

## 1 **Electronic Supplementary Information (ESI)**

# 2 **Healable thermo-reversible functional polymer via RAFT** 3 **polymerization and ultrafast ‘Click’ Chemistry using triazoline** 4 **derivative**

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8

## 9 **Experimental**

### 10 **Materials**

11 2-Hydroxyethylmethacrylate (HEMA, 97 %) was purchased from Aldrich Chemical, USA and  
12 further purified by passing through basic alumina column to make it inhibitor-free. 4-cyano-4-  
13 [(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTSPA), 4,4'-azobis(4-cyanovaleric  
14 acid) (ABCVA), 4,4'-Methylenebis(phenyl isocyanate), 4-(Dimethylamino)pyridine (DMAP)  
15 and 1,4-Diazabicyclo[2.2.2]octane (DABCO) were purchased from Aldrich Chemical, USA and  
16 used as received. Bromine (>99 %) was purchased from S. D. Fine Chemical Ltd. Ethyl  
17 carbazate and N,N'-Dicyclohexylcarbodiimide (DCC) were purchased from Spectrochem, India  
18 and used as received. Indole-3-butyric acid (IBA), DMF (> 99 %) and n-Hexane (> 99 %) were  
19 purchased from Merck, India and used as received. DABCO-Br, 4,4'- (4,4'- diphenylmethylene)-  
20 bis(carbethoxysemicarbazide), 4,4'-(4,4'-diphenylmethylene)-bis(urazole) and 4,4'-(4,4'-  
21 diphenylmethylene)-bis-(1,2,4-triazoline-3,5-dione) were synthesized as reported in literature<sup>1</sup>.

### 22 **Characterization**

23  $^1\text{H}$  NMR spectra were recorded in Bruker 600 MHz spectrometer at room temperature using  
24 DMSO- $d_6$  solvent. Fourier Transform Infrared spectroscopy (FT-IR) was recorded using Perkin-  
25 Elmer, Inc. version 5.0.1, in attenuated total reflection (ATR) mode. All the IR spectra were  
26 recorded within the range of 4000 – 400  $\text{cm}^{-1}$ . The molecular weights of the polymers were  
27 determined by Gel Permeation Chromatography (GPC) (Agilent 1260 Infinity GPC instrument)  
28 using THF as an eluent at a flow rate of 1  $\text{mL min}^{-1}$  and a narrow disperse polystyrene as a  
29 calibration standard. The polymer solutions were passed through three PL gel 10  $\mu\text{m}$  MIXED-B  
30 columns (300 x 7.5 mm) connected in series, which were preceded by a PL gel 10  $\mu\text{m}$  guard  
31 column (50 x 75 mm). An RI detector was used to record the signal. Before injecting the  
32 polymer solution into the GPC instrument, it was thoroughly filtered using a regenerated  
33 cellulose filter having a pore size of 0.2  $\mu\text{m}$ . Differential Scanning Calorimetry (DSC) analysis  
34 of the polymer samples was carried out using DSC 200 F3 instrument (Netzsch, Germany). All  
35 the polymer samples (~6 mg) were heated from -25  $^{\circ}\text{C}$  to +180  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C / min}$   
36 under  $\text{N}_2$  atmosphere. Nitrogen was used as an inert atmosphere with a flow rate of 50  $\text{mL min}^{-1}$ .  
37 The temperature against heat flow was recorded. The enthalpy was calibrated by indium standard  
38 supplied by Netzsch. TGA analysis was carried out on a TGA-50 instrument (Shimadzu). In this  
39 case, a small amount (~8 mg) of sample was taken and heated from 25  $^{\circ}\text{C}$  to 600  $^{\circ}\text{C}$  at a rate of  
40 10  $^{\circ}\text{C/min}$  under nitrogen atmosphere. MALDI-TOF-MS analysis was performed using  
41 Ultraflex extreme mass-spectrometer (Bruker). 2,5-Dihydroxybenzoic acid (DHB) and sodium  
42 trifluoroacetate was used as matrix and cationic agent. The ethanol solution of polymer and DHB  
43 were mixed at 1:1 ratio by volume. The cationic agent was added to enhance the ionization of  
44 polymer. The healing capability of the crosslinked polymer was studied via ZEISS FESEM at an  
45 accelerating voltage of 5 kV scanning electron microscope. A scratch was made on the surface of

46 the polymer sample and then it was healed by heating the sample at 130 °C for 1 h followed by  
47 cooling at room temperature. Healing study was also carried out using optical microscopy  
48 analysis (Leica DMLM, made in Germany) in Optical Microscopy and Mechanical Testing  
49 laboratory (OMMT), Central Research facility (CRF), IIT Kharagpur.

