Electronic Supporting Information

Synthesis of Soluble Core Cross-Linked Polystyrene Star Polymer by Application of Acrylate-Nitrile Oxide ‘Click Chemistry’ Using Metal-Free Reagents

Rakesh Banerjee, Saikat Maiti and Dibakar Dhara*
Department of Chemistry, Indian Institute of Technology Kharagpur
West Bengal 721302, India

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1.0. (a) Model reaction with Poly (4-vinyl benzylchloride) and Anisaldehyde oxime:

To confirm the formation of isoxazoline ring in the polymeric system via nitrile oxide-alkene 'click chemistry', a model reaction was carried out with acryloyl-functionalized homopolymer modified from poly(4-vinyl benzylchloride) (MA) and anisaldehyde oxime (MO).

Preparation of anisaldehyde oxime: In a 25 mL single necked round-bottomed (r. b.) flask anisaldehyde (1 g, 7.4 mmol) was mixed with 5 mL of ethanol. On the other hand $NH_2OH.HCl$ (0.767 g, 11.2 mmol) and sodium acetate (1.21 g, 14.7 mmol) were dissolved in minimum volume of water. Then these two solutions were mixed and the reaction mixture was stirred overnight at room temperature. After completion of the reaction, EtOH was removed under vacuum and the remaining reaction mixture was extracted with diethyl ether. The diethyl ether extracts were combined and was washed thoroughly with water. The organic part was concentrated in a rotary evaporator under reduced pressure. It was then dried and anisaldehyde oxime obtained as a pale yellow liquid (0.97 g, 87 %). ^{1}H NMR ($CDCl_3$): δ 3.774 (s, 3H), 6.884 (d, 2H, J= 8.0 Hz), 7.471 (d, 2H, J= 8.0 Hz), 8.073 (s, 1H), 8.5 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 55.22, 114.22, 124.3, 128.47, 149.5, 161.04.

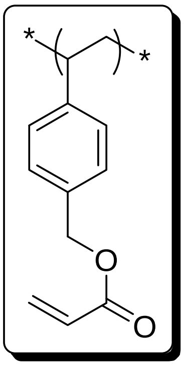
Preparation of acryloyl-functionalized homopolymer from poly (4-vinyl benzylchloride) (MA): Acrylic acid (0.384 g, 5.33 mmol) was taken in a 25 mL two-necked r. b. flask. in dry DMF (6 mL) under nitrogen atmosphere and heated to 60 °C. Potassium carbonate (K_2CO_3) (1.03 g, 7.46 mmol) was added slowly followed by addition of KI (0.04 g, 0.28 mmol) and the mixture was stirred for another 30 min at that temperature. Then a solution of poly (4-vinyl benzylchloride) ($M_n \sim 5800$) (0.4 g, 2.63 mmol) in dry DMF (2 mL) was added dropwise for about 30 minutes and the reaction was left to stir at 100 °C for 36 h. Then the reaction was quenched and the product was then precipitated out from cold methanol, washed and dried under high vacuum. ^{1}H NMR ($CDCl_3$): δ 1.10 (br, $CHCH_2$ polymer backbone), 1.68 (br, $CHCH_2$ polymer backbone), 5.14 (br, -CH_2O-(acrylate), polymer), 5.8 (br, alkene, polymer), 6.2 (br, alkene, polymer), 6.5 (br, Ar, polymer), 7.07 (br, Ar, polymer). ^{13}C NMR ($CDCl_3$): 40.7, 66.3, 126.3, 128.5, 130.6, 131.4, 133.5, 135.2, 166.2.

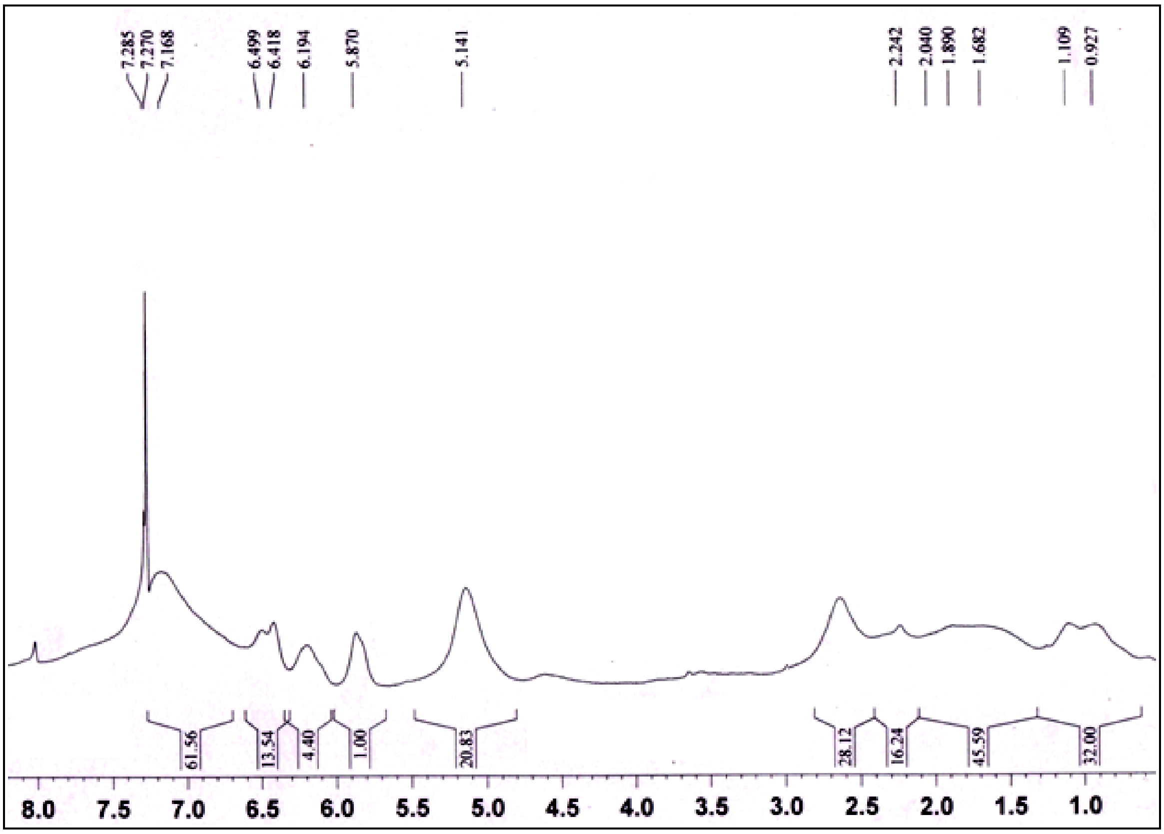
Synthesis of isoxazoline ring in polymeric scaffold: In a 25 mL two-necked r. b. flask anisaldehyde oxime (0.16 g, 1.07 mmol) in dry DCM (5 mL) was taken under nitrogen atmosphere with continuous stirring. Then iodosobenzenediacetate (0.72 g, 2.24 mmol) and $MgSO_4$ (0.4 g, 3.33 mmol) were added into the solution at 0 °C for 10 min with vigorous stirring. **MA** (0.08 g, 0.425 mmol) in 2 ml of dry DCM was added slowly for 15 min at 0 °C and the post reaction mixture was stirred for overnight at room temperature. Unreacted $MgSO_4$ was then removed by filtration and the solvent was evaporated under reduced pressure. The residue was dissolved in 3 ml of THF and the product was precipitated out from cold hexane and dried under high vacuum.

