Electronic Supplementary Material (ESI) for Chemical Communications

SUPPLEMENTARY MATERIAL

A novel photodegradable hyperbranched polymeric photoresist

Saptarshi Chatterjee and S. Ramakrishnan
Department of Inorganic and Physical Chemistry
Indian Institute of Science
Bangalore 560012, INDIA

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Chemical Communications

EXPERIMENTAL SECTION

Materials

Terephthalaldehyde, sodium borohydride, trimethylorthoformate, propargyl alcohol, 4-*N*,*N*-dimethylamino-1,8-naphthalic anhydride were purchased from Sigma-Aldrich Chemical Co. and used directly. Benzene, acetic acid, sodium acetate, dimethyl amine aqueous solution, acrylonitrile, potassium nitrate were purchased from Spectrochem Chemicals Ltd, while common organic solvents and reagents were procured from Ranbaxy, Spectrochem or SD fine chemicals. Solvents were distilled prior to use and, if necessary, were dried following the standard procedures.

Methods

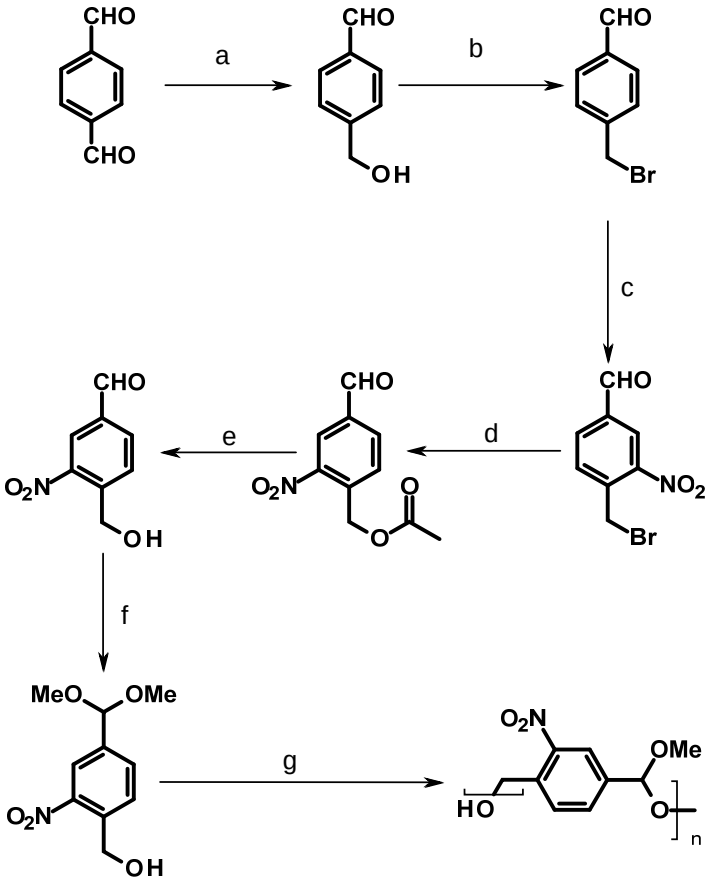
^{1}H NMR spectra were recorded using a Bruker 400 MHz spectrometer using $CDCl_3$ as the solvent and TMS as internal reference, unless otherwise mentioned. The absorption spectra were recorded using Cary UV-Vis spectrophotometer. GPC measurements were carried out using Viscotek triple detector analyzer (TDA) model 300 system, that has a refractive index (RI), a differential viscometer (DV) and light scattering (LS) connected in series. The separation was achieved using a series of two PL gel mixed bed columns (300 X 7.5mm) operated at 30 ^{o} C using THF as the eluent. Molecular weights were determined using a universal calibration curve based on the data from the RI and DV) detectors using narrow polystyrene standards. The glass transition temperature of the sample was determined using a Mettler Toledo DSC instrument at a heating rate of 10 °C/min, under dry N_2 atmosphere. The samples were first heated to 100 °C (to ensure that the sample flows and makes the contact with the pan) and quenched prior to recording the T_g. IR spectrum was recorded in a Brukar Alpha ATR-IR machine. Photopatterning was carried out using an EVG double sided mask aligner. SEM images were recorded in a FEI ESEM Quanta scanning electron microscope with accelerating voltage 5KV.

