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Synthesis, characterization and structural modification of Nanophilic Poly(epichlorohydrin)

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ABSTRACT

The solution polymerization of epichlorohydrin (ECH) in the presence of thioglycolicacid (TGA) as an initiator at 45^{o}C for four hours under nitrogen atmosphere was carried out. Further, the structure of poly(epichlorohydrin) (PECH) is modified by nano silver end capping process. Thus obtained polymer was characterized by various analytical techniques. In order to improve the application of PECH in the biological field, the structure of PECH was extended by the ring opening polymerization (ROP) of ε-caprolactone (CL). The antimicrobial property of nano silver end capped PECH before and after structural modification was also tested. In order to improve the water solubility, the structure of the diblock copolymer was modified by p-hydroxy benzoic acid and succinimide.

Keywords: PECH, DSC, TGA, SEM, structural modification

INTRODUCTION

The synthesis of nanophilic polymeric systems with tailor made properties and study positive signals towards the applications in targeted product is a fascinating field of interest. Among those, PECH is one of the most valuable polymers because of its applications in various science and engineering fields [1, 2]. Unfortunately, the applications of PECH is restricted to some extent in the bio-medical field due to the hydrophobicity, low drug carrying ability and unwanted side products by the chlorine atom. The above said problem of PECH was outwitted by the introduction of poly(caprolactone) (PCL) with good drug carrying ability, succinimide with good water miscibility and nano Ag with good antimicrobial activity. The PECH was synthesized and further modified to poly (glycidyl azide) for the production of energetic materials [3]. Singfield et al [4] synthesized PECH with multiple melting behaviors. Effect of water on the synthesis of energetic PECH was studied by Sciamareli and co-workers [5]. Solubilization of PECH in ionic liquid was reported by Kim and research team [6]. Alkyl alumino phosphonate catalyzed ring opening polymerization of ECH was reported in the literature [7]. Stannic chloride initiated hydroxyl terminated PECH was synthesized and characterized by Francis and research team [8]. Other authors also reported about the synthesis, characterization and applications of PECH [9, 10]. By thorough literature survey, we could not find any report based on the succinimide or p-hydroxy benzoicacid and PCL modified PECH with good antimicrobial property.

The nano structured materials, particularly nano Ag plays a vital role in catalysis and electronics field [11, 12] due to its unique properties like antimicrobial and photo sensitizer [13, 14]. Highly fluorescent Ag nano clusters were synthesized by Xin et al [15]. Seed mediated method was adopted for the synthesis of Ag nano wire [16]. Tartrate reduction route was followed for the synthesis of Ag nano rod and nano wire by Gu et al [17]. Synthesis of Ag nano particles and its antibacterial effect against S.aureus was published by Li and co-workers [18]. Norvancomycin

capped Ag nano particles was synthesized and its antibacterial activity against E-coli was tested [19]. Antifungal activity of Ag nano particle against candida Spp. was reported in the literature [20]. The above literature survey represents the synthesis and characterization of PECH and Ag nano particle. To the best of our knowledge, nono Ag end capped PECH report is not available in the literature. The novelty of the present investigation is the synthesis of nanophilic (nano Ag end capped) PECH by using the TGA as a bridging agent, for the first time. Thus synthesized nano Ag end capped PECH was structurally modified and characterized by various analytical techniques like FTIR, UV-visible, DSC, TGA, FESEM and NMR. The antimicrobial action of the same against E-coli was tested. The combination of both hydrophobic and hydrophilic segments lead to the formation of nano micelle and the same is responsible for the effective drug delivery.

MATERIALS AND METHODS

Materials

Epichlorohydrin (ECH, Spectrochem, India), Thioglycolic acid (TGA, Lobachemie, India), Silver nitrate ($AgNO_3$, Spectrum), Sodium Hydroxide (NaOH, Spectrum), ε-caprolactone (CL, Merck, India), stannous octoate (S.O, Sigma Aldrich, USA), p-hydroxy benzoic acid (PHBA, Spectrum) and succinimide (SI, Nice chemicals, India) were purchased and used as received without any further purification. Double distilled water (DDW) was used for the preparation of the solution. Chloroform and diethylether were purchased from Spectrum chemicals.

Solution polymerization of ECH with TGA initiator

A 100 mL round bottomed (RB) flask equipped with a magnetic stirrer and a lateral neck with tap was used. The system was vacuumed and backfield with dry nitrogen several times. Thioglycolic acid (1 mL), ECH (5 mL) and DDW (25 mL) were introduced under inert atomosphere. The reaction mixture was stirred by magnetic bar for 4h at 70^oC and neutralized with NaOH solution. 4.5 g highly viscous PECH was obtained after drying the sample for 6 hours (8). The reaction is mentioned in Scheme-1.

Silver end capping of PECH

PECH (1.0 g) was dissolved in 50 mL THF. 0.06 g $AgNO_3$ was dissolved in 25 mL DDW and introduced in to a 250 mL RBF under stirring condition to obtain a homogeneous mixture under nitrogen atmosphere for 30 min. The mixture was heated to 45^0C for further 2 hours. During this mixing process, the thiol end capped PECH reduced the $AgNO_3$ and formed the nano Ag end capped PECH. The products were freeze dried. 0.82 g dark brown silver end capped PECH viscous liquid was obtained and stored under nitrogen atmosphere. The chemical reaction involved is mentioned in Scheme-1.

Synthesis of PECH-b-PCL block copolymer

1.0g of above synthesized PECH was taken in a 25 mL RBF. 1.0 CL monomer was charged with the RBF. With this 0.001 g S.O was added and the contents were heated to 160^oC under nitrogen atmosphere with mild stirring for 2 hours (21). At the end of the reaction time, PECH-b-PCL was obtained as a highly viscous liquid. It was further purified by adding 25 mL chloroform and re-precipitated by the addition of 250 mL diethylether. The contents were transformed into a 500 mL beaker and kept under fume hood over night. Thus obtained white crystalline powder copolymer was dried, weighed and stored in a zipper lock cover. The reaction is mentioned in Scheme-1.

Structural modification of PECH-b-PCL by succinimide or p-hydroxy benzoicacid

1.0 g of above synthesized block copolymer was dissolved in 100 mL THF. 1.0g succinimide or p-hydroxybenzoicacid was dissolved in 50 mL DDW and mixed with the copolymer solution. With this 0.2g NaOH pellet was added and stirred well under nitrogen atmosphere for 10 min at room temperature. Then, the temperature was raised to 45^oC and stirred for 6 hours. At the end of the reaction, the contents were evaporated to dryness. After drying, the powder mass was obtained, weighed and stored in a zipper lock cover. The reaction is mentioned in Scheme-1.