Formation of isoxazoline was confirmed by ^1H NMR and ^{13}C NMR analysis. ^1H NMR (DMSO-d_6): δ 1.00 (br, $CHCH_2$ polymer backbone), 1.62 (br, $CHCH_2$ polymer backbone), 3.80 (br, -CCH_2CH-isoxazoline), 5.10 (br,-CHO-(isooxazoline), 5.20 (br, -CH_2O-(isoxazoline), polymer) 6.94 (br, Ar, polymer), 7.11 (br, Ar, polymer). ^{13}C NMR (DMSO- d_6): 29.7, 55.8, 56.1, 68.8, 114.5, 123.7, 129.1, 129.9, 131.9, 132.4, 133.5, 161.5, 170.6.

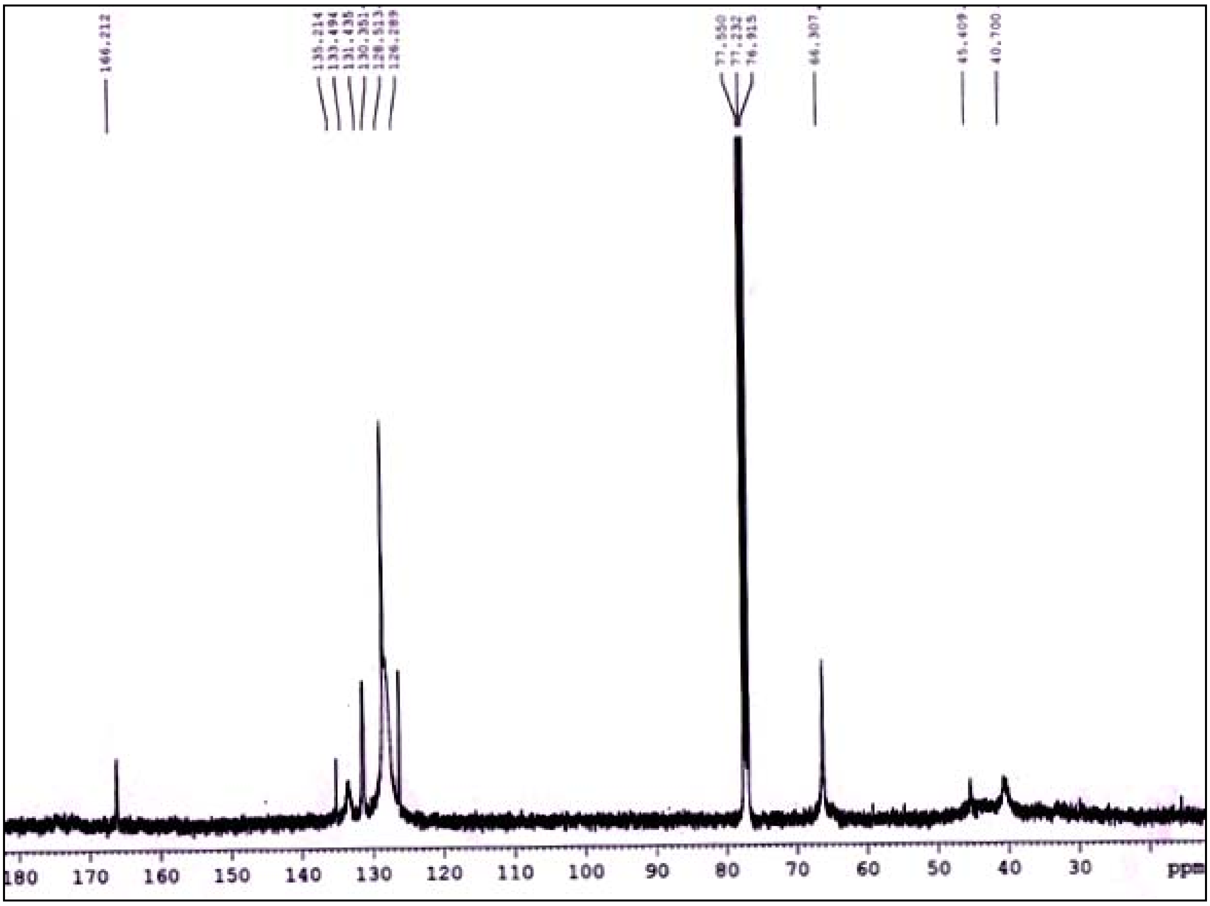
NMR spectra:

(b) ^{1}H NMR spectra of acryloyl-functionalized homopolymer from poly(4-vinyl benzylchloride)