Synthesis of the monomers

4-(Hydroxymethyl)benzaldehyde.[1] $NaBH_4$ (0.35 g, 9.25 mmol) was added at –5 °C with continuous stirring for 30 min to a solution of terepthalaldehyde (5 g, 37.3 mmol) in a mixture of 95% EtOH (70 mL) and THF (100 mL). Then the mixture was stirred for 6 h, while the

temperature was maintained 0°C. Then the reaction mixture was neutralized with 2 M HCl to pH 5, the solvents were evaporated, water (200 mL) was added to the residue, and products were extracted with ethylacetate. Combined organic extracts were dried with $MgSO_4$, and the solvent was evaporated. The product was purified by column chromatography using an AcOEt-Petether (2 : 1) mixture of solvents. Yield was 4.1 g (82%), m.p. 40 °C.

NMR (400 MHz, $CDCl_3$, δ ppm): 10 (s , 1H, C**H**O) 7.88 (d, 2 H, Ar-**H**'s), 7.54 (d, 2 H, Ar-**H**'s), 4.80 (d, 2 H, ArC$\mathbf{H_2}$).



Scheme S1. Synthesis of the AB_2 monomer (A) and its polymerization to form hyperbranched nitro-polyacetal. (a) $NaBH_4$/THF, EtOH (b) HBr in Water/ Tolune (c) KNO_3/H_2SO_4 (d) CH_3COONa/ CH_3COOH (e) KOH/MeOH (f) MeOH / $HC(OMe)_3$, H^+(f) PCS.

4-(Bromomethyl)-benzaldehyde.[1] 4-(Hydroxymethyl)benzaldehyde (2.5 g, 18.38 mmol) was taken in 10 ml of toluene in a round bottom flask and 5 ml of 48% Aqueous HBr was added to it. The mixture was refluxed for 3 hrs. 100 ml chroloform was added to it and the organic layer was washed with sodium bicarbonate water until it was neutral. Then it was passed through

anhydrous sodium sulphate and solvent was evaporated and dried under vacuum. Product obtained as pale yellow crystalline solid. Yield was 3 g (82%), m.p 94 ^{o}C.

NMR (400 MHz, $CDCl_3$, δ ppm): 10.02 (s , 1H, C**H**O) 7.88 (d, 2 H, Ar-**H**'s), 7.57 (d, 2 H, Ar-**H**'s), 4.52 (s, 2 H, ArC$\mathbf{H_2}$).

4-(Bromomethyl)-3-nitrobenzaldehyde.[2] The bromide (4.1 g, 20.6 mmol) was added at 0 °C to a solution of KNO_3 (2.49 g, 24.7 mmol) in 40 mL of H_2SO_4, and the mixture was stirred for 4 h at room temperature, poured into ice-water, and extracted with CH_2Cl_2. The extract was washed with water, saturated $NaHCO_3$ (aq), water, and brine and dried over $MgSO_4$. The solvent was removed and dried over vacuum pump. Product was obtained as yellow solid. Yield was 2.9 g (58%).

NMR (400 MHz, $CDCl_3$, δ ppm): 10.1 (s, 1H, C**H**O) 8.55 (s, 1H, Ar-**H**), 8.15 (s, 1H, Ar-**H**), 7.80 (s, 1H, Ar-**H**), 4.89 (s, 2H, ArC$\mathbf{H_2}$).

4-Formyl-2-nitrobenzyl acetate. 4-(Bromomethly)-3-nitrobenzaldehyde (2.9 g, 11.8 mmol) was taken in a round bottom flask along with anhydrous sodium acetate (9.7 g, 118 mmol) and 50 ml of glacial acetic acid. The reaction mixture was refluxed for 24 h. The reaction mixture was extracted with chloroform (100 ml x 3). The chloroform layer was washed twice with 5 % NaHCO3 solution and finally with water. Solvent was removed and product was dried under vacuum. Product obtained as dark yellow liquid. Yield was 2.3 g (94%).