Characterization

FTIR spectrum was recorded for the samples by using Shimadzu 8400 S model (Japan) instrument through KBR pelletisation method. The spectrum was measured between 4000 and 400 cm^{-1}. The surface morphology and particle sizes of the grafted samples were determined by FESEM Hitachi S4800 Japan instrument. Differential scanning calorimetry (DSC) and Thermogravimetric analysis were measured by using Universal V4.4A TA Instruments (simultaneous DSC and TGA analyzer) under nitrogen atmosphere at the heating rate of 10K/min from room

temperature to 373K. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) (500 MHz) spectra were obtained using an NMR apparatus (Varian, Unity Inova-500 NMR) at room temperature in $CDCl_3$ solvent. Antimicrobial study was carried out as mentioned below: 0.1ml (100µml) diluted Klebsiella broth was spread over the fresh nutrient agar plate. 0.3 mm of well was cultured in the centre of the broth spread plate. 20µml of prepared test sample was added into the well. Then the plate was incubated at 37^{o}C for monitoring the antimicrobial property of the sample. At different interval of time the antimicrobial property of the sample was noted. At 4 and 96 hours antimicrobial property of the sample was photographed. The diameter of the black spot has been increased with time. A Waters 2690 gel permeation chromatography (GPC) instrument was used to determine the M_n and M_w of the polymer samples by using tetrahydrofuran (THF) as an eluent at room temperature at the flow rate of 1 $mLmin^{-1}$ against polystyrene (PS) standards. A Zetasizer (Nano-ZS Malvern Instrument USA) was used to measure the zeta potential of dispersions. To determine the particle size distribution, the dispersion was analyzed by laser diffraction technique using a particle size analyser (Microtrac, Bluewave, Japan). The binding energy of diblock copolymer system was determined by X-ray photoelectron spectroscopy, (XPS, Thermo Scientific, Theta Probe, and UK). Field emission scanning electron microscopy (FESEM) was used to examine morphological behaviour of copolymer with the help of FESEM – Hitachi S4800 Japan, instrument.

RESULTS AND DISCUSSION

In the present investigation, the TGA initiated PECH was prepared and further the structure of PECH was modified in order to improve the processability and bio-compatibility. The Cl atom of PECH unit was replaced by succinimide and p-hydroxy benzoic acid. In order to improve the bio-compatibility the PCL units were introduced. In order to improve the processability the p-hydroxy benzoicacid or succinimide units were introduced via chemical grafting reaction. The structure-property relationship of PECH before and after modification is studied here.

FTIR Analysis

The FTIR spectrum of PECH before and after the structural modification is given in Figure 1. Figure 1(a) indicates the FTIR spectrum of TGA initiated ROP of ECH. The broad peak around 3400 cm^{-1} confirmed the OH stretching of PECH attached at the chain end. The C-H symmetric and anti-symmetric stretching is observed at 2865 and 2937 cm^{-1} respectively. The carboxyl stretching of TGA appeared at 1727 cm^{-1}. The C-S and Cl stretching of PECH are observed at 1384 and 667 cm^{-1} respectively. The C-O-C ether linkage is appeared at 1042 cm^{-1}. Figure 1(b) represents the PECH after the structural modification with PCL. The increase in C-N symmetric (2866 cm^{-1}), anti-symmetric (2943 cm^{-1}), carbonyl stretching (1721 cm^{-1}) and the C-H out of plane bending vibration (722 cm^{-1}) confirmed the structural modification of PECH by PCL moieties. The aromatic C-H stretching of p-hydroxy benzoicacid units are observed at 820 cm^{-1}. The appearance of doublet peak around 1080 cm^{-1} confirmed the C-O-C ester linkage of both PCL and p-hydroxy benzoicacid units. The appearance of new peaks confirmed the structural modification of PECH. Figure 1(c) indicates the FTIR spectrum of PECH after the structural modification with succinimide and PCL units. Here also one can see the above said peaks corresponding to PECH and PCL units. A new peak at 1357 cm^{-1} confirmed the C-N stretching of succinimide units. Recently, Ferrahi et al [22] explained the C-Cl and C-O-C stretching of ECH units in the copolymer structure. By using the FTIR spectra the functionalities of PECH before and after structural modification was confirmed.

NMR Study

The proton and carbon NMR spectra confirmed the chemical modification of PECH by p-hydroxy benzoicacid and PCL units. Figure 2(a & b) represents both the ^{1}H and ^{13}C-NMR of PCL and p-hydroxy benzoicacid modified PECH. The alkoxy proton of PCL was appeared at 4.2 ppm. The aromatic proton of p-hydroxy benzoicacid was appeared between 6.5 and 7.3 ppm. The aromatic carbons of p-hydroxy benzoicacid units were appeared between 125 and 130 cm^{-1}. The carbonyl carbon of PCL was appeared at 173 cm^{-1}. According to the literature, the C-H carbon signal was appeared at 79.07 ppm [22]. The presence of both aromatic carbon signals and aliphatic carbonyl signals confirmed the chemical modification of PECH by PCL and p-hydroxy benzoicacid units. Figure 3 represents the both ^{1}H and ^{13}C-NMR spectrum of PECH, after the chemical modification with PCL and succinimide units. Again the alkoxy proton of PCL was appeared at 4.2 ppm. The methylene protons of succinimide units can be seen around 1.3 ppm (Figure 3(a)). Figure 3(b) confirmed the ^{13}C-NMR spectrum of PECH after the structural modification with succinimide and PCL units. The carbonyl stretching of PCL and succinimide units were appeared around 173 cm^{-1}. The carbonyl stretching of PCL and succinimide units were appeared around 173 ppm. The alkoxy carbon signal of PCL segments are appeared around 62 ppm. Thus both hydrogen and carbon NMR

confirmed the chemical modification of PECH by succinimide and PCL units. For the sake of convenience the ^{1}H and ^{13}C-NMR spectra of PECH-TGA-Ag system is shown in Figure 4(a & b).