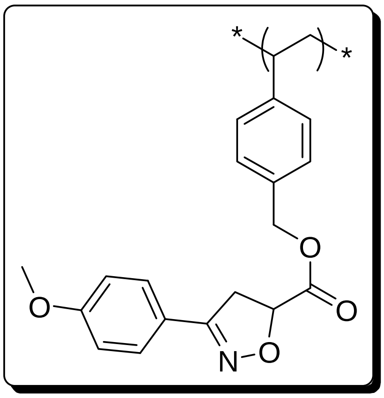


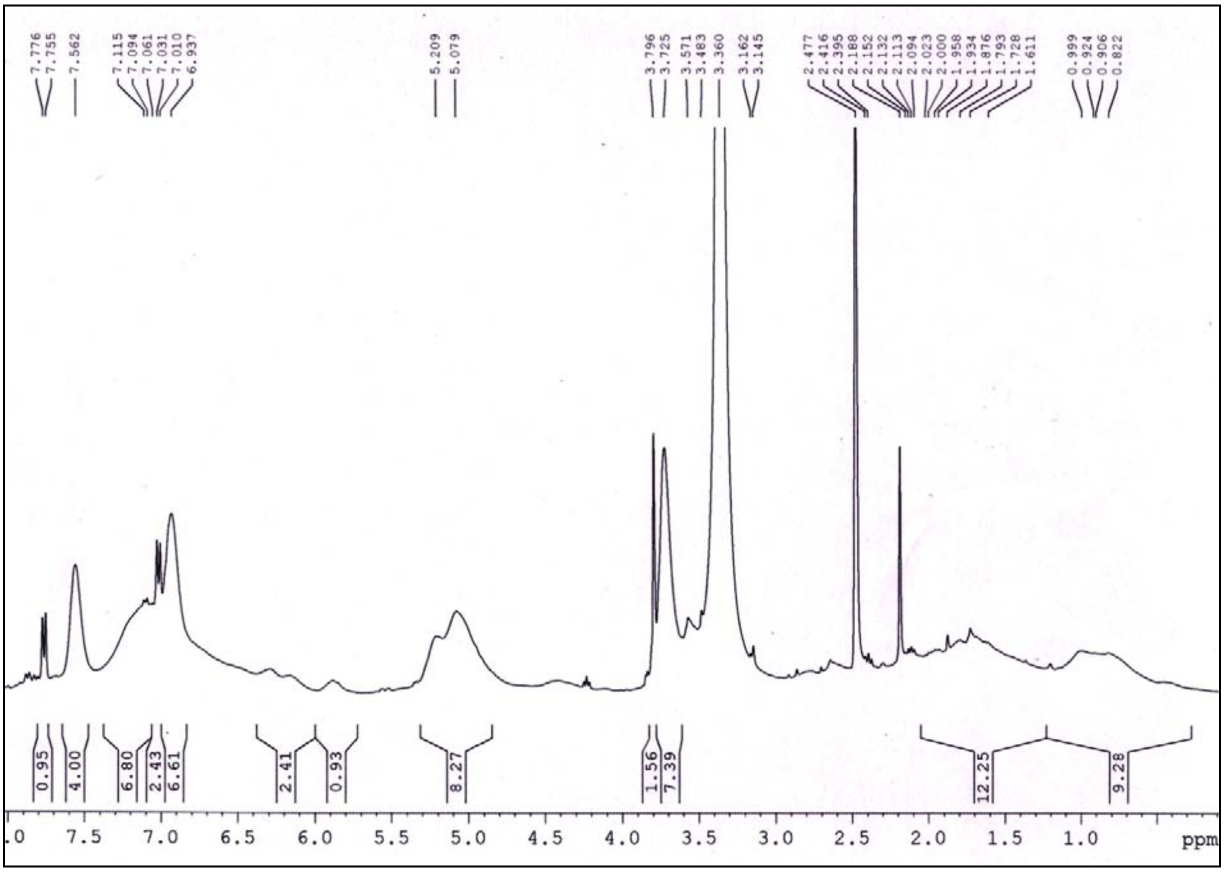


^{13}C NMR spectra of acryloyl-functionalized homopolymer from poly(4-vinyl benzylchloride)

