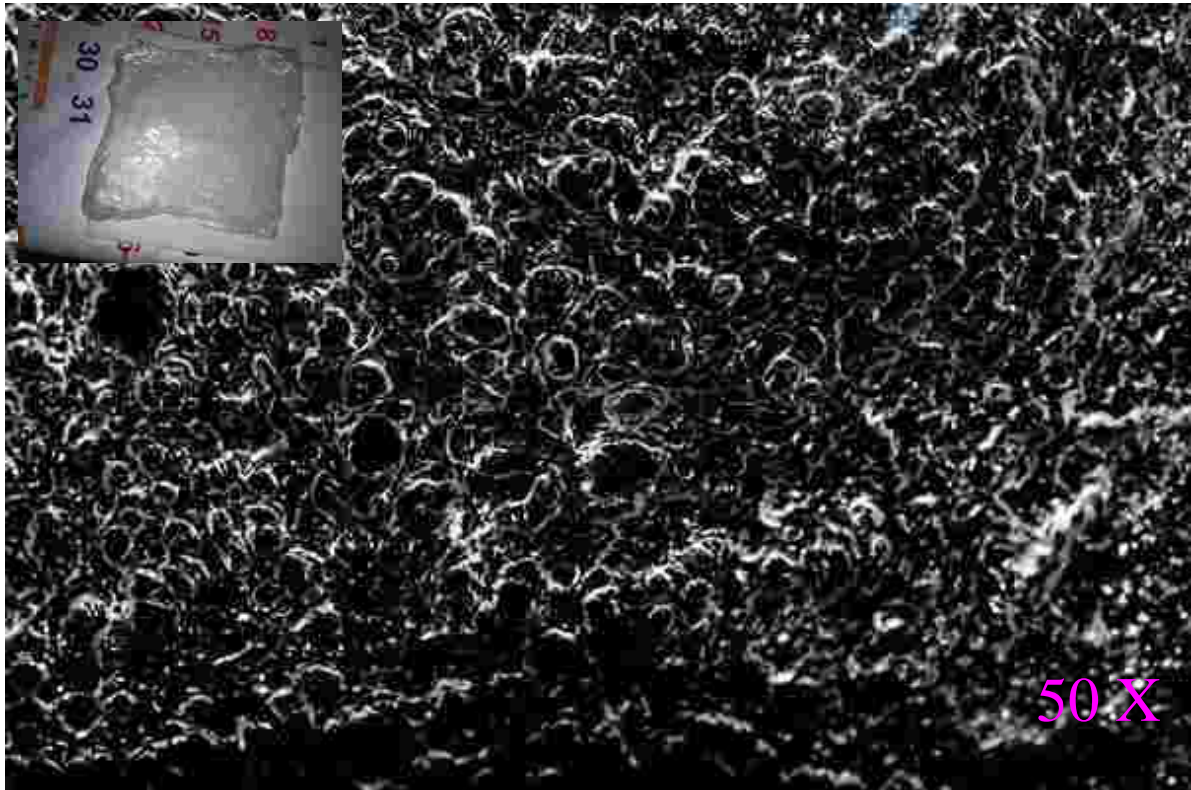(31) FTIR Spectrum of Chitosan-BPDGE -PVA film (ATR mode)

(32) Optical microscopic image of Chitosan Film

(33) Optical microscopic image of Chitosan-BPDGE-PVA film

(34) Optical microscopic image of Chitosan-BPDGE film

SECTION 15

CONTRIBUTION TO THE SOCIETY

Green chemistry work with eco-friendly catalysts, eco-friendly solvents, and experiment with flow processes which is scalable to kilogram scale, without huge factory premises. Some of this research is adopted by the chemical industry, particularly in pharmaceuticals and biomaterials. Huge factories are always a social peril. It creates a lot of air pollution and problems on waste disposal. Installation of flow reactors to can create livelihood materials, without occupying large compound. We are trying to incorporate the flow process for large scale production of bioplastics. Also we are in touch with the incorporation of flow process to Ayurvedic pharma and food processing, to enhance productivity. The sustainable process has following implications on society as given below.
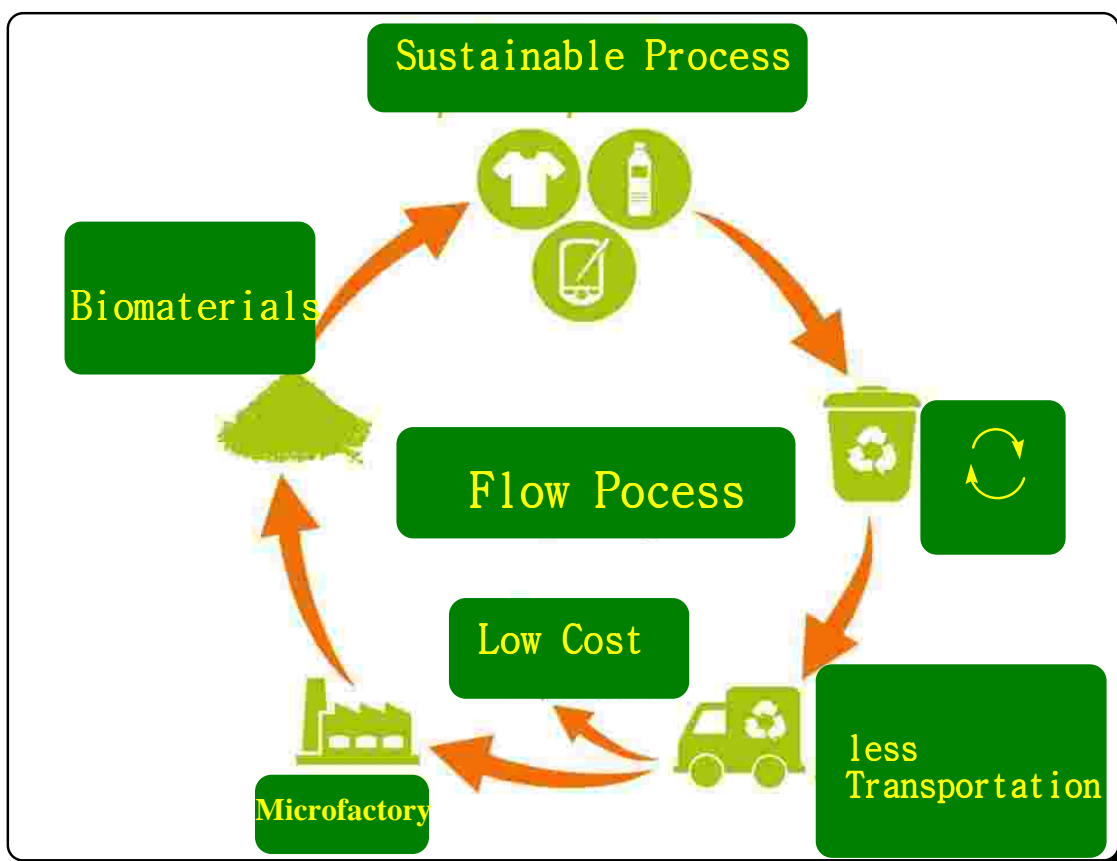
Figure1: The societal implication of flow process

16	WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT	**NIL**
17	NO. OF PUBLICATIONS OUT OF THE PROJECT ………………. (PLEASE ATTACH)	**NIL**

(PRINCIPAL INVESTIGATOR)　　　　　　　　　　**(REGISTRAR/PRINCIPAL)**

(Seal)