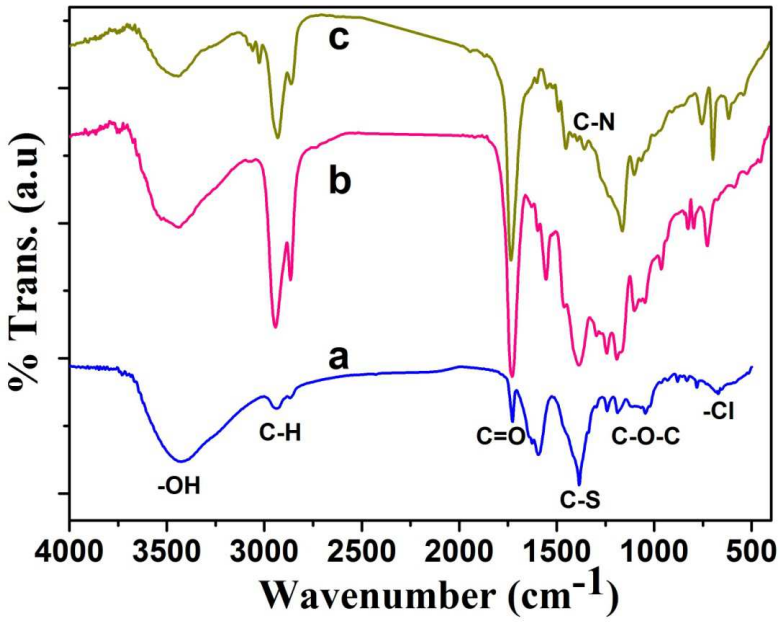


Figure 1: FTIR spectrum of (a)Ag-TGA-PECH, (b)PECH-g-PHBA-b-PCL, (c)PECH-g-SI-b-PCL system

