

Supplementary Information

Novel application of Fe-Zn double-metal cyanide catalyst in the synthesis of biodegradable, hyperbranched polymers

Joby Sebastian^a and Darbha Srinivas*^a

Catalysis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411 008, India.

E-mail: d.srinivas@ncl.res.in; Fax: +91 20 2590 2633; Tel: +91 20 2590 2018.

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S1: Method for the preparation of Fe-Zn double-metal cyanide (DMC) catalyst

In a typical preparation of Fe-Zn DMC,^{11(b)} solution 1 was made by dissolving 0.01 mol of $K_4[Fe(CN)_6]$ (Merck, India) in 40 ml of double-distilled water. Solution 2 was prepared by dissolving 0.1 $ZnCl_2$ (Merck, India) in a mixture of distilled water (100 ml) and *tert.*-butanol (20 ml). Polyethylene glycol (PEG – 4000) (15 g) was separately dissolved in 2 ml of distilled water and 40 ml of *tert.*-butanol to prepare solution 3.

Solution 2 was added slowly to solution 1 at 50 °C over 1 h with vigorous stirring. White precipitation occurred during the addition. Then, solution 3 was added to the above reaction suspension over a period of 5 min and stirring was continued for another 1 h. The solid cake formed was filtered, washed with 500 ml of distilled water, and dried at 25 °C for 2-3 days. This material was activated at 180 – 200 °C for 4 h prior to using in the reactions or for characterization. Color: white; yield = 98%.

S2: Catalyst characterization

X-ray diffraction (XRD) patterns of the powdered samples were recorded in the 2θ range of 5 – 85° with a scan speed of 2°/min on a Philips X'Pert Pro diffractometer using $Cu-K_{\alpha}$ radiation ($\lambda = 0.15406$ nm) and a proportional counter detector. Surface area of the sample was estimated by BET method from the N_2 -adsorption-desorption isotherms, measured at -196 °C (NOVA 1200 Quanta Chrome equipment). Prior to N_2 -adsorption, the sample was evacuated at 373 K. Average pore diameter was determined by the BJH method and micropore surface area was calculated from the t-plot. Infrared spectrum of the sample, as KBr pellet, was recorded on a Shimadzu 8201 PC FTIR spectrophotometer in the region of 400 – 4000 cm^{-1} . The morphological characteristics of the samples were determined using a scanning electron microscope (SEM; Leica 440)

and high resolution transmission electron microscope (HRTEM; FEI Technai F 30). In HRTEM studies, the catalyst sample were dispersed in isopropyl alcohol, deposited on a Cu grid, dried and imaged. The type and density of the acid sites were determined by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy of adsorbed pyridine and temperature-programmed ammonia desorption (NH_3 -TPD) techniques. Details of the experimental procedures were reported by us earlier.^{12(b)} In water adsorption studies, the Fe-Zn catalysts were first activated at 180 °C for 4 h and then exposed to water vapor at 100 °C. Water adsorbed on the catalysts was monitored by gravimetry.

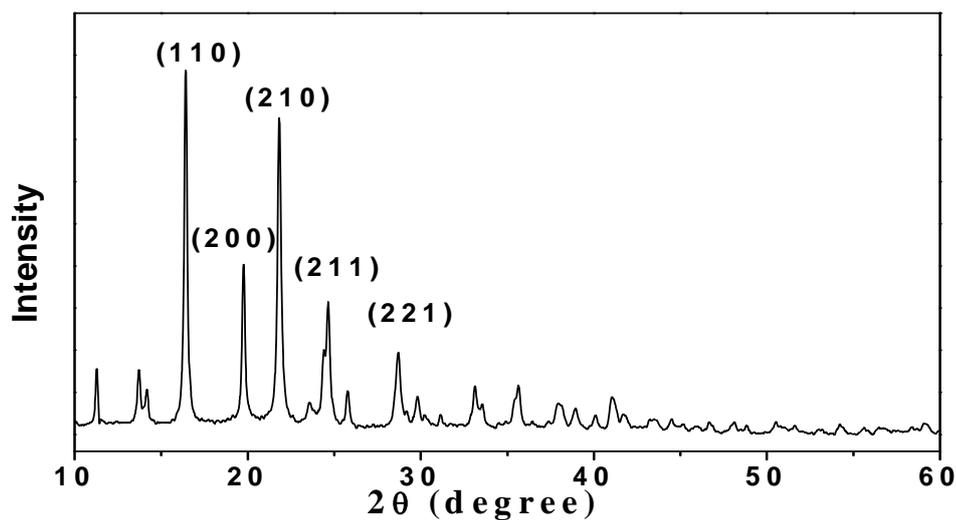


Fig. 1. XRD pattern of Fe-Zn DMC catalyst.