#### 50 **Synthesis of PHEMA using RAFT polymerization**

51 PHEMA was prepared using different molar ratios of RAFT: Initiator. HEMA (1 g,  $7.68 \times 10^{-3}$   
52 mol), CDTSPA (0.0413 g,  $1.02 \times 10^{-4}$  mol), ABCVA (0.0072 g,  $2.56 \times 10^{-5}$  mol) and DMF (2  
53 mL) were taken in a Schlenk tube supplied with a magnetic stirring bar. The tube was then sealed  
54 with silicone rubber septum and degassed by purging N<sub>2</sub> gas for 15 min. The polymerization was  
55 carried out for 3 h at 70°C and then quenched by immersing the tube in an ice bath and exposing  
56 to air. The highly viscous polymer was solubilized in small volume of DMF and precipitated in a  
57 non-solvent like n-hexane. The polymer was dried in vacuum oven at 60°C for 24 h. Conversion  
58 (~75 %),  $M_{n, \text{Theo}} = 7720 \text{ g mol}^{-1}$ ,  $M_{n, \text{NMR}} = 7690 \text{ g mol}^{-1}$ .

#### 59 **Synthesis of PHEMA – Indole**

60 PHEMA (0.1560 g, 0.0196 mmol, 1eq), Indole-3-butyric acid (IBA) (0.4873 g, 2.39 mmol, 2eq)  
61 and 4-dimethylamino pyridine (DMAP) (0.0580 g, 0.47 mmol, 0.2 eq) were dissolved in 5 mL  
62 DMF and cooled in an ice bath. N,N-dicyclohexylcarbodiimide (0.5300 g, 2.56 mmol, 2eq) was  
63 dissolved in 5 mL DMF and then added dropwise to the above mixture. The reaction was then  
64 continued for 24 h at an ambient temperature. Then the polymer solution was filtered and  
65 precipitated in cold hexane. The modified polymer was dried in vacuum oven at 40 °C. The  
66 conversion was measured via <sup>1</sup>H NMR analysis (~78.7 %),  $M_{n, \text{NMR}} = 16900 \text{ g mol}^{-1}$ ;  $M_{n, \text{GPC}} =$   
67  $15920 \text{ g mol}^{-1}$ ; PDI= 1.23).

#### 68 **Synthesis of DABCO-Br**

69 In a 100 mL round bottomed flask, 1,4-Diazabicyclo[2.2.2]octane (1.3477 g, 12 mmol, 1eq) was  
70 dissolved in 20 mL chloroform followed by dropwise addition of Br<sub>2</sub> solution (4.7 g, 58 mmol,  
71 4.8 eq) in 20 mL of chloroform using an additional funnel. The reaction was continued for 4 h  
72 under nitrogen atmosphere. Finally, the yellow precipitate was filtered off and washed with  
73 chloroform (100 mL) and kept in vacuum oven at 40°C for drying (Yield: 4.023 g, 99 %).

#### 74 **Synthesis of 4,4'-(4,4'-diphenylmethylene)-bis-(carbethoxysemicarbazide)**

75 In a 100 ml 2 neck round bottomed flask, ethyl carbazate (4 g, 38 mmol, 2eq) was dissolved in  
76 30 mL of toluene and placed in an ice bath. A solution of 4,4'-Methylenebis(phenyl isocyanate)  
77 (4.8 g, 19.2 mmol, 1eq) in 20 mL toluene was prepared and taken in an additional funnel, which  
78 was equipped to flask. The overall mixture was put under nitrogen atmosphere. The isocyanate  
79 solution was added dropwise under vigorous stirring. After complete addition of isocyanate, the  
80 overall mixture was allowed to stir for 5 hours at room temperature followed by 2 h at 90°C.  
81 Then the reaction mixture was cooled to room temperature, and the desired product was filtered  
82 off followed by washing with toluene (Yield: 8.1 g, 99 %). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ (ppm): 8.89  
83 (s, 2H), 8.63 (s, 2H), 7.93 (s, 2H), 7.35 (d, *J* = 8.1 Hz, 5H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.13  
84 (m, 1H), 7.07 (d, *J* = 8.3 Hz, 4H), 4.05 (q, *J* = 7.0 Hz, 4H), 3.78 (s, 2H), 1.19 (t, *J* = 7.3 Hz, 6H).