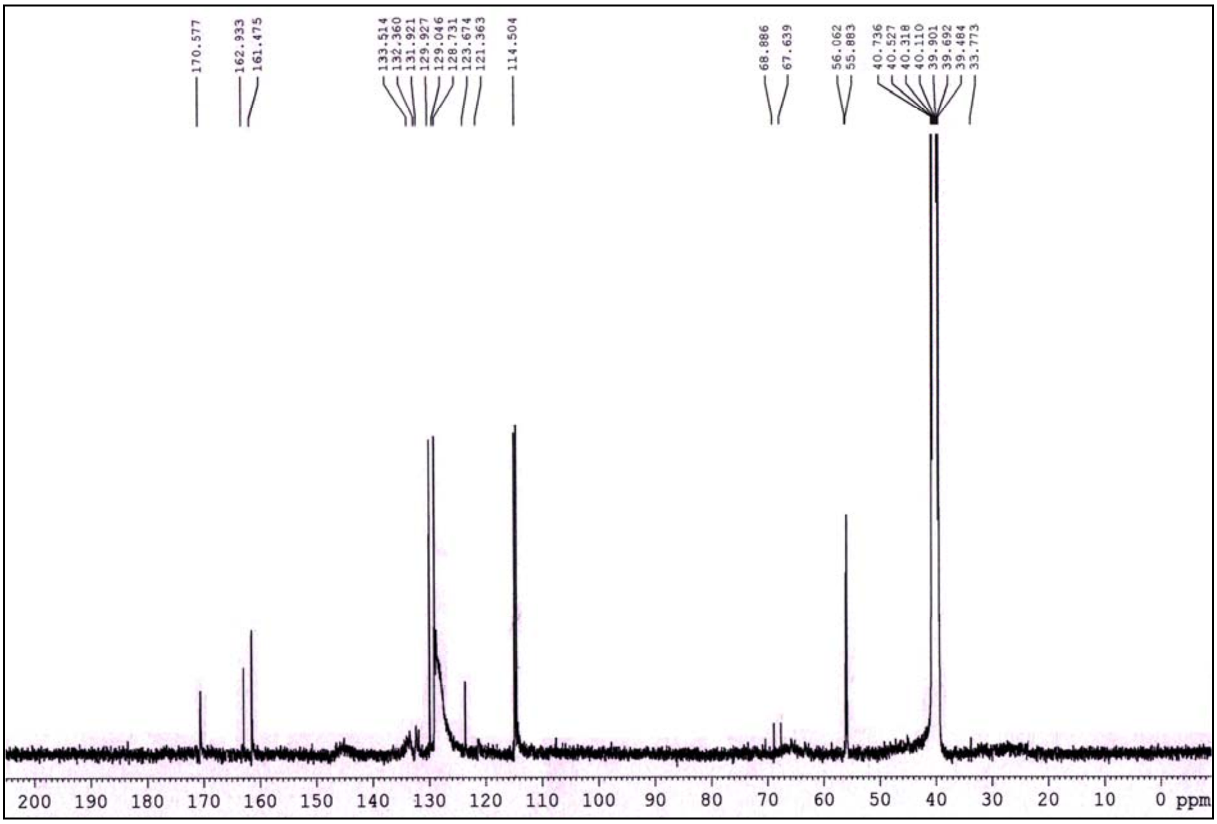


(c) ^{1}H NMR spectra of polymer containing isoxazoline ring



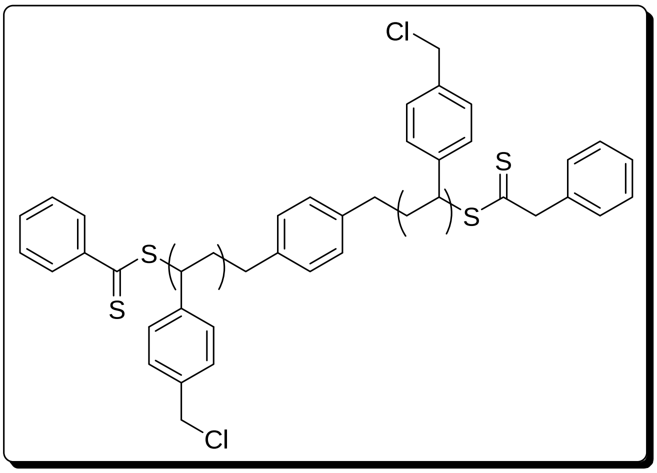


^{13}C NMR spectra of polymer containing isoxazoline ring



2.0. NMR spectra of the various compounds are given below:

Figure S1: ^{1}H NMR of poly(4-vinylbenzyl chloride) macro-CTA



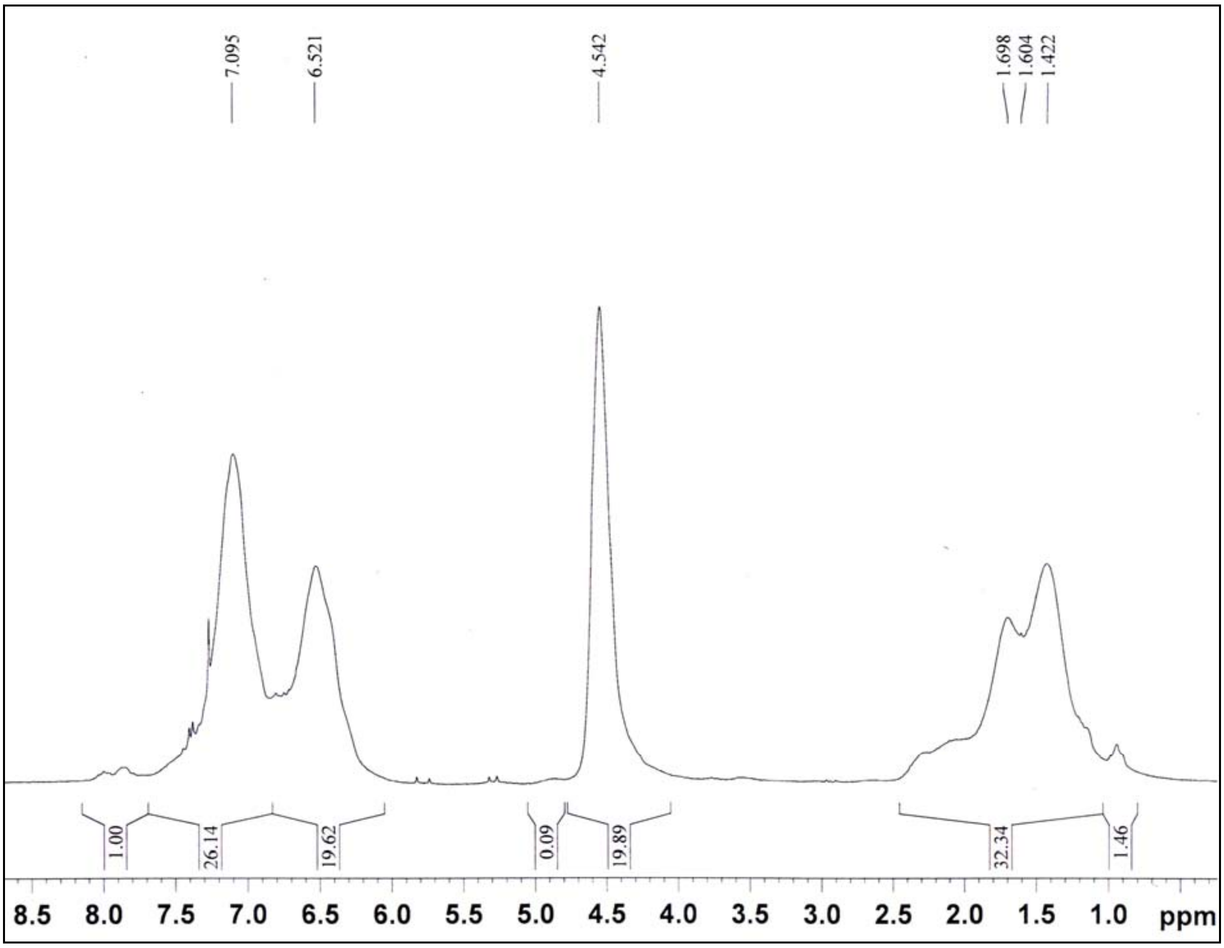


Figure S2: ^{1}H NMR of polystyrene-*block*-poly(4-vinylbenzyl chloride)