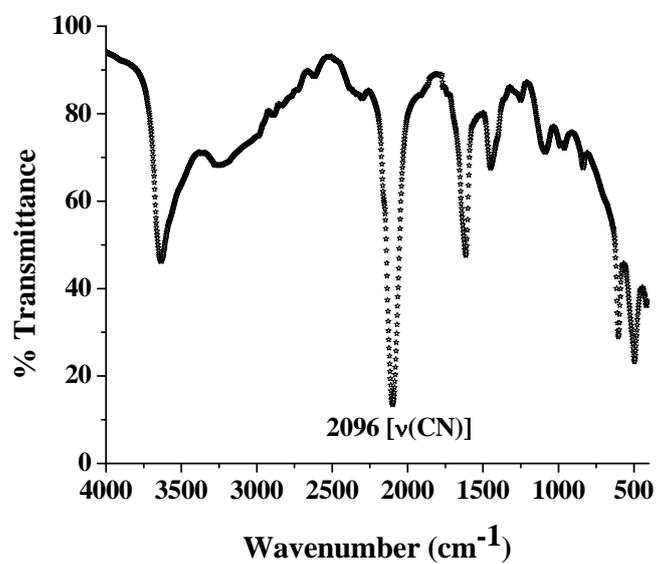


Fig. 2: FTIR spectrum of DMC as KBr pellet.

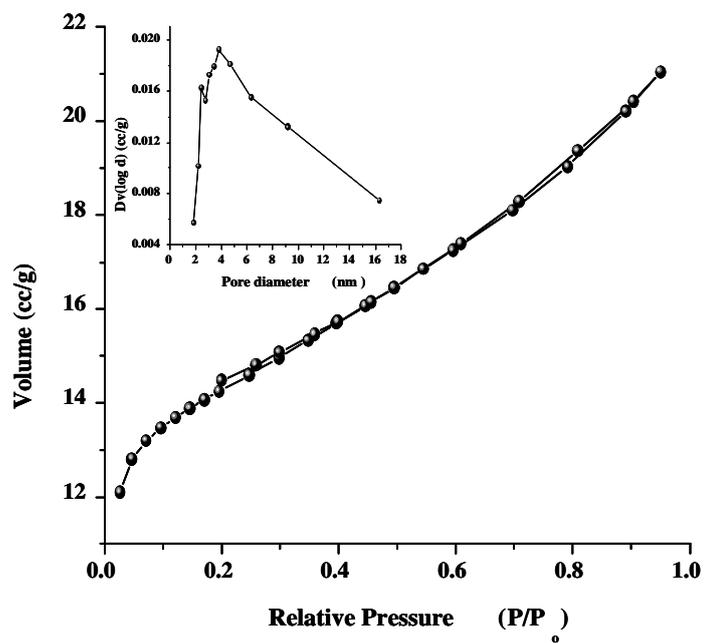


Fig. 3: N₂-physisorption of DMC

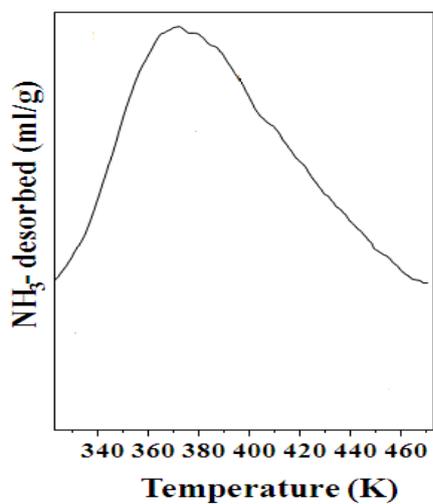


Fig. 4: NH_3 -TPD of DMC.