#### 85 **Synthesis of 4,4'-(4,4'-diphenylmethylene)-bis-(urazole)**

86 In 100 mL round bottomed flask, bisfunctional semicarbazide (4.1 g, 9mmol) was dissolved in  
87 20 mL aqueous potassium hydroxide solution (4 M) under nitrogen atmosphere. Then the  
88 solution was allowed to reflux for 2 h at 100°C. The mixture was warm filtered and cooled to  
89 room temperature followed by acidification using conc. HCl until pH of the solution became 1.  
90 The mixture was cooled to room temperature and the white product was filtered off and dried in

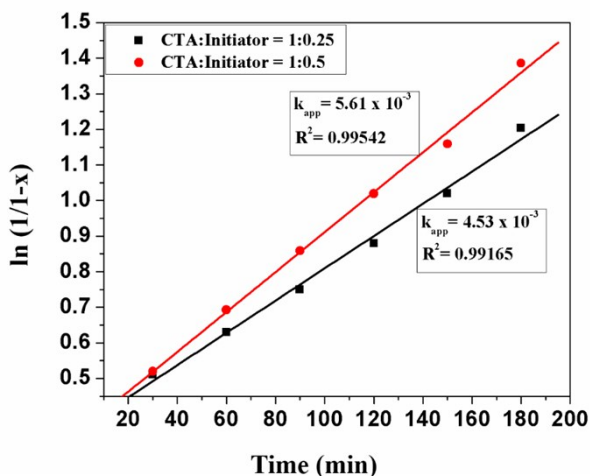
91 vacuum oven (Yield: 4 g, 99 %).  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ )  $\delta$  (ppm): 10.46 – 10.41 (m, 4H), 7.39 –  
92 7.25 (m, 8H), 4.03 (s, 2H), 3.34 (s, 1H).

### 93 Synthesis of 4,4'-(4,4'-diphenylmethylene)-bisTAD

94 In a 100 mL round bottomed flask, the mixture of bifunctional urazole (1 g, 2.7 mmol, 1eq) and  
95 DABCO-Br (2.5 g, 1.6 mmol, 0.59 eq) in 20 mL dichloromethane. The reaction mixture was  
96 allowed to stir for 5 h at room temperature under nitrogen atmosphere. The mixture was then  
97 filtered off and the residue was washed with dichloromethane. The filtrate was then dried in a  
98 rotary evaporator at  $40^\circ\text{C}$  to obtain the pink coloured product (Yield: 0.92 g, 97 %).  $^1\text{H}$  NMR  
99 ( $\text{DMSO-d}_6$ )  $\delta$  (ppm): 7.46 – 7.24 (m, 8H), 4.05 (d,  $J = 13.9$  Hz, 2H).

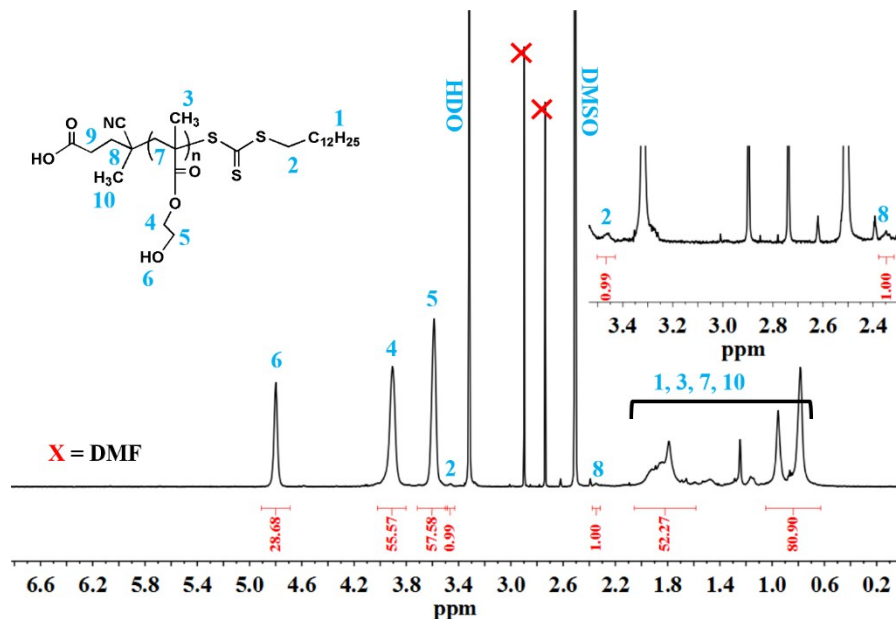
### 100 Synthesis of reversible network of PHEMA – Indole – bisTAD

101 To achieve the crosslinked adduct, the indole polymer and bifunctional TAD were dissolved in  
102 minimal volume of THF and mixed at room temperature at 1:1 molar ratio. After the reaction  
103 was complete (indicated by noticing disappearance of the red colour of bis TAD derivative<sup>1</sup>)  
104 within less than 5 seconds, the crosslinked polymer was dried in vacuum oven at  $40^\circ\text{C}$  for  
105 overnight. The product was further analyzed via FTIR spectroscopy.