NMR (400 MHz, $CDCl_3$, δ ppm): 10.1 (s, 1H, C**H**O) 8.65 (s, 1H, Ar-**H**), 7.87 (d, 1H, Ar-**H**), 7.31 (d, 1H, Ar-**H**), 5.64 (s, 2H, ArC$\mathbf{H_2}$), 2.26 (s, 3H, $ArCH_2COC\mathbf{H_3}$).

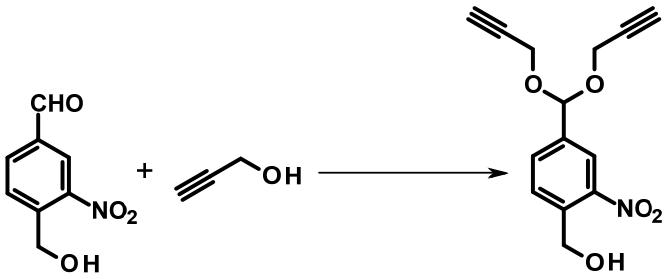
4-(Hydroxymethyl)-3-nitrobenzaldehyde. 4-Formyl-2-nitrobenzyl acetate (3 g, 14.5 mmol) was dissolved in 20 ml methanol. Potassium hydroxide (163 mg, 2.9 mmol) was added into it. The reaction mixture was stirred in room temperature for 4 h. Methanol was removed at room temperature under vacuum. 30 ml of water was added into it. Product was extracted in ethylacetate. The organic layer was washed with brine. Then it was passed through anhydrous sodium sulphate and solvent was evaporated and dried under vacuum. Product obtained as pale yellow solid. Product was further purified passing through the column at 3:1 pet-ether ethyl acetate. The yield was 1 g (41%).

NMR (400 MHz, $CDCl_3$, δ ppm): 10.1 (s, 1H, C**H**O) 8.6 (s, 1H, Ar-**H**), 8.21 (d, 1H, Ar-**H**), 8.07 (d, 1H, Ar-**H**), 5.14 (d, 2H, ArC**H**$_2$), 2.39 (s, 1H, $ArCH_2O$**H**).

(4-(Dimethoxymethyl)-2-nitrophenyl)methanol. 4-(Hydroxymethyl)-3-nitrobenzaldehyde (1 g, 4.4 mmol) was taken in 10 ml dry methanol in a round bottomed flask and 3.2 g (30.3 mmol) of trimethyl orthoformate was added to it. A catalytic amount of methanolic HCl was added and it was refluxed for 24 h. A small amount of $NaHCO_3$ was added into it and stirred for half an hour to neutralize the acid. The reaction mixture was filtered and solvent was removed using a rotary evaporator and dried in vacuum pump. The yield was 1 g (80%).

NMR (400 MHz, $CDCl_3$, δ ppm): 8.21 (s, 1H, Ar-**H**) 7.76 (d, 2H, Ar-**H**'s), 5.48 (s, 1 H, ArC**H**$(OCH_3)_2$), 4.98 (d, 2 H, ArC**H**$_2$), 3.34 (s, 6H, ArCH$(OC$**H**$_3)_2$).

Hyperbranched nitropolyacetal. (4-(dimethoxymethyl)-2-nitrophenyl)methanol (1 g, 4.4 mmol) was taken in a polymerization flask along with 2 mol % of p-toluenesulphonic acid. The reaction mixture was degassed by purging N_2 for 10 min and then heated to 80 ^oC under N_2 atmosphere to ensure homogeneous mixing of the catalyst and monomers. Then the polymerization was carried out at 100 ^oC for 30 min under N_2 purging. Then the polymerization tube was connected to a Kugelrohr apparatus and the polymerization was continued at 100 ^oC under reduced pressure of 20 Torr for 30min. The polymer was dissolved in THF and the solution of the polymer was neutralized by solid $NaHCO_3$ and filtered. The filtrate was concentrated and poured into dry methanol to obtain the polymer. This polymer was further purified through dissolution followed by reprecipitation using THF-methanol. Yield was 0.7 g (82%).