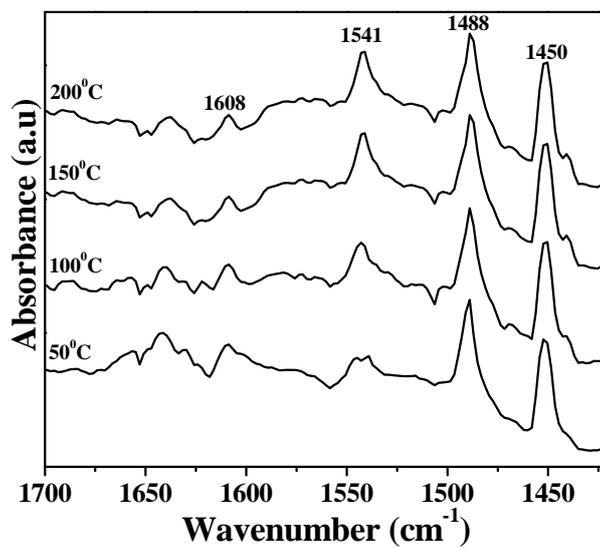


Fig. 5: DRIFT of adsorbed pyridine

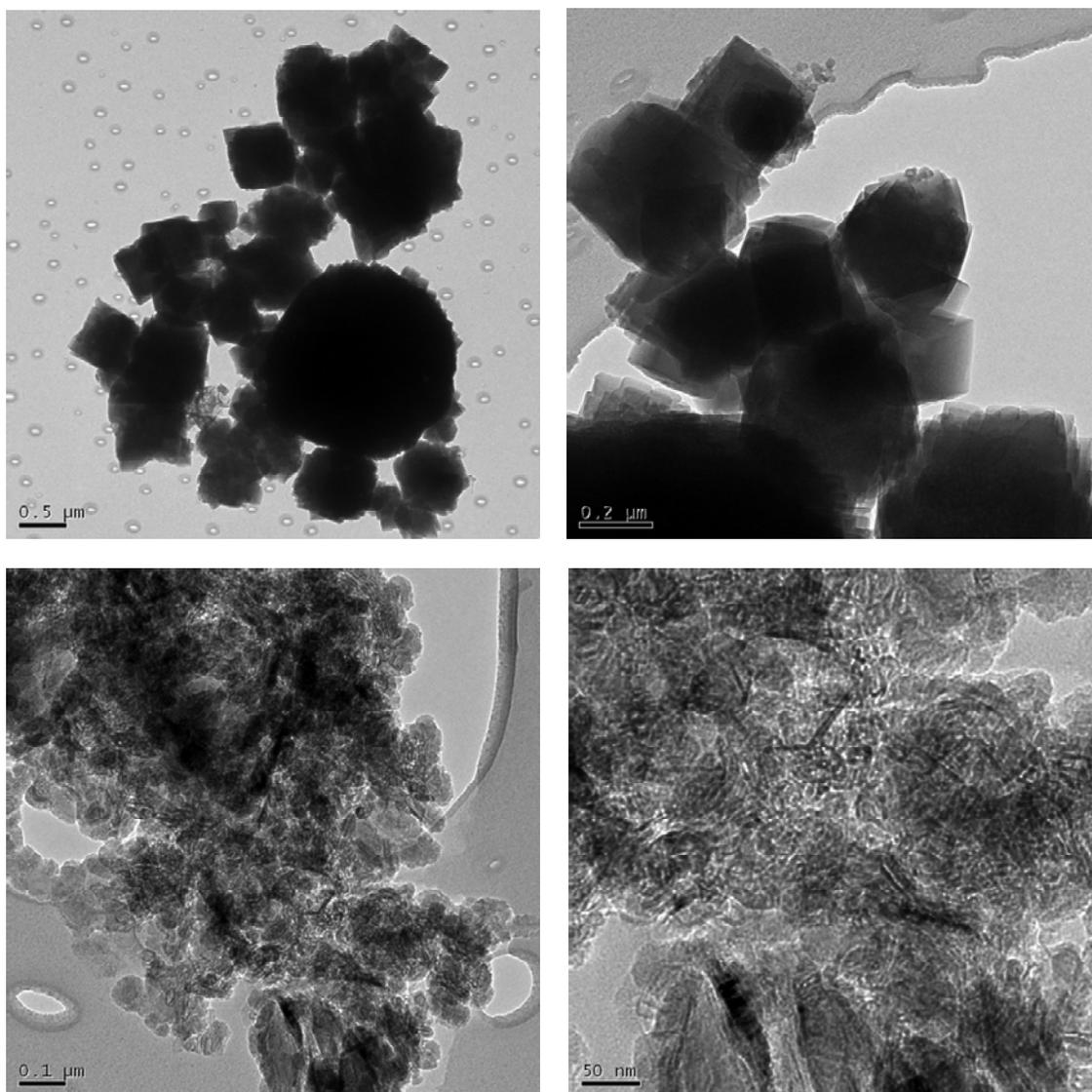


Fig. 6: HRTEM images of Fe-Zn DMC at different resolutions.