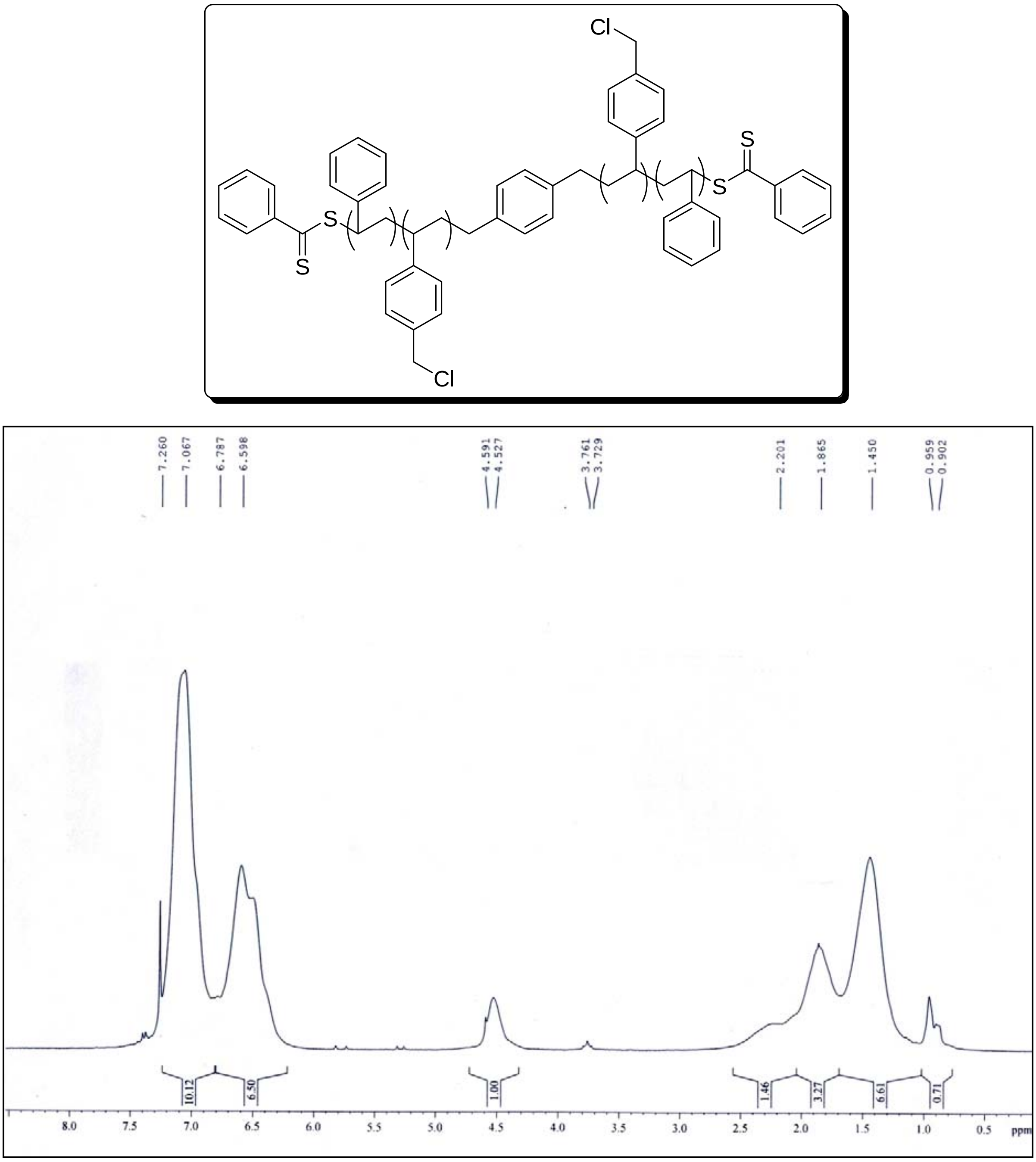
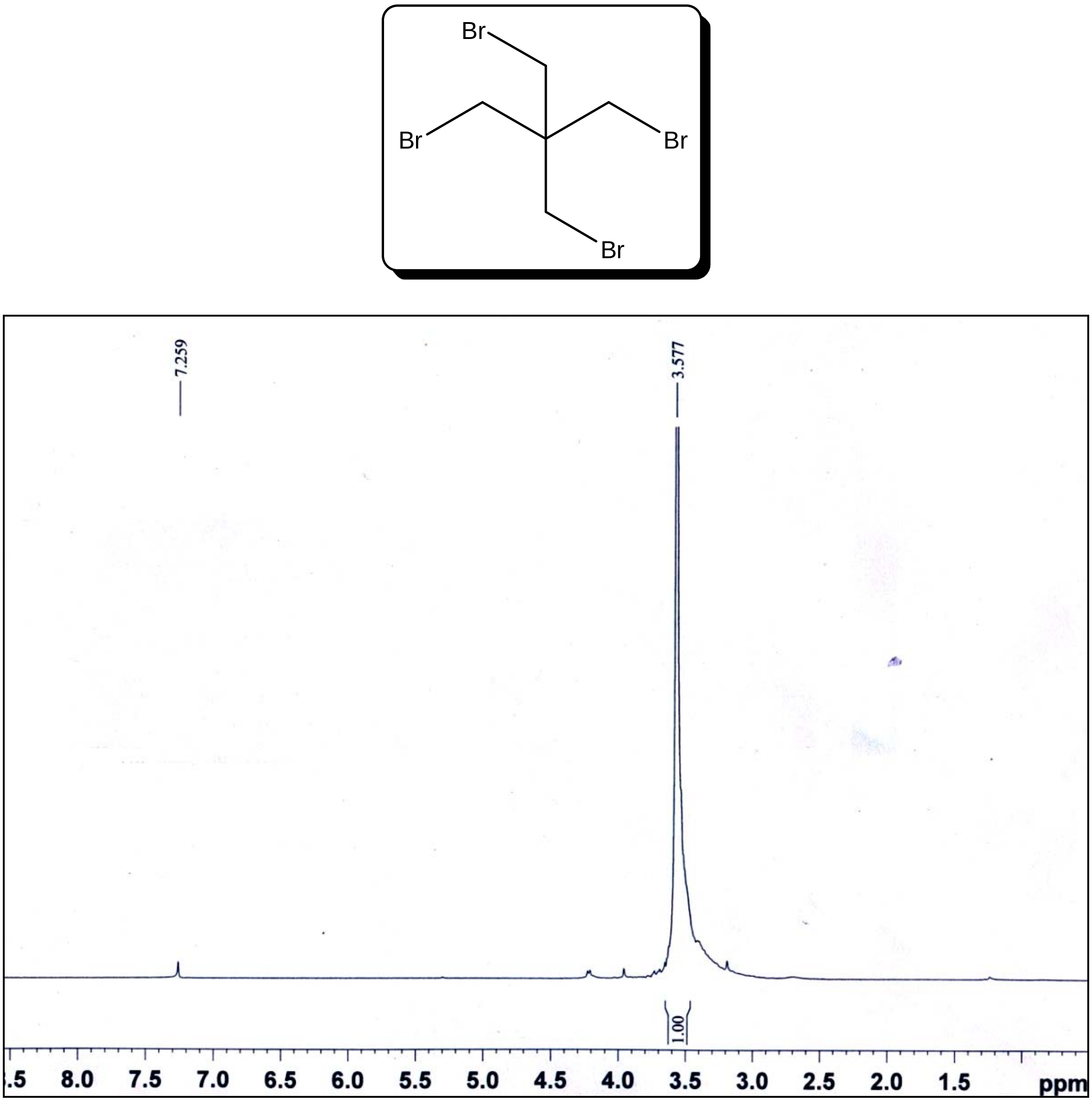