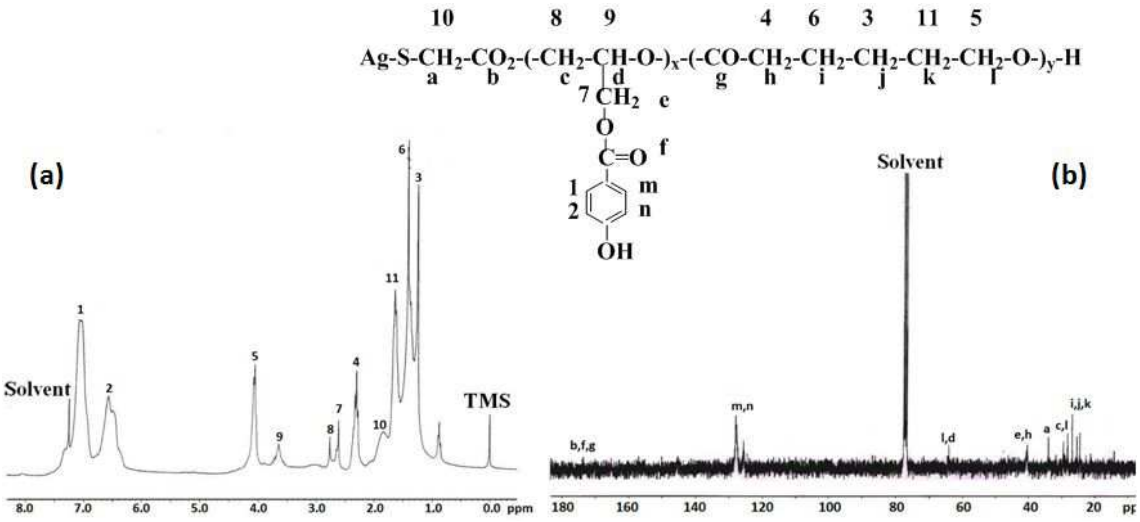


Figure 2: ^{1}H-NMR (a) and ^{13}C-NMR (b) spectrum of PECH-g-PHBA-b-PCL system

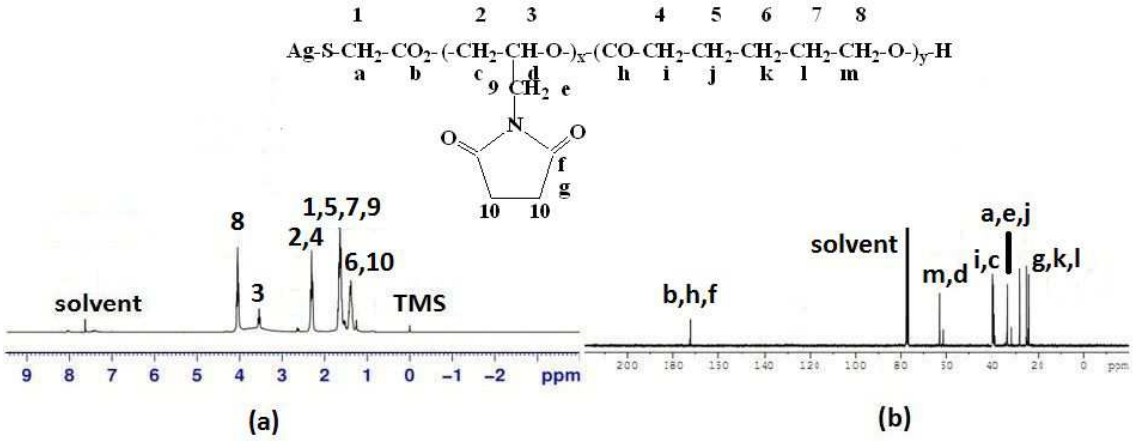


Figure 3: ^{1}H-NMR (a) and ^{13}C-NMR (b) spectrum of PECH-g-SI-b-PCL system

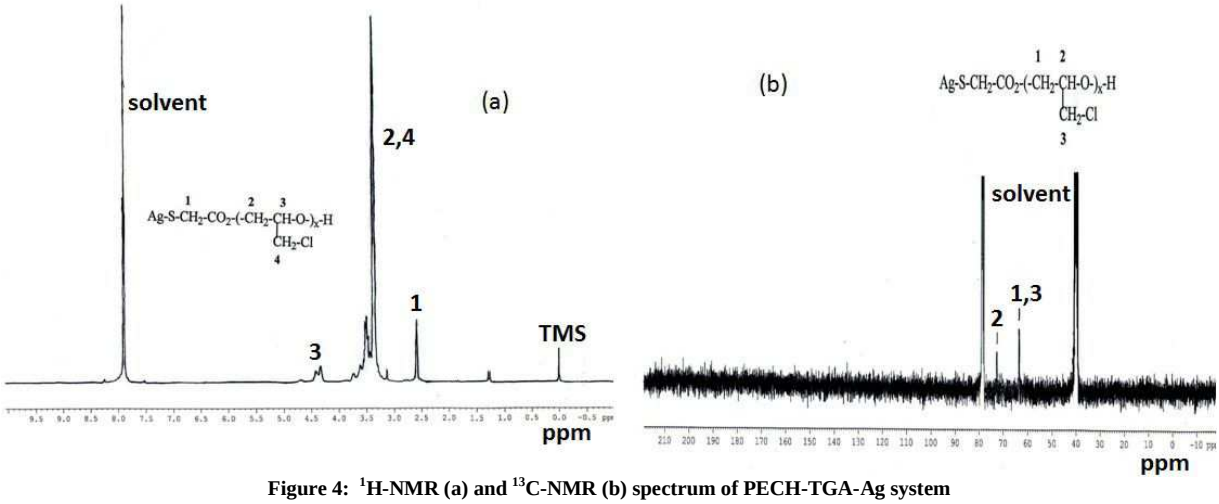


Figure 4: ^{1}H-NMR (a) and ^{13}C-NMR (b) spectrum of PECH-TGA-Ag system

DSC Study

The phase transition of PECH before and after the structure modification is given in Figure 5. The DSC of Ag nano particle end capped PECH is shown in Figure 5(a) without any T_g or T_m. PECH after the structural modification with PCL, p-hydroxy benzoicacid (Figure 5(b)) and succinimide and PCL (Figure 5(c)) exhibits the T_m value of 48.8 and 61.3^o C respectively. The phase transition below 100^{o}C is associated with the T_m of PCL units. The appearance of melt transition below 100^{o}C confirmed the chemical modification of PECH by PCL units. The succinimide grafted PECH-PCL block copolymer exhibited the highest T_m with peak broadening due to the more moisture absorbance. Singfield and co-workers [2] reported about the multiple melting behavior of PECH. The poly(s-epichlorohydrin) exhibited a single endothermic peak at 112°C, ascribed to the T_m of poly(s-epichlorohydrin). In the present investigation, the T_m of PECH is not appeared and obviously confirmed the amorphous nature of PECH.

TGA Profile

The thermal stability of PECH before and after chemical modification is shown in Figure 6. Figure 6(a) indicates the TGA thermogram of pristine Ag nano particle end capped PECH. The thermogram exhibits a three step degradation process. The first minor weight loss below 150^o C is due to the removal of moisture and physisorbed water molecules. The second minor weight loss is ascribed to the breaking of Cl atom from the PECH backbone. The third major weight loss around 266^{o}C is due to the breaking of ether linkage. Above 450^{o}C the system exhibits 74% weight residue remained. Eroglu and co-workers [1] reported the single step degradation for PECH with ~10% weight residue remained above 500^{o}C. Figure 6b indicates the p-hydroxy benzoicacid grafted PECH-PCL block copolymer system. The system shows a three step degradation processes. The first major degradation weight loss around 240^{o}C is due to the breaking of ester linkage between PECH and p-hydroxy benzoicacid units. The second

minor weight loss around 315° C can be explained on the basis of degradation of ether linkages present in PECH. The third major weight loss around 370°C can be explained on the basis of degradation of ester units present in the PCL. Above 450°C, the system exhibits 42% weight residue remained. Figure 6(c) explains the TGA thermogram of succinimide grafted PECH-PCL block copolymer. Here one can see a three step degradation process. The first major weight loss around 220°C is due to the degradation of succinimide units. The second minor weight loss around 290°C is associated with the degradation of ether linkage present in PECH. The third major weight loss around 411°C is due to in the breaking of ester linkages present in the PCL units. Above 450°C, the system shows 15.6% weight residue remained. In comparison, the pristine PECH exhibited the highest thermal stability due to the presence of inter molecular forces like hydrogen bonding. After the structural modification the succinimide grafted system exhibited the highest thermal stability due to the presence of more inter molecular hydrogen bonding.

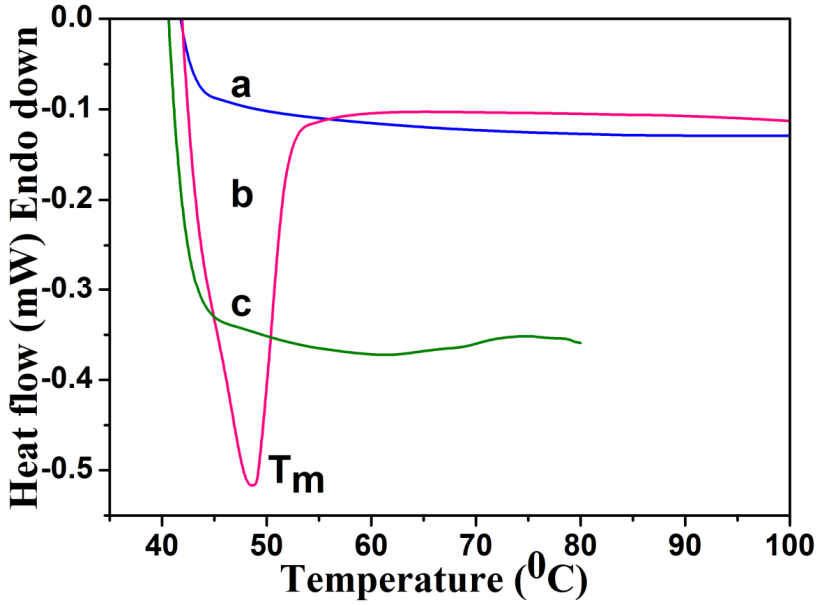


Figure 5: DSC thermogram of (a)TGA-PECH-Ag, (b)PECH-g-PHBA-b-PCL,(c)PECH-g-SI-b-PCL system

GPC Analysis

The ROP of ECH and CL monomers were confirmed by GPC analysis. (Figure 7). The pristine Ag nano particle end capped PECH (Figure 7(a)) exhibits the M_n, M_w and PD values of 2214, 2998 g/mol and 1.35 respectively. This confirmed the oligomerization of ECH [23]. The p-hydroxy benzoicacid grafted PECH (Figure 7(b)) PCL system shows the M_n, M_w and PD values of 6766, 10701 g/mol and 1.58 respectively. The succinimide grafted PECH-PCL block copolymer (Figure 7(c)) system shows the M_n, M_w and PD values of 7348, 10396 g/mol and 1.41 respectively. The PD values confirmed that the obtained polymer is having linear structure without any cross linking and branching.