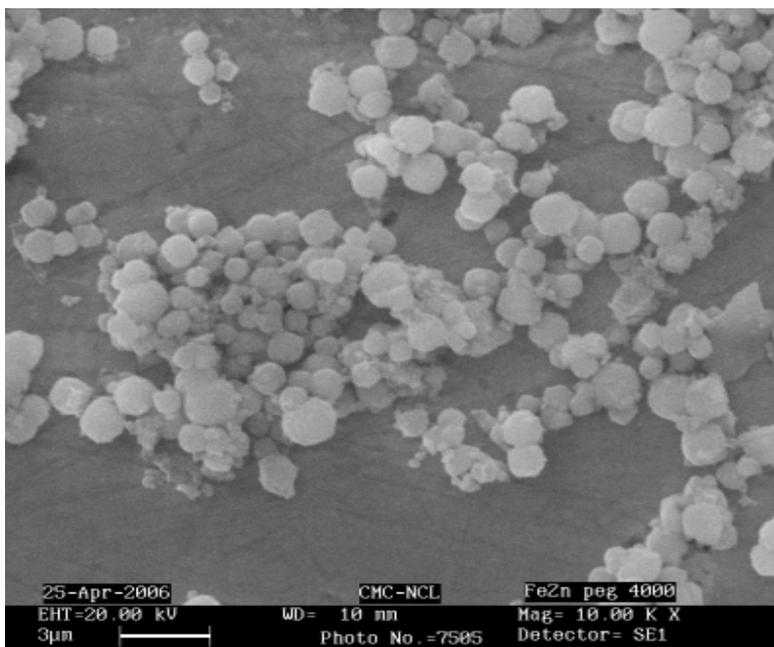


Fig. 7: SEM image of the Fe-Zn DMC catalyst

S3: Procedure for product analysis

Inverse gated ^{13}C nuclear magnetic resonance (NMR) spectroscopy was used to analyze the degree of branching in the hyperbranched polymer. The measurements were done on a Bruker AV 500 NMR spectrometer: pulse program: Zgig 30, aquisition time = 1.1 s, time delay = 5 s, number of scans = 4180. The various branching and linear segments of the polymer were assigned with the help of distortionless enhancement polarization transfer (DEPT) experiments. In correlation spectroscopy (COSY; program = gpqf) and total correlation spectroscopy (TOCSY; program = gpphw5) the following parameters were used: Acquisition time = 0.297 s (F2) and 0.037 s (F1), spectral width = 6.8947 ppm, receiver gain = 8, O1(Hz) = 1751.3. For heteronuclear single quantum correlation (HSQC; program = ctgp) acquisition time = 0.045 s (F2) and 0.0057 s (F1), spectral width = 9.997 ppm, receiver gain = 18400, O1 = 2496 Hz and O2 = 12106 Hz. In heteronuclear multiple-bond correlation (HMBC, program = gp12ndqf) the spectral

parameters used are: acquisition time = 0.59397 s (F2) and 0.0047 s (F1), spectral width = 6.8947 ppm, receiver gain = 16400, O1 = 1751.3 Hz and O2 = 13619.9 Hz.

Inherent viscosity (η) of the polymer product was measured in tetrahydrofuran at 30°C using an Ubbelohde viscometer. The viscosity measurements were repeated three times and the average of the reading is reported.

FTIR spectra of the polymer were recorded on a Shimadzu 8201 PC spectrophotometer by placing the sample in between the KBr discs.

Mass Spectra from matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) with automated tandem TOF fragmentation of selected ions were acquired with a Voyager-DE STR (Applied Biosystems Voyager System 4383) in positive reflector mode with a laser intensity of 2324, accelerating voltage of 20000 V and number of laser shots of 50/spectrum. An aliquot (1 μ L) of polymer solution (1 mg/ mL in acetone) was mixed with 24 μ L of 2,5-dihydroxybenzoic acid (DHB) matrix solution (10 mg/ mL, acetonitrile-water 50:50 v/v) and 1 μ L of the resulting solution was spotted on the MALDI plate for analysis.

S4: FTIR spectra of hyperbranched polymers

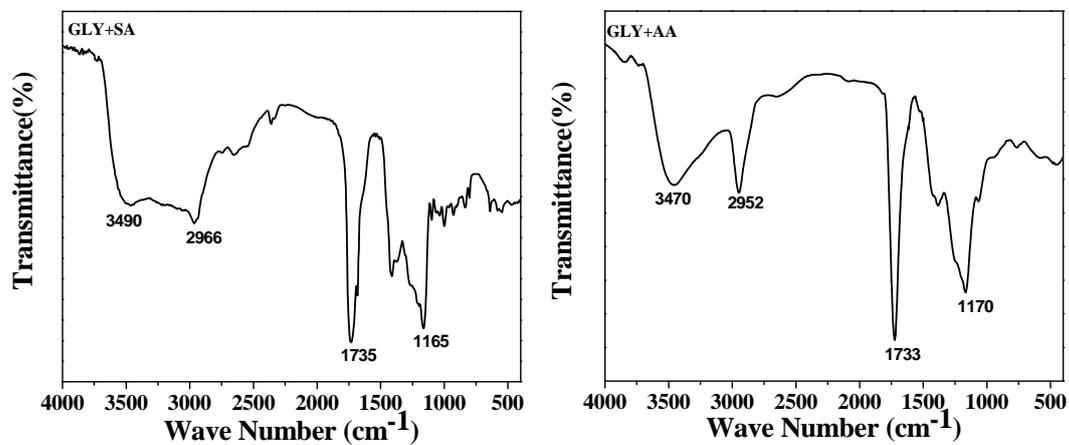


Fig. 8: FTIR spectra of G-SA and G-AA polymers obtained over DMC. The characteristic peaks due ester linkage, terminal OH groups and -CH stretching vibrations are marked.