Figure S3: ^{1}H NMR of Pentaerythrityl tetrabromide



^{13}C NMR of pentaerythrityl tetrabromide

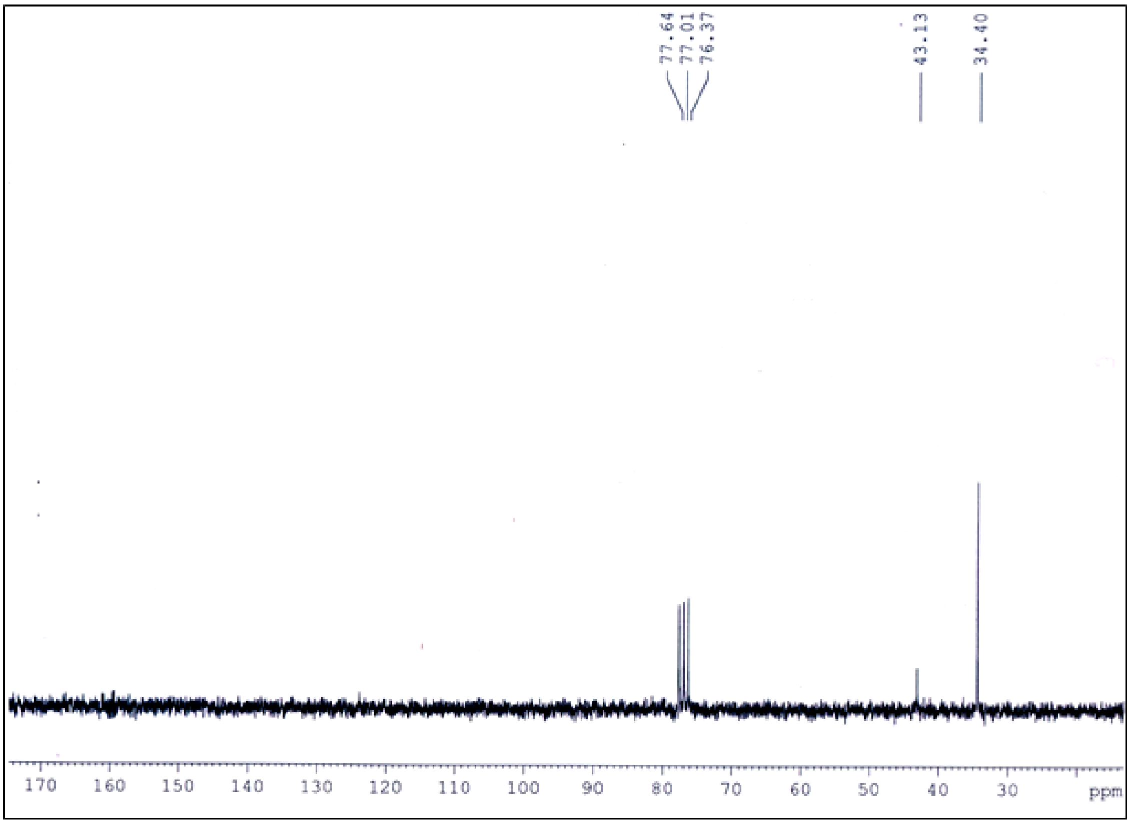
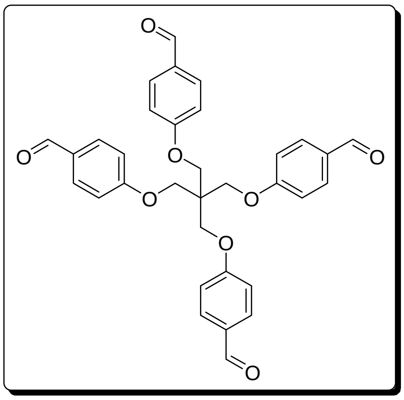
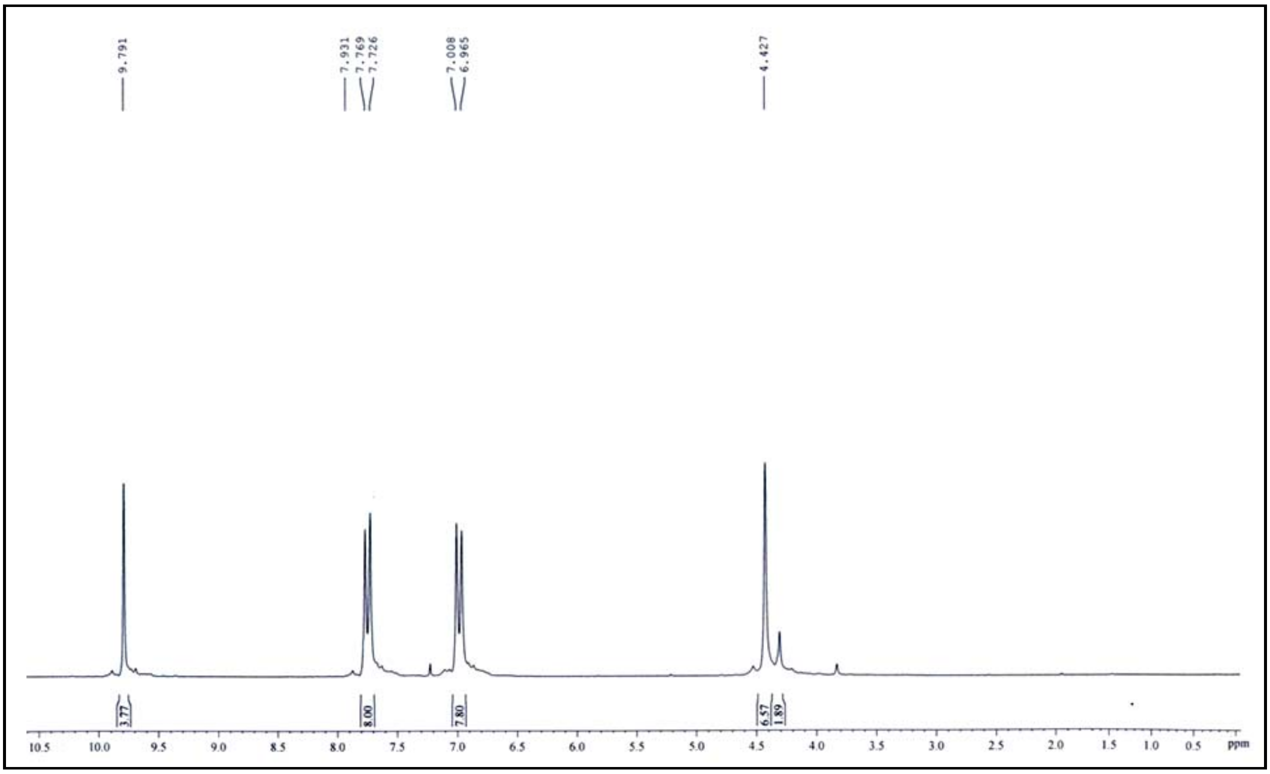