FESEM Study

The surface morphology of PECH before and after structure modification is given in Figure 8. Figure 8(a) indicates the FESEM image of pristine Ag nano particle end capped PECH. The silver nano particles attached at the chain end of PCL or TGA are having different size varied between 40 and 103.1 nm. The variation in size of silver nano particle can be explained as follows: i) the silver nano particle formation was accelerated through the thiol group of TGA initiator. Thiol group is mild reducing agent and hence lead to the formation of silver nano particle with the lowest size of 41.2 nm. ii)The silver nano particle formation was also enhanced by polyol methodology. The polyol methodology is slow process and lead to the formation of larger size silver nano particle. Figure 8(b) confirms the surface morphology of p-hydroxy benzoicacid grafted PECH-PCL block copolymer. Now the bigger sized silver nano particle was reduced to some extent. It means the particle size greater than 100 nm was reduced approximately to 75 nm. The reduction in the size of silver nano particles can be explained as follows: i) During the ROP of CL, the temperature was maintained at 160° C for 2 hours. This high thermal energy might involve in the size reduction

process. ii) During the ROP of CL, there will be a generation of high stress inside the reaction vessel and this mechanical force might reduce the size of the silver nano particle. Figure 8c indicates the surface morphology of succinimide grafted PECH-PCL block copolymer. Here one can see the silver nano particle with the size of less than 80 nm with some voids on the surface. The voids present on the surface of PCL helped to carry the drug during the drug loading process. This type of material is having high bio-medical value. In the present investigation, in addition to the mild reduction by the thiol group and polyol methodology two more forces were acted as a size reducing factors [24]. They are claimed as thermal energy and mechanical forces. The presence of micro voids increases the applications of PECH in the medicinal field.

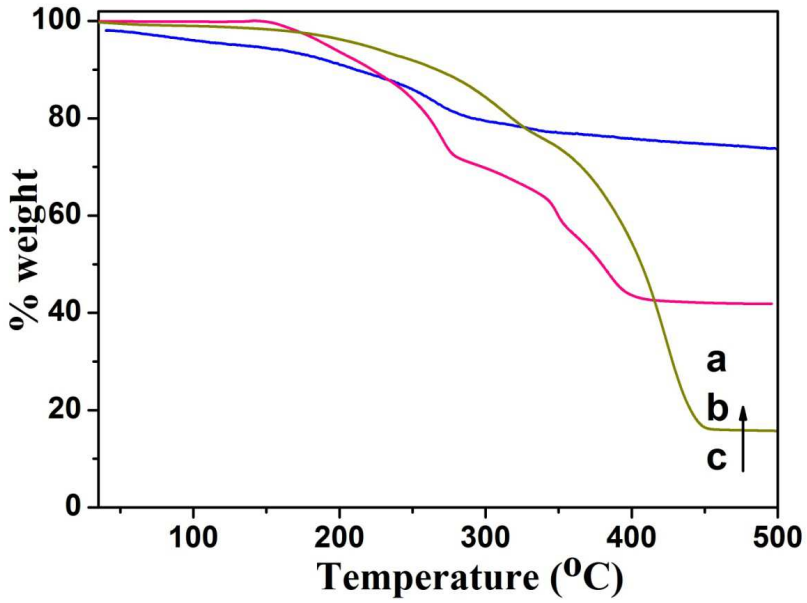


Figure 6: TGA thermogram of (a)TGA-PECH-Ag, (b)PECH-g-PHBA-b-PCL, (c)PECH-g-SI-b-PCL system

XPS Analysis

Figure 9 explains the XPS of PECH before and after structural modification. Figure 9(a) indicates the XPS of pristine Ag nano particle end capped PECH. The O1S, Ag3d, C1S, Cl2P and S2P energy levels are observed at 531, 369, 283, 200.7 and 161 eV respectively. The appearance of Ag3d confirmed the silver nano particle formation. Figure 9(b) indicates the XPS of p-hydroxy benzoicacid grafted PECH-PCL block copolymer. Here also one can see the above said peaks. Important point noted here is the intensity of O1S, C1S at 531, 283 eV respectively were increased due to the block copolymerization with CL and grafting with p-hydroxy benzoicacid. The increase in C1S and O1S peak intensity confirmed the ROP of CL. One more point is peak corresponding Cl2P at 200.7 eV was disappeared. It means that the Cl atom of ECH segment was replaced by the p-hydroxy benzoicacid. Again this confirmed the chemical modification of PECH-PCL block copolymer. Figure 9(c) represents the XPS of succinimide grafted PECH-PCL diblock copolymer. Here also one can see the above said peaks with an appearance of new peak corresponding to N1S at 349 eV confirmed the chemical grafting of succinimide unit on the ECH segment. The Cl2P peak at 200.7 is not appeared here. Moreover, the peak intensity of C1S and O1S were increased. Recently, Sribala and co-workers [25] explained the XPS of PECH. Our report is coinside with their report. The disappearance of Cl2P peak and increase in C1S and O1S peak confirmed the chemical modification of PECH by succinimide and CL units.

Antimicrobial Study

The silver nano particle has a unique property such as antimicrobial property. Figure 10(P1a & b) indicates the antimicrobial zone of pristine Ag nano particle end capped PECH for 24 and 48 hour respectively. Here one can see a block dot corresponding to the antimicrobial activity of silver nano particle. Unfortunately after 48 hour of incubation the antimicrobial zone growth was not observed. This is due to the polydispersity of silver nano particle. Figure 10(P2a & b) indicates the antimicrobial activity of PECH after the structural modification with p-hydroxy

benzoicacid and CL units for 24 and 48 hours respectively. The antimicrobial activity against E-Coli was observed with successful growth. Figure 10(P3 a & b) indicates the antimicrobial activity of PECH after structural modification with succinimide and CL segments for 24 and 48 hours respectively. Here one can see a considerable growth in the antimicrobial properties of silver nano particle against E-Coli. In comparison, the succinimide grafted system exhibits excellent antimicrobial property due to the good bio-compatibility. Satiriou et al [26] studied about the antimicrobial activity of silver ion and nano particle against E-coli and concluded that the antimicrobial activity depends on the size of the material because of the curvature that facilitates the mass transfer from their surface. Our results are in accordance with their report.