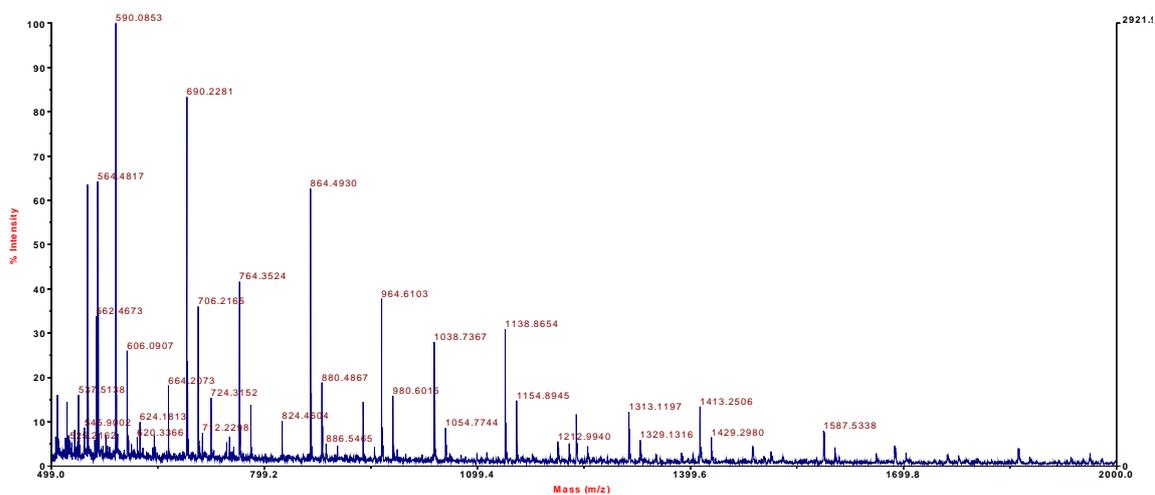


Fig. 9(a): MALDI-TOF-mass spectrum of G-SA polymer obtained over DMC

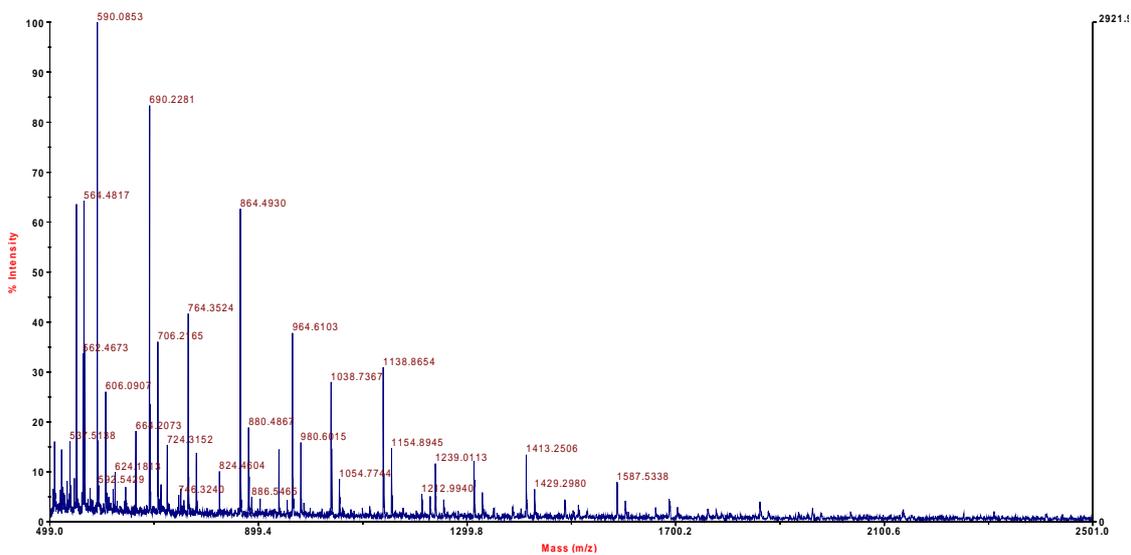
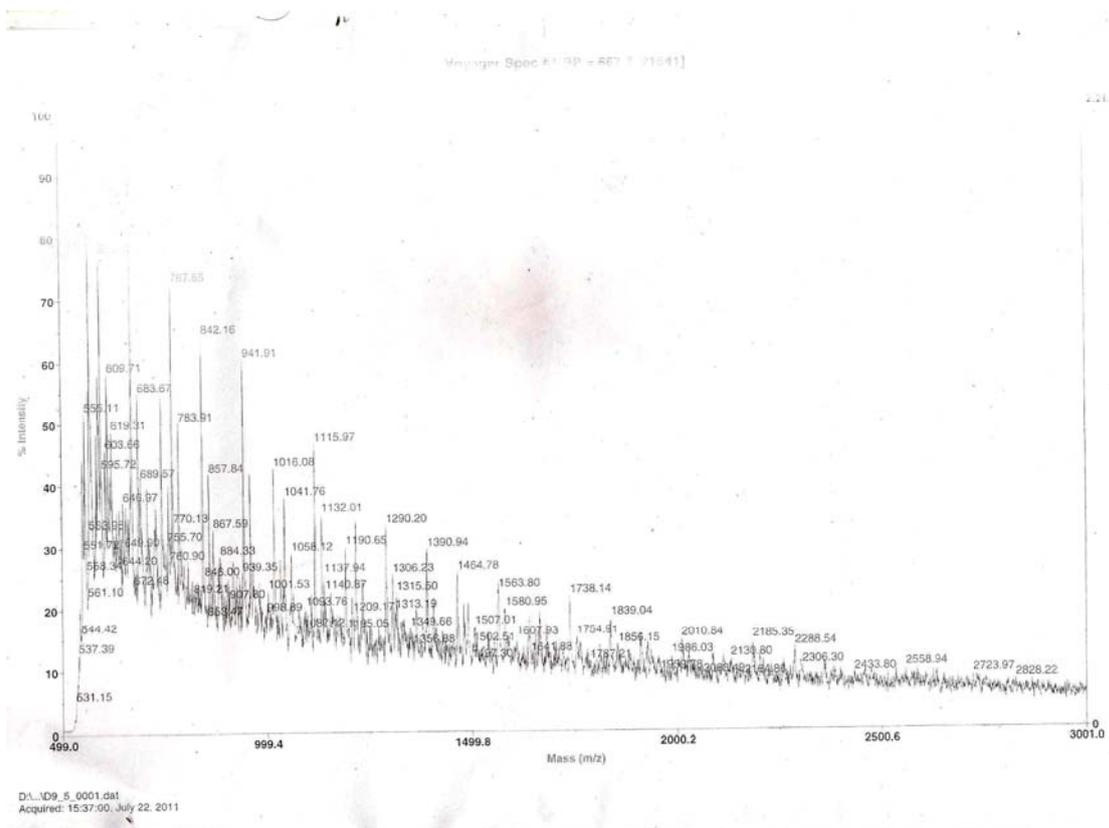