Figure S4: ^{1}H NMR of Tetra-arm aldehyde





^{13}C NMR of Tetra-arm aldehyde

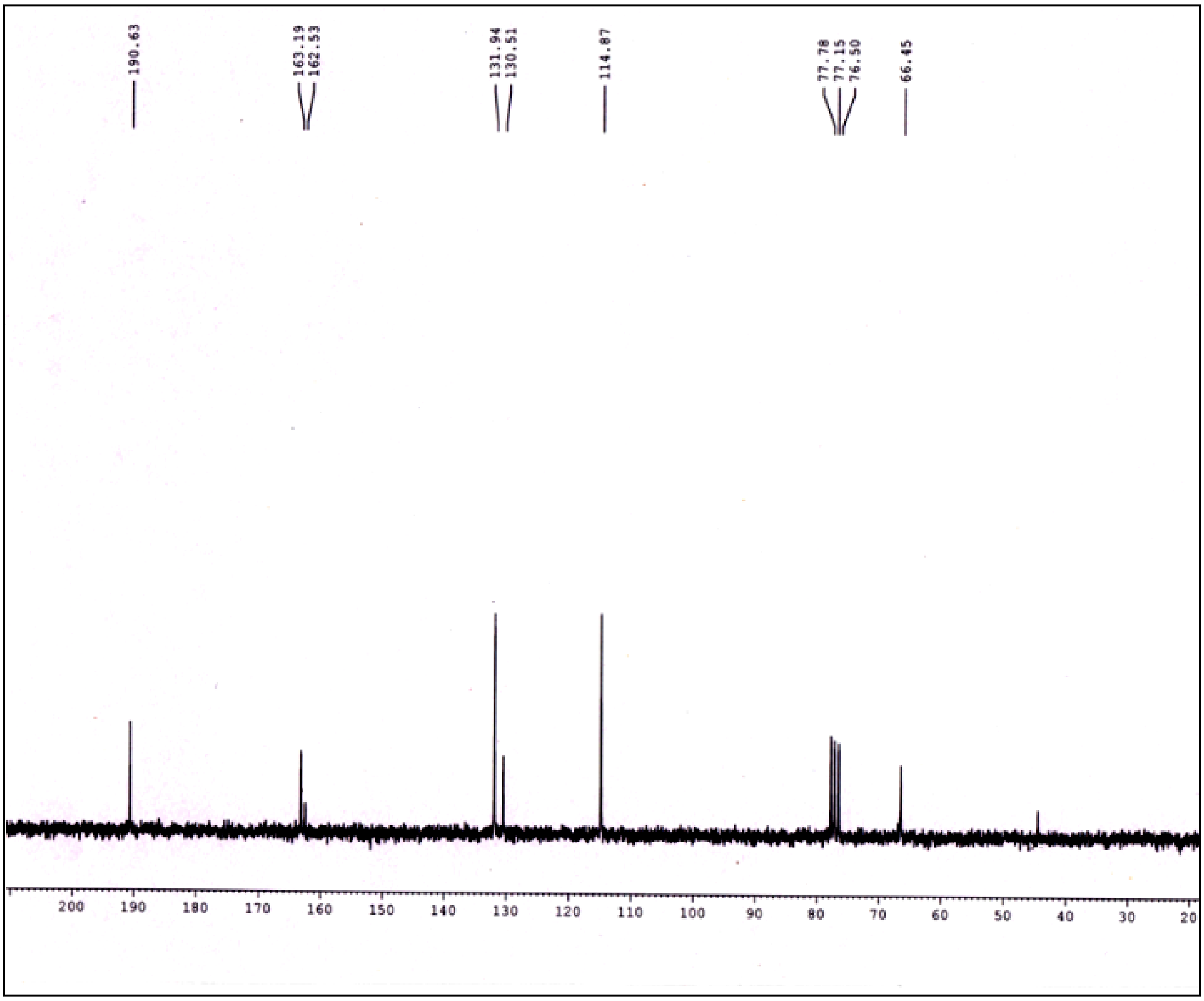
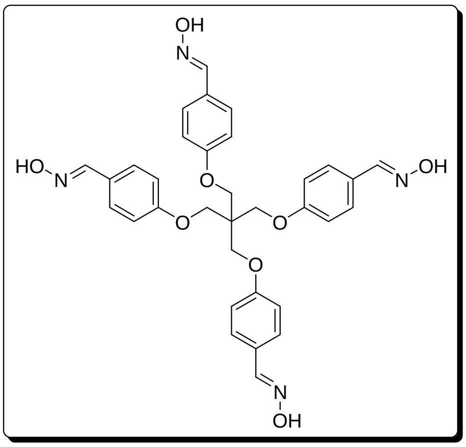
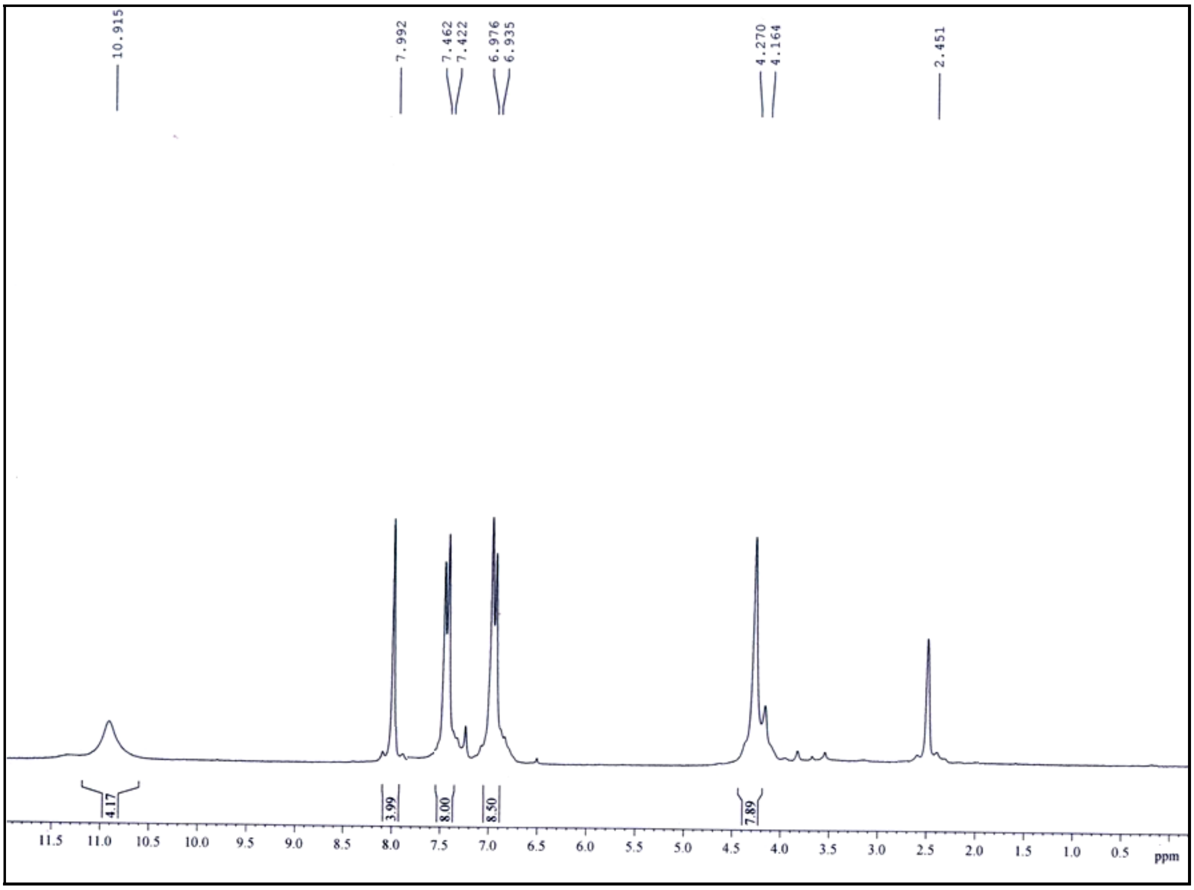