107 **Figure S1:** Kinetic study of the PHEMA prepared via CDTSPA RAFT agent and ABCVA  
108 initiator at different CTA: Initiator molar ratios. (X = conversion of HEMA)

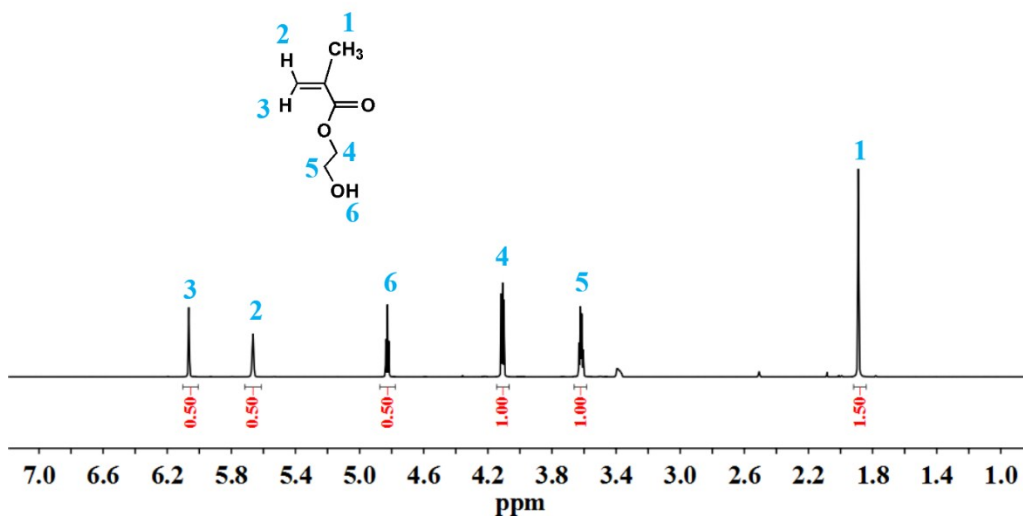
109 **<sup>1</sup>H NMR analysis of PHEMA**



110

111 **Figure S2:** <sup>1</sup>H NMR analysis of HEMA in DMSO-d<sub>6</sub>.

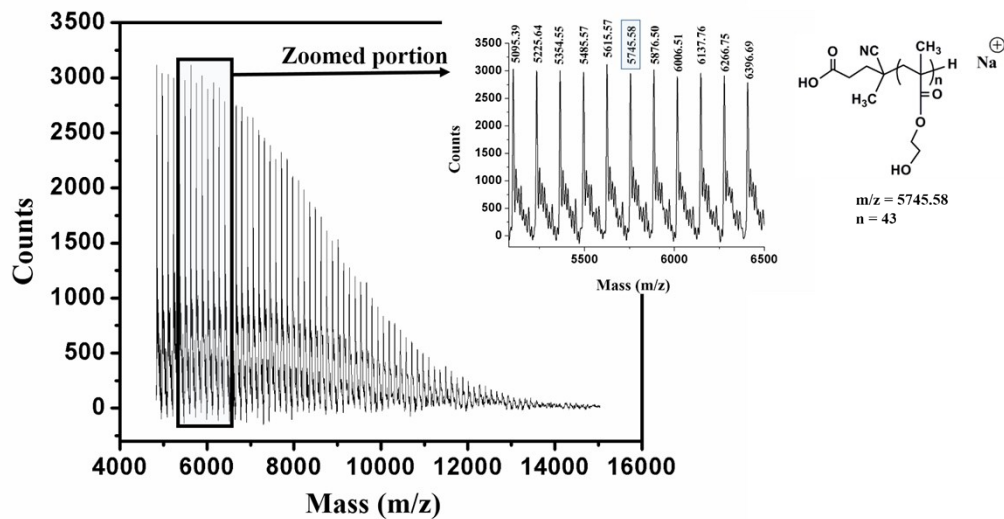
112 **<sup>1</sup>H NMR analysis of HEMA**



113

114 **Figure S3:**  $^1\text{H}$  NMR analysis of HEMA in  $\text{DMSO-d}_6$ .