Fig. 9(b): MALDI-TOF-mass spectrum of G-AA polymer obtained over DMC



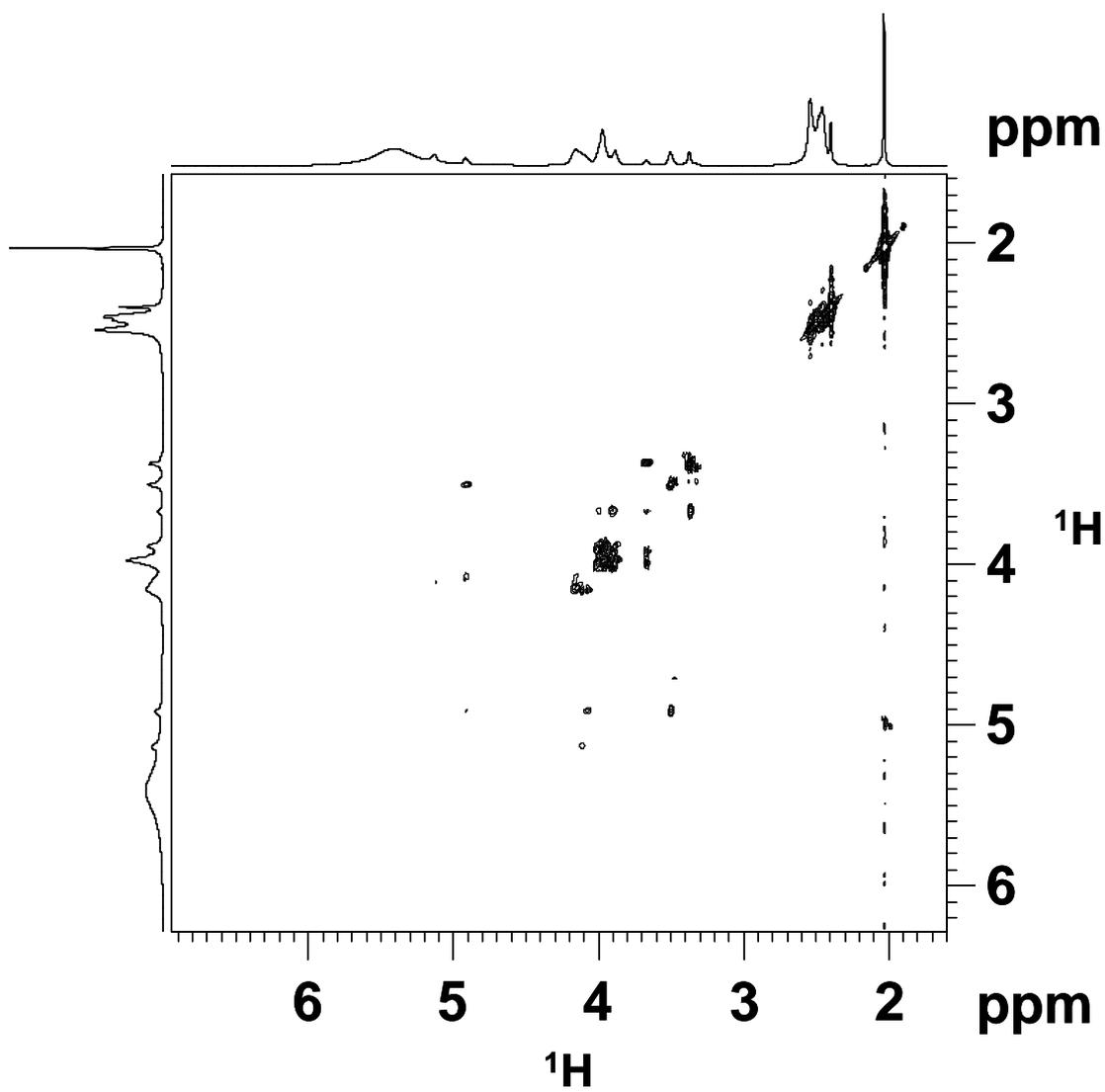


Fig. 10(a): COSY of G-SA polymer

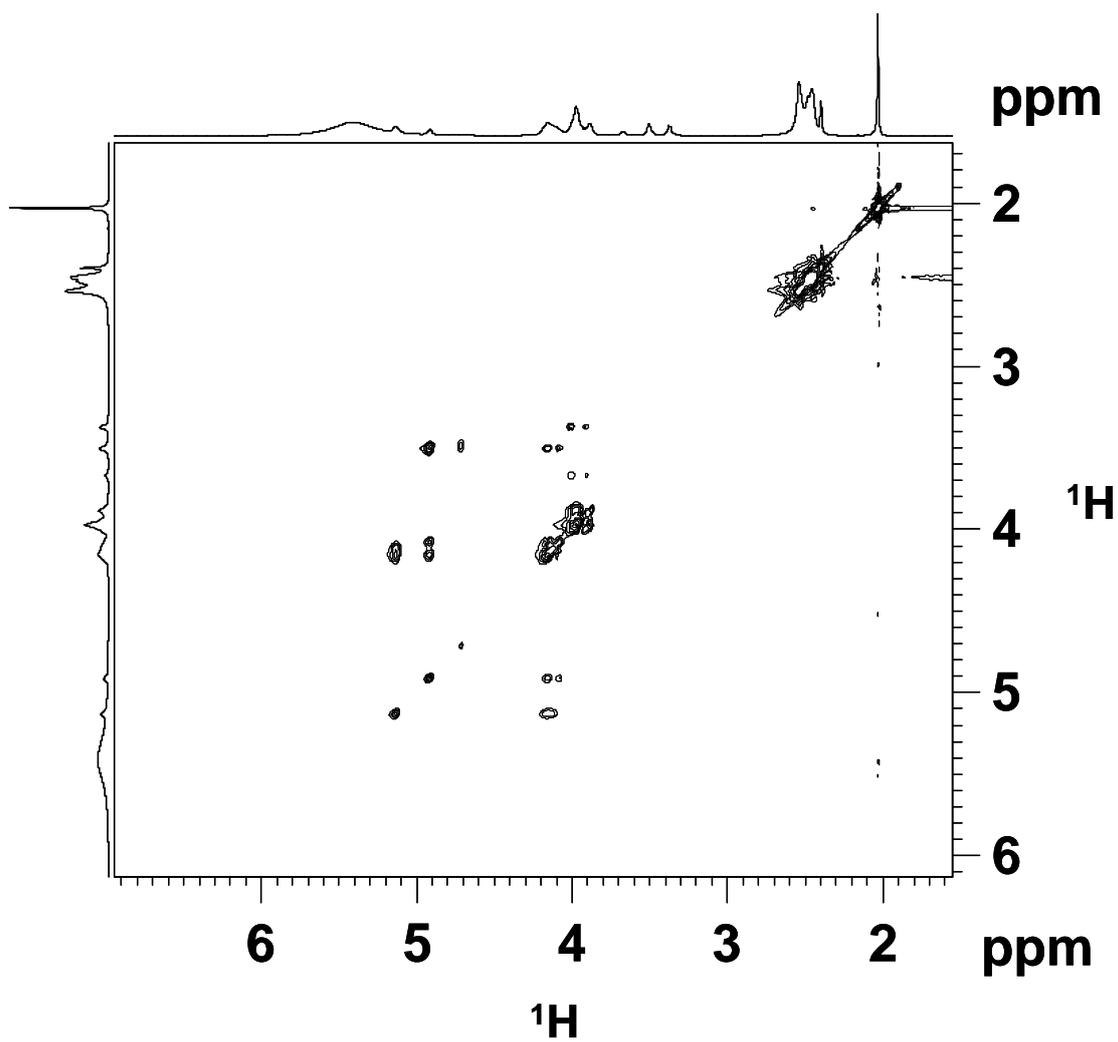


Fig. 10(b): TOCSY of G-SA polymer

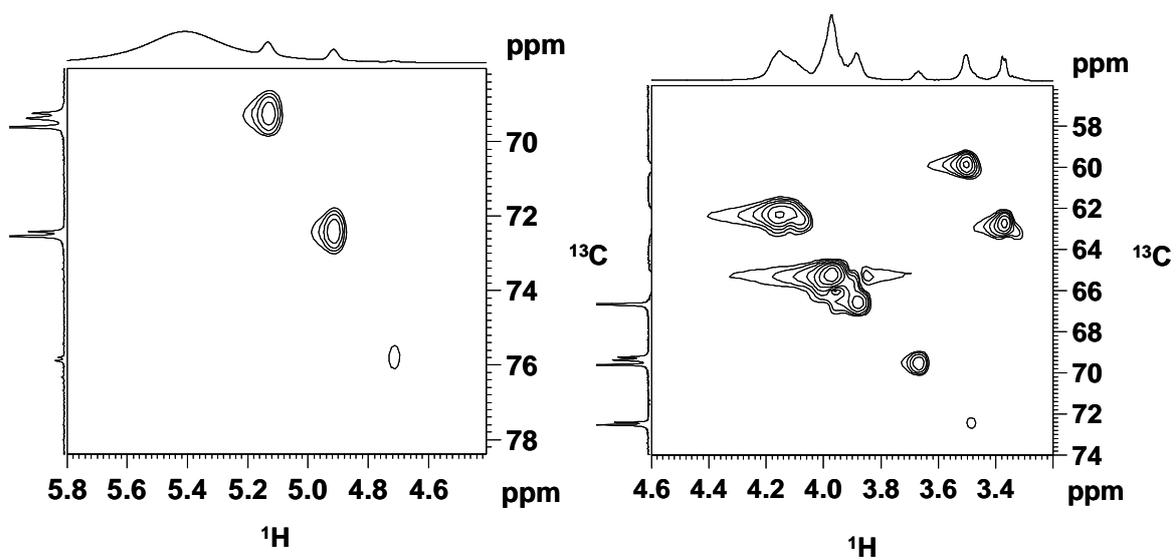