Figure S5: ^{1}H NMR of tetra-arm oxime





^{13}C NMR of tetra-arm oxime

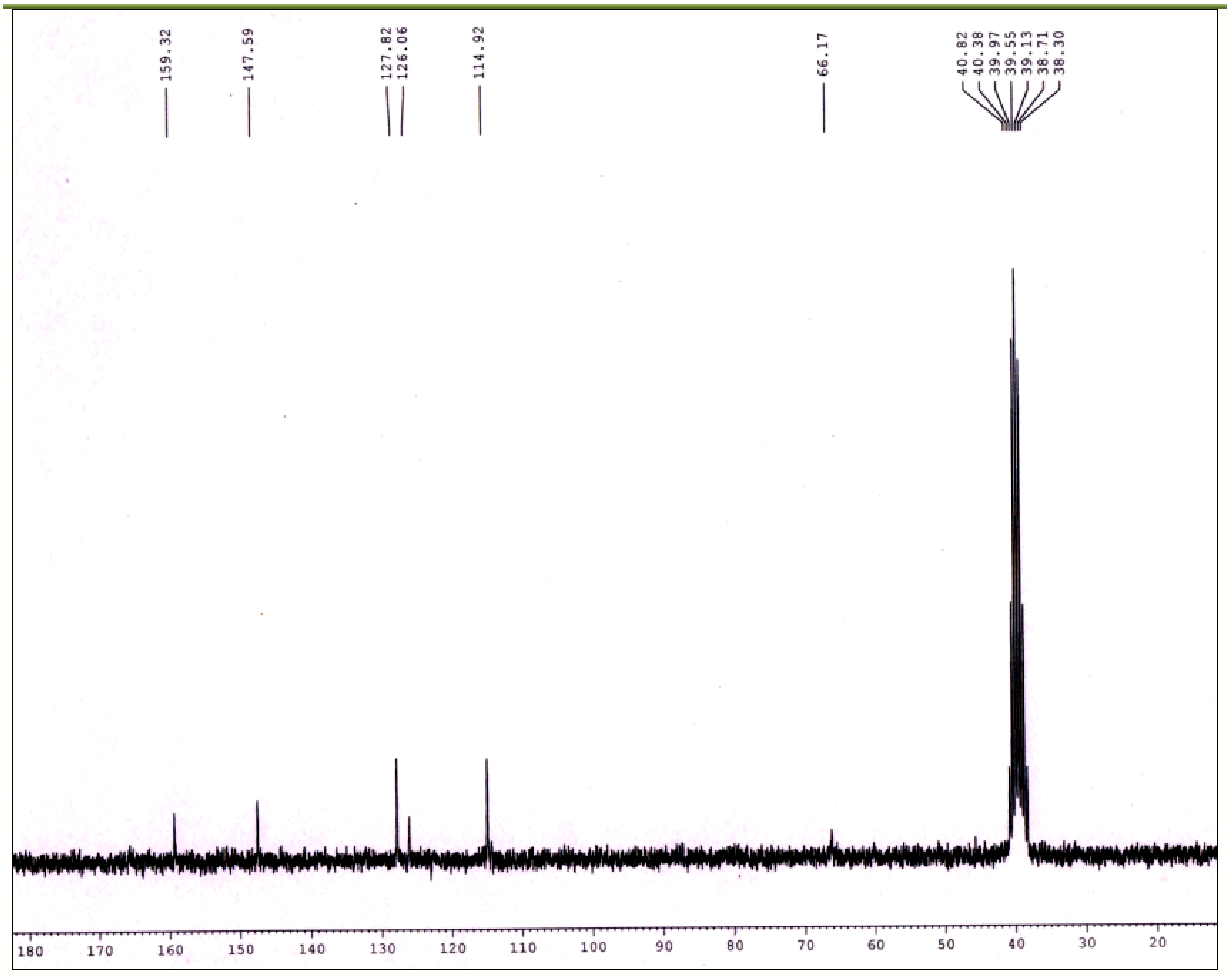


Figure S6. Molecular weight (Mn) vs. percentage conversion for the synthesis of P2 using XBDTB as chain transfer agent.