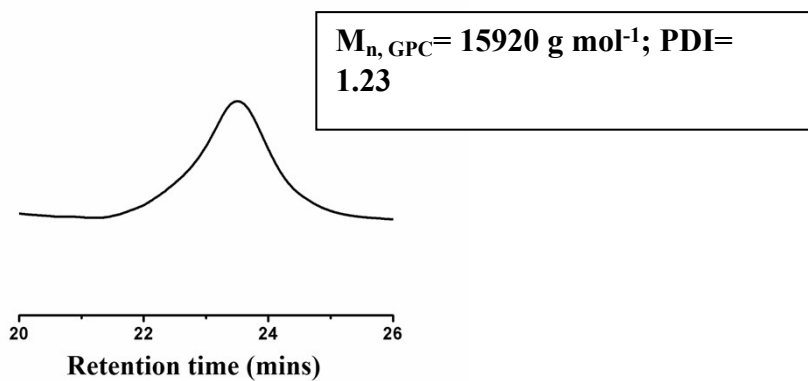
115 **MALDI-Tof analysis of PHEMA polymer prepared via CDTSPA as RAFT agent**



116

117 **Figure S4:** Full scale of MALDI-Tof analysis of PHEMA.

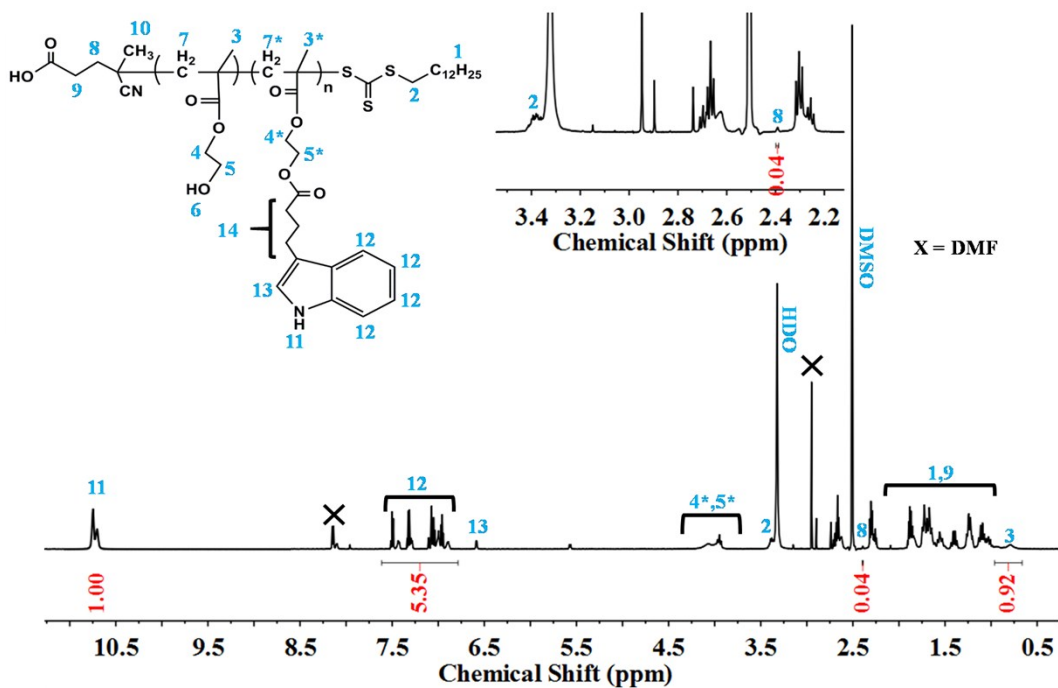
118 **GPC traces of PHEMA-Indole polymer**



119

120 **Figure S5:** SEC traces of PHEMA-indole polymer.

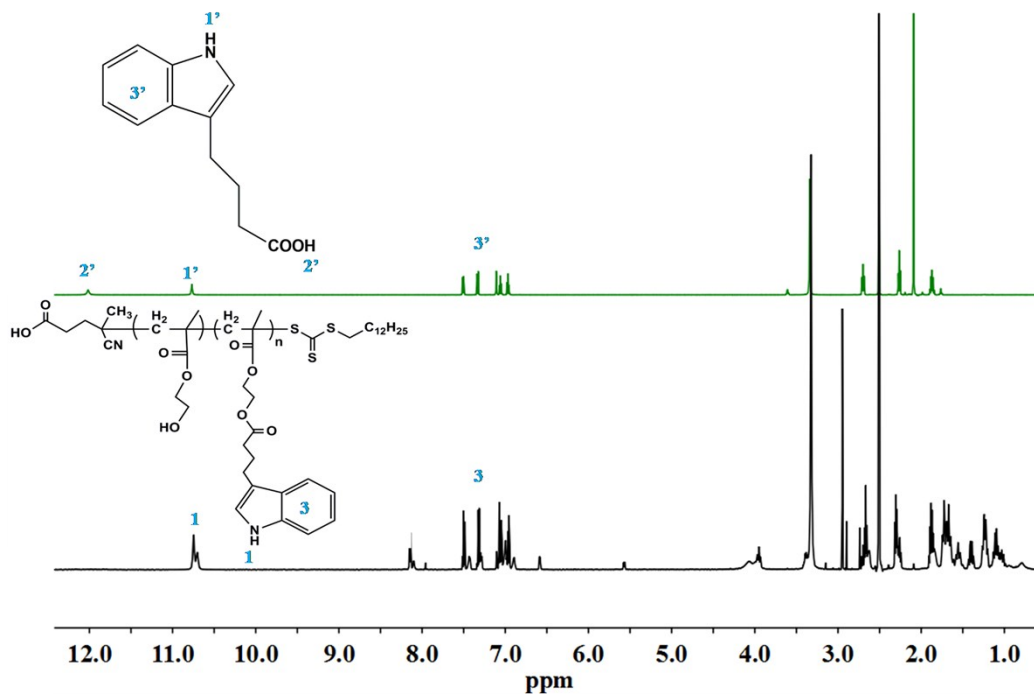
121  $^1\text{H}$  NMR analysis of PHEMA-Indole