Fig. 10(c): HSQC of G-SA polymer

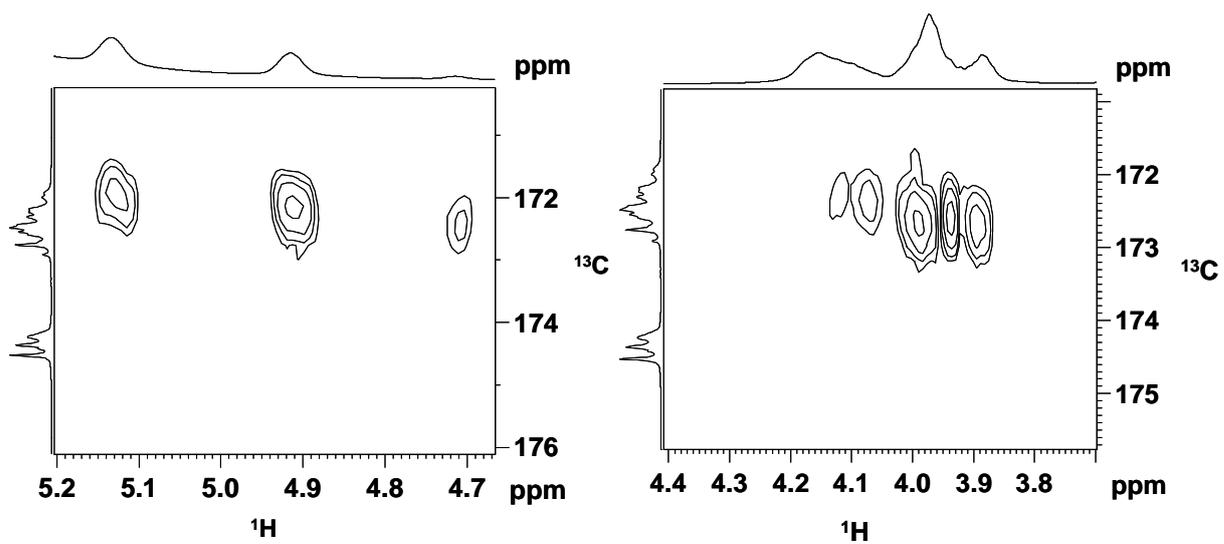


Fig. 10(d): HMBC of G-SA polymer

S5: Characterization data of reused DMC catalyst

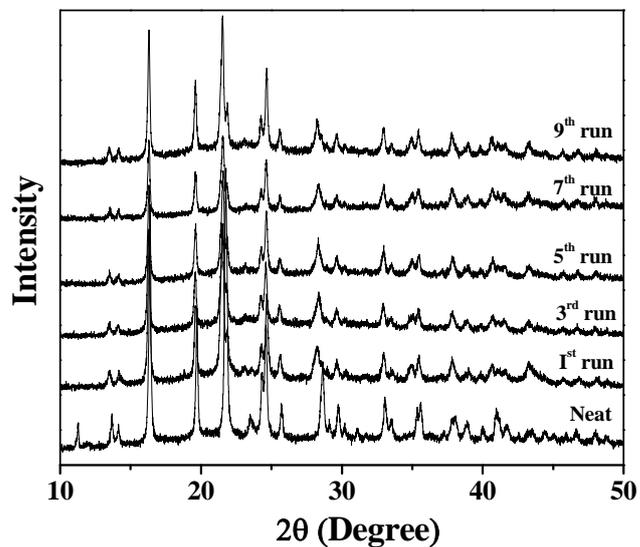


Fig. 11: XRD of reused DMC in G-SA reaction showing structural integrity