Scheme S2. Synthesis of hyperbranched nitro propargyl monomer.

(4-(Bis(pro-2-ynyloxy)methyl-2-nitrophenyl)methanol. 3 g (16.5 mmol) 4-(hydroxymethyl)-3-nitrobenzaldehyde was taken in a RB along with 10 ml of dry propargyl alcohol. 80 ml of dry benzene was added into it. A catalytic amount of PTSA was added in it. The reaction mixture was then heated to 85 °C for 24hrs and the water formed during this step was azeotropically removed using a Dean-Stark's apparatus. The acid was neutralized using $NaHCO_3$. Benzene and excess propargyl alcohol was removed under reduced pressure. Product was purified as pale yellow oil by column chromatography using AcOEt-Petether (1:9) mixture of solvents. The yield was 1.8 g (39%).

NMR (400 MHz, $CDCl_3$, δ ppm): 8.22 (s, 1H, Ar-H's) 7.79 (s, 2 H, Ar-H's), 5.93 (s, 1 H, ArC**H**(OPropargyl)$_2$), 4.97 (s, 2H, ArC**H$_2$**), 4.35 (d, 2H, OC**H$_2$**CCH), 4.22 (d, 2H, OC**H$_2$**CCH), 2.48 (t, 2H, OCH_2CC**H**).

Hyperbranched nitro-dipropargypolylacetal – Nitro-HPBA-P

Polymerization of this monomer was performed similarly. Yield was 66%.

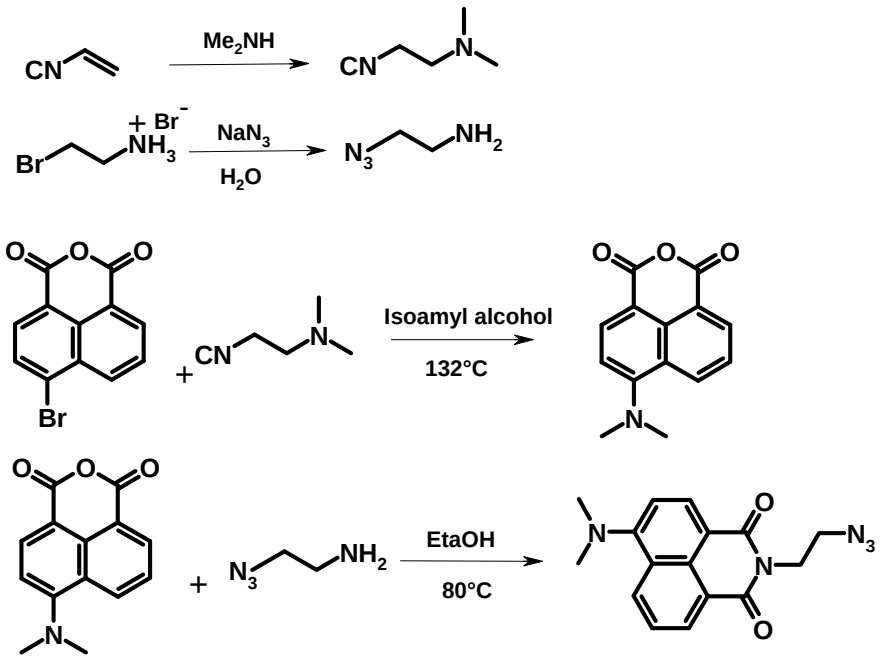
Synthesis of 4-*N*,*N*-dimethylamino-*N*-(2-azido-ethyl)-1,8-naphthalimide: Fluorescent dye.[3,4]

3-Dimethylaminopropionitrile. 5.3 g (0.1 mol) of acrylonitrile was added drop