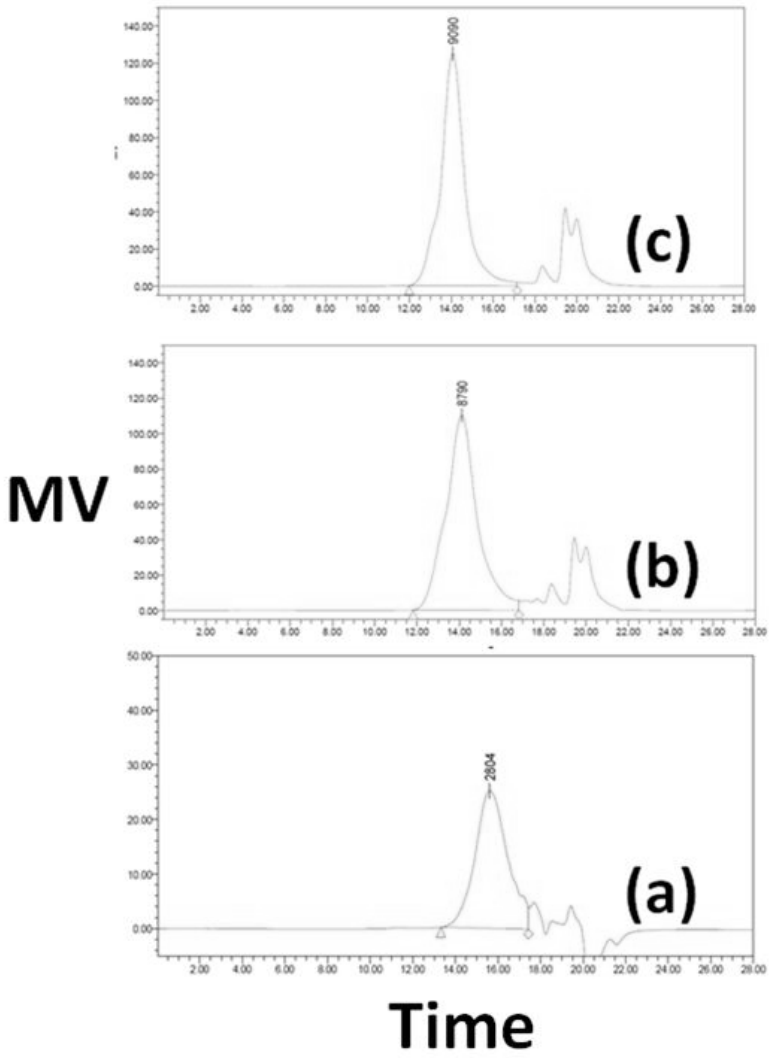


Figure 7: GPC of (a)Ag-TGA-PECH, (b)PECH-g-PHBA-b-PCL, (c)PECH-g-SI-b-PCL system

Zeta Potential Report

Figure 11 indicates the particle size and zeta potential diagram. Figure 11(a) represents the particle size of approximately 100 nm corresponding to the succinimide grafted PECH-PCL block copolymer system. Figure 11(b) confirms the zeta potential value of the above said polymer. The system exhibits two peaks at zero and -25 mV. This indicates that the present polymer system exhibits total negative charges. So that a drug with a positive charge can easily approach the polymer system in order to act as an effective drug carrier. Also indicates that a drug with neutral charge can also approach the polymer system with effective drug carrying systems. The zeta potential measurement confirmed that a drug with positive charge can easily approach the succinimide grafted polymer

system for an effective drug carrying process. The zeta potential value of polyamide-ECH diblock copolymer was reported in the literature [27]. This explains the drug carrying ability of the present diblock copolymer.

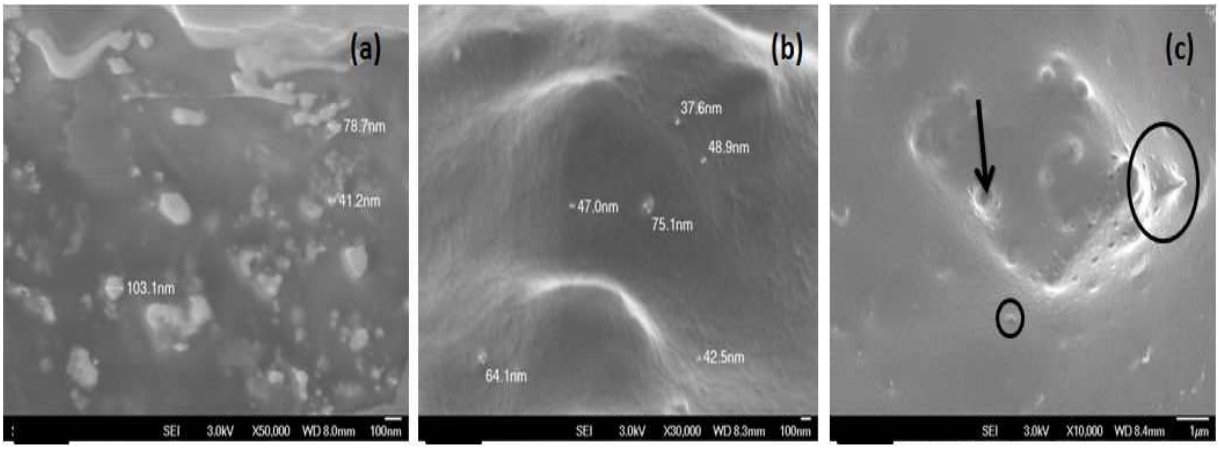


Figure 8: FESEM of (a)Ag-TGA-PECH, (b)PECH-g-PHBA-b-PCL, (c)PECH-g-SI-b-PCL system

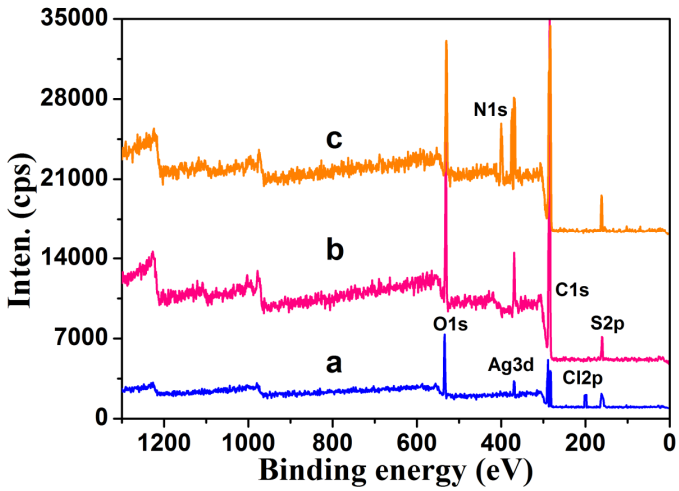


Figure 9: XPS of (a)Ag-TGA-PECH, (b)PECH-g-PHBA-b-PCL, (c)PECH-g-SI-b-PCL system

Ultrasonic Velocity Study

The inter and intra molecular hydrogen bonding as well as the interaction between the polymer and solvent (THF) can be explained on the basis of determining acoustic parameters. The pristine PECH exhibits the ultrasonic velocity, compressibility and refractive index value of $1.23x10^{-3}$ m/s, $2.13x10^{-11}$ N/m^2 and 0.81 respectively. The p-hydroxy benzoicacid grafted PECH-PCL block copolymer exhibits the values of $1.56x10^{-3}$ m/s, $4.58x10^{-11}$ N/m^2 and 1.064 respectively. The succinimide grafted PECH-PCL block copolymer exhibits the values of $1.28x10^{-3}$ m/s, $6.87x10^{-11}$ N/m^2 and 0.85 respectively. The p-hydroxy benzoicacid grafted systems exhibited the highest values due to the presence of rigid phenyl ring and which causes sterric effects and kinked the structure with certain stereo regularity. The high ultrasonic velocity explains the less favorable interaction between polymer and solvent. This infers that during the structural modification of PECH both the size and charge of the modifying agent is an important point. The succinimide grafted system exhibits good interaction with solvent and exhibits better dissolution. Again this is due to the presence of more and more hydrogen bonding with the succinimide group.

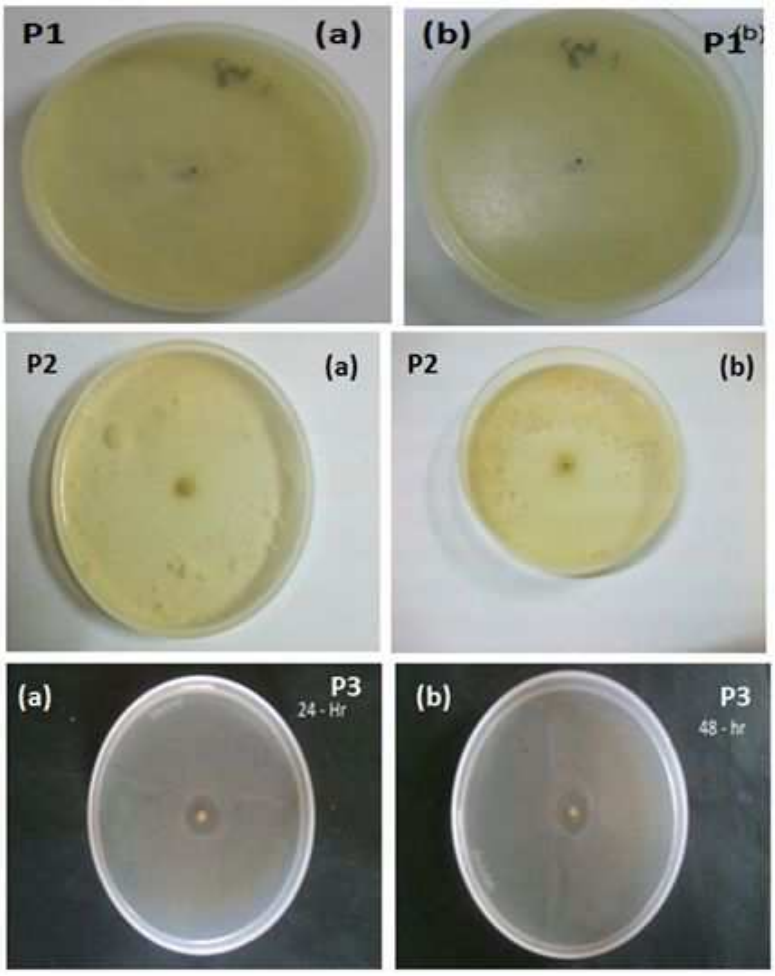


Figure 10: Antimicrobial activity of (a)Ag-TGA-PECH, (b)PECH-g-PHBA-b-PCL, (c)PECH-g-SI-b-PCL system

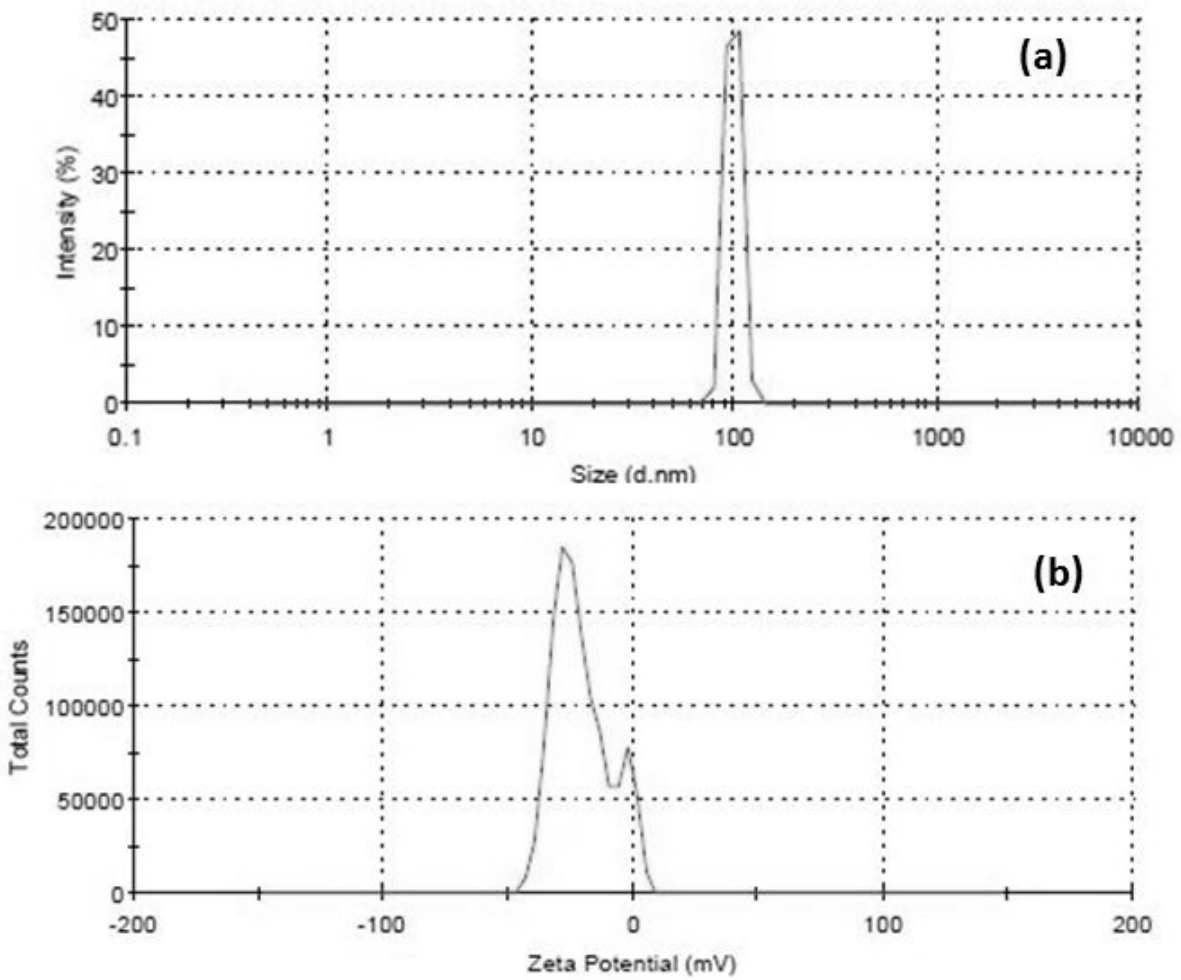
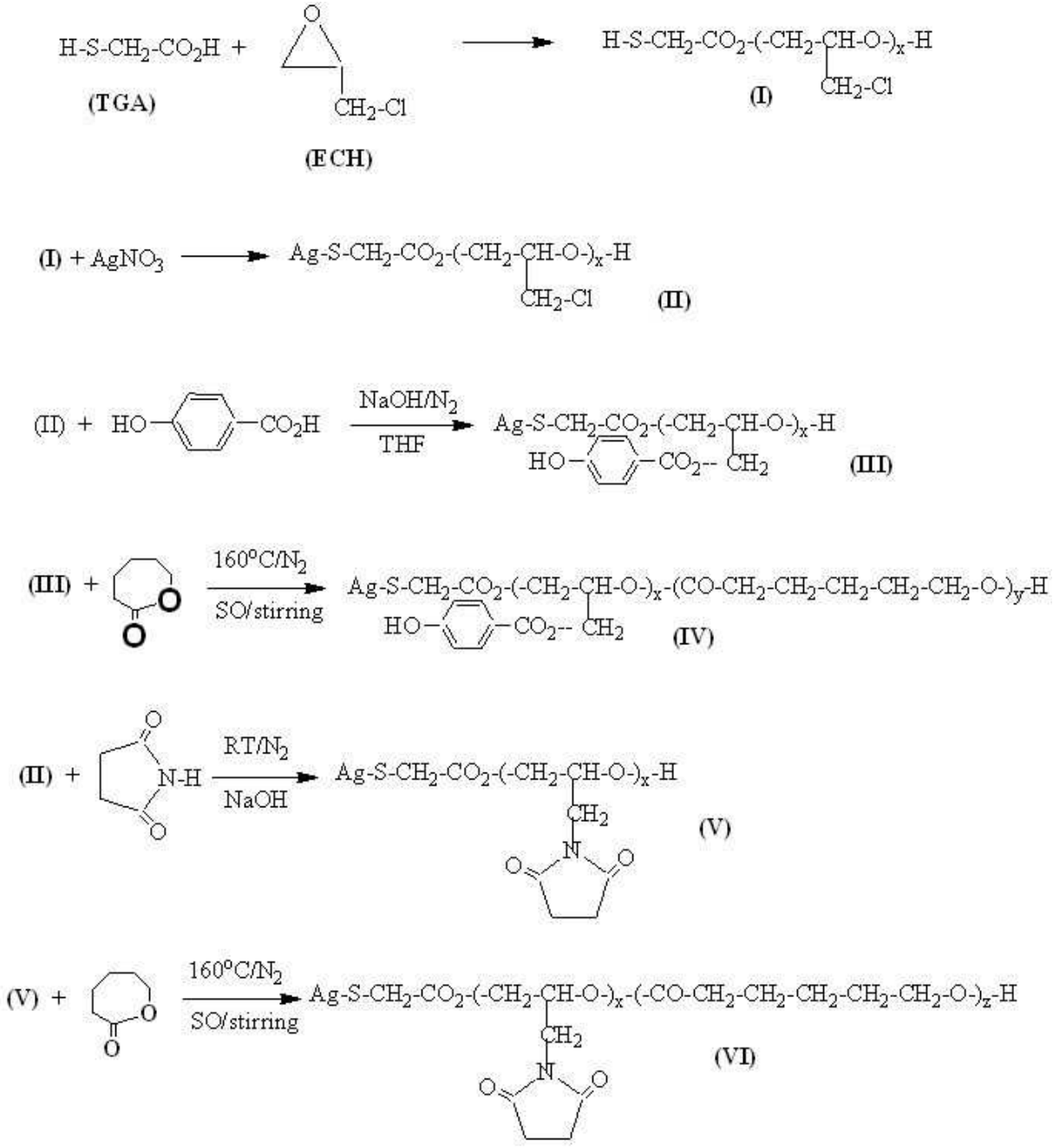


Figure 11: Particle size analysis (a) and zeta potential (b) of PECH-g-SI-b-PCL system



Scheme 1: Synthesis of structurally modified nanophilic Poly(epichlorohydrin)

CONCLUSION

From the above study the important points are summarized here as conclusions. The FTIR spectrum confirmed the structural modification of PECH by PCL, by noting a carbonyl peak at 1729 cm^{-1}. The ^{1}H-NMR (alkoxy proton signal at 4.2 ppm) and ^{13}C –NMR (aromatic signal of p-hydroxy benzoicacid, 125-130 ppm) spectra confirmed the chemical modification of PECH by PCL and p-hydroxy benzoicacid. The DSC study exhibited a T_m below 100^{o}C confirmed the presence of PCL segments in the diblock copolymer. The % weight residue remained above 450^{o}C was increased after the structural modification of PECH. The GPC results confirmed the structural modification of PECH by increase in molecular weight. FESEM results declared the presence of Ag nano particle. The

disappearance of Cl2p in the XPS confirmed the structural modification of PECH by p-hydroxy benzoicacid or succinimide. The antibacterial property was imported to the diblock copolymer by Ag nano particle. The ultrasonic velocity values explained the interaction between the diblock copolymer and the solvent, THF. In such a way one can improve the bio-medical value of PECH.

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