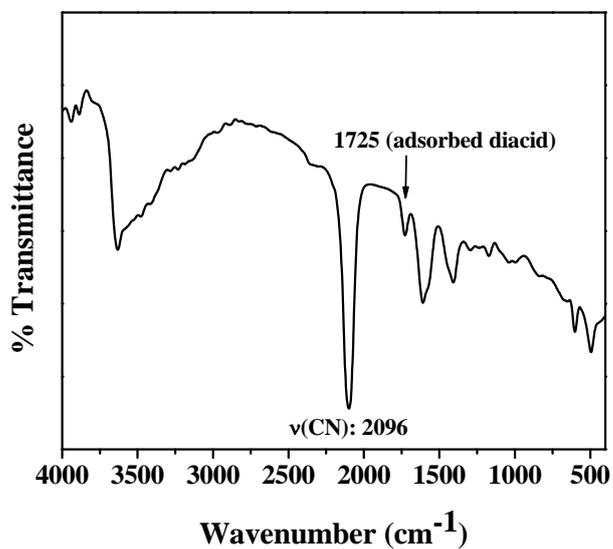


Fig. 12: FTIR of reused DMC (9th run). Band at 1725 cm⁻¹ is due to adsorbed and activated succinic acid.

S6: Tentative mechanism of polyesterification over tetrahedral Zn^{2+} ions in DMC