122

123 **Figure S6:**  $^1\text{H}$  NMR analysis of PHEMA-Indole in DMSO- $d_6$ .

124 **Comparison of  $^1\text{H}$  NMR analyses of IBA with PHEMA-indole polymer**



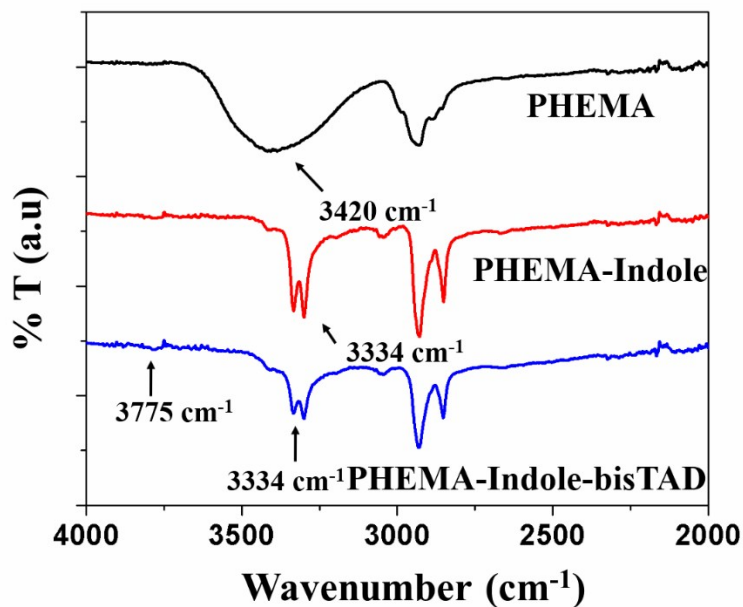
125

126 **Figure S7:**  $^1\text{H}$  NMR comparison of Indole-3-butyric acid and PHEMA-Indole in DMSO- $d_6$

127 solvent.



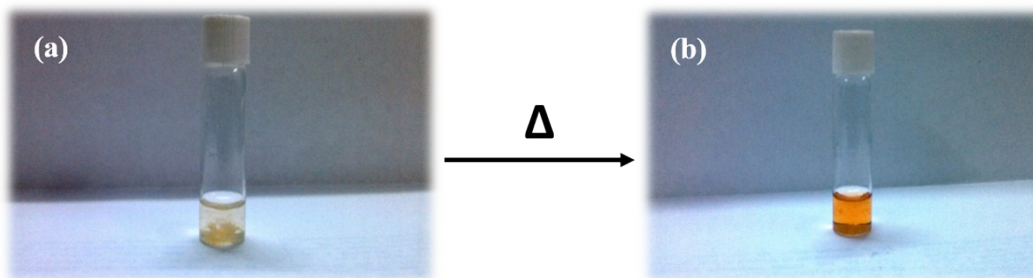
128 FTIR analysis



129

130 **Figure S8:** FTIR analysis of the respective polymers in ATR mode.

131 **Solution property study of PHEMA-Indole-bisTAD crosslinked polymer**

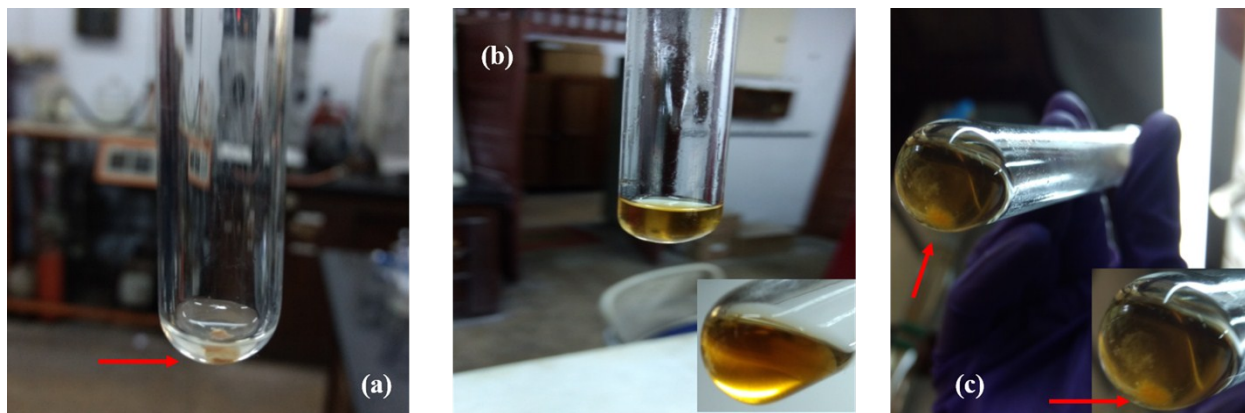


(a) Crosslinked polymer insoluble at 30 °C

(b) Crosslinked polymer soluble in DMF after heating at 130 °C for 45 m

132

133 **Figure S9:** (a) Crosslinked polymer insoluble in DMF at 30 °C; (b) Crosslinked polymer become  
134 soluble after heating at 130 °C for 45 m.



135

136 **Fig S10:** (a) Insoluble Alder-ene crosslinked product in DMF solvent at room temperature; (b)  
137 Soluble adduct after heating at 130 °C in DMF solvent and (c) Repeat crosslinked product after  
138 cooling to room temperature in DMF solvent.

139 **Image of bifunctional TAD solution in DMF at room temperature**



Figure S11(a): bisTAD  
in DMF

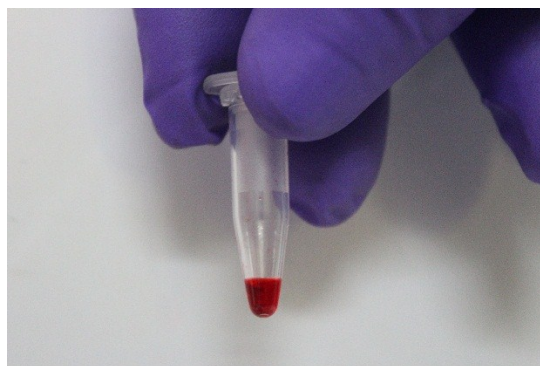
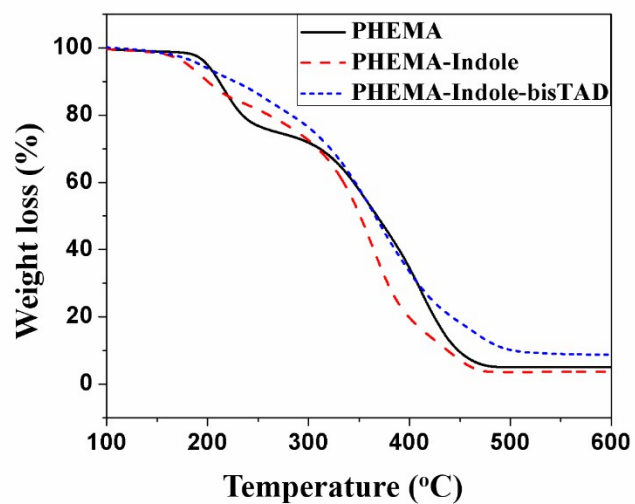


Figure S11(b): bisTAD in THF

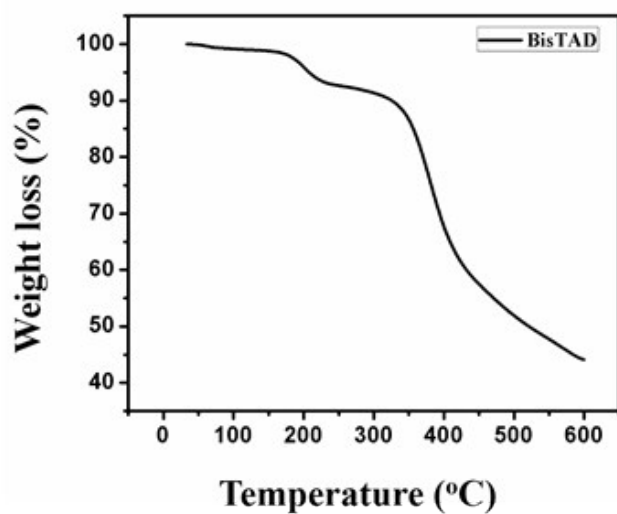
140 **Figure S11:** Image of bisTAD in DMF and THF solvent.

141 **TGA analysis of the polymers and bisTAD**



142

143 **Figure S12:** TGA analysis of the polymers.

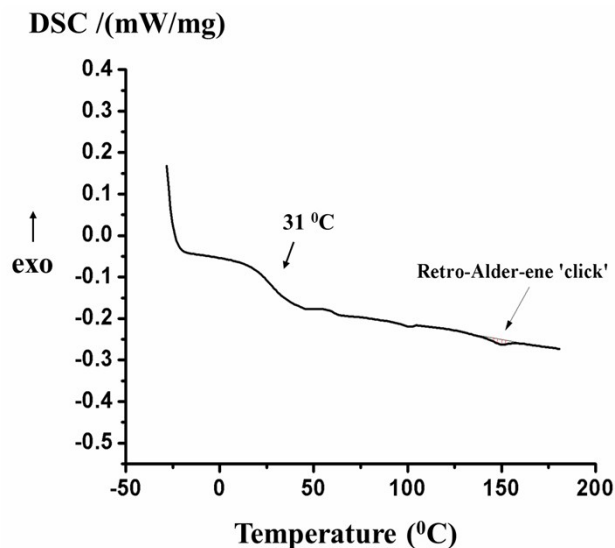


144

145 **Figure S13:** TGA analysis of bisTAD done at 20 °C / min under nitrogen atmosphere (30 °C to  
 146 600 °C), showing that the initial decomposition temperature of bisTAD starts at 191 °C.

147 **DSC analysis of PHEMA-Indole-bisTAD polymer after 12 h**

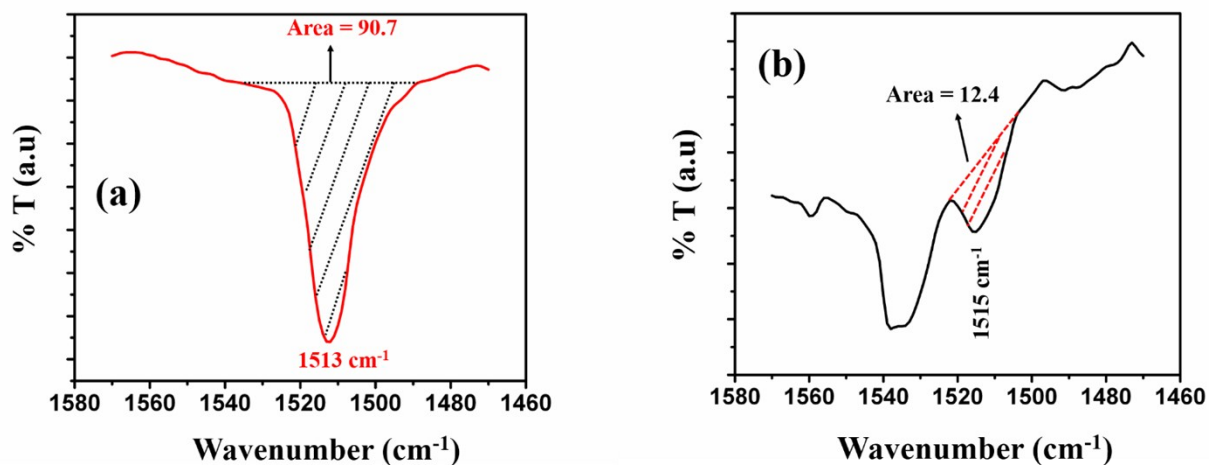
148 The DSC analysis of the same sample (DSC analysis of sample as shown in fig 4 of main  
 149 manuscript) done after keeping at room temperature for 12 h.



150

151 **Figure S14:** DSC analysis of the sample done at 10 °C / min under nitrogen atmosphere (-25 °C  
 152 to +180 °C).

153 **FTIR analysis of PHEMA-Indole and PHEMA-Indole-bisTAD**



154

155 **Figure S15:** FTIR analysis of polymers indicating ~90% conversion from PHEMA-Indole to  
 156 PHEMA-Indole-bisTAD adduct, fig S14 (a): FTIR analysis of PHEMA-Indole and fig s14 (b):  
 157 FTIR analysis of PHEMA-Indole-bisTAD.

158 **Reference**

159 1. S. Billiet, K. De Bruycker, F. Driessen, H. Goossens, V. Van Speybroeck, J. M. Winne and F.  
160 E. Du Prez, *Nat. Chem.*, 2014, **6**, 815-821.