

2.1. Materials

2.1.1. Chemicals, reagents and their purification

Biopolymer:

Starch (starch soluble) was purchased from Rankeem (India) and was used as received.

Polymer:

Polyethylene glycol-600 (PEG-600) (Mean $M_w = 570-630$) was purchased from Merck (India) and was used as received.

Monomer:

Methyl methacrylate (MMA) (99%, Aldrich, India) was purified by passing through basic alumina packed column and stored at 0°C.

Ligand:

N,N'',N'',N',N'-pentamethyl diethylenetriamine (PMDETA) (99%, Aldrich, India) was used as received.

Catalyst:

Cupric bromide (CuBr_2) (99%, SRL, India) was used as received.

Initiator:

Methyl-2-chloro propionate (MCP) (97%, Alfa Aesar, India) was used as received. 2-bromopropionyl bromide (97%, Aldrich, India) was used as received.

Solvents:

N,N-Dimethylformamide (DMF) (99%, Emplura, India), Toluene (99.7%, Merck, India), Tetrahydrofuran (THF) (99.5%, Rankeem, India) and Methyl ethyl ketone (MEK) (99.5%, Merck, India) were used as received.

Reducing agent:

L-ascorbic acid (99.7%, Extrapure, AR) was purchased from SRL (India) and was used as received.

Other chemicals:

Methanol (> 99%, Fisher Scientific, India), Acetone (99%, Merck, India), Basic alumina (Laboratory Reagent, India), Triethylamine (99%, Merck, India), Dichloromethane (DCM) (99%, Merck, India), Ethyl acetate (99.5%, Merck, India), Potassium hydroxide

(KOH) (85%, Rankeem, India) and Carbon disulphide (CS₂) (99%, Merck, India) were used as received.

2.2. Characterization:

2.2.1. Fourier transform infrared (FT-IR) spectroscopy:

Some of the Infrared spectra of the polymer thin film were recorded on a Perkin Elmer, Spectrum RX I, FT-IR spectrometer, as a thin film on KBr plate at a range of 400 to 4000 cm⁻¹ and some were recorded on Bruker's fourier transform infrared spectrometer. To record spectrum, the samples were dissolved in chloroform and were cast film onto KBr pellet.

2.2.2. Nuclear magnetic resonance (NMR) spectroscopy:

Both solid and liquid states NMR were used to record NMR spectra. For some polymer liquid state, ¹H and ¹³C NMR spectra were recorded on Jeol 9.4 Tesla/400 MHz Bruker NMR spectrometer using CDCl₃ as solvent and Tetramethylsilane (TMS) as the internal standard. The solid state ¹H NMR for some polymer was recorded on Bruker ULTRASHEILD WB 11.7 Tesla/MHz using TMS as an internal standard.

1D and 2D NMR spectra were also recorded on Bruker NMR Spectrometer in solvent CDCl₃. ¹H and ¹³C experiments were carried out at frequencies of 400 and 800 MHz, respectively and calibrated with respect to the solvent signal. Gradient Heteronuclear Multiple Bond Correlation (HMBC) and Heteronuclear Single Quantum Coherence (HSQC) experiments were recorded using the pulse sequence *hmbcgpndqf* and *hsqcetgp* of Bruker software, respectively. The spectra acquired in HMBC with 1200 increments in the F1 dimension and 1216 data points in F2 dimension. Total correlation spectroscopy (TOCSY) experiment was performed using standard pulse sequence of 8 scans, accumulated for 440 experiments with 1.5 delay time. HSQC experiment was acquired with 100 increment in F1 dimension and 1208 data points in F2 dimension.

2.2.3. Thermogravimetric analysis (TGA):

Thermal study of the samples was done by STA 6000 model for Thermogravimetric analysis (TGA). Thermogravimetric analysis of the polymer approximately weight 2.048 mg was subjected to heat from 30°C to 800°C at 10°C/min under nitrogen atmosphere.

2.2.4. Differential scanning calorimetry (DSC):

Differential scanning calorimetry (DSC) was carried out on a TA (DSC Q100 V8.1 Build 251) instrument at a heating rate of 10°C/min under nitrogen atmosphere. In this case the sample was heated to +200 °C then cooled to -50 °C. The sample was again heated to +200 °C at the heating rate of 10°C/min.

2.2.5. Gel permeation chromatography (GPC):

Gel permeation chromatography (GPC) was performed in an Agilent GPC system, using a 50µl manual sampler, Isocratic pump and 1260 infinity II refractive index (RI) detector. GPC analysis was carried out using THF as eluent at a flow rate of 1mL/min at room temperature.

2.2.6. Matrix Assisted Laser Desorption/Ionization-Time of Fragmentation-Mass Spectroscopy (MALDI-TOF-MS):

MALDI-TOF-MS analysis was carried out using Applied Biosystems 4800 Plus MALDI-TOF/ TOF mass spectrometry using 2, 5-dihydroxybenzoic acid (DHB) and salt (Sodium trifluoroacetate).

2.2.7. Scanning electron microscopy (SEM):

The surface study of the polymer was performed using ZEISS ULTRA PLUS Scanning electron microscopy (SEM). Dry solid sample of polymer was put on silicon vapor and then it was coated with gold before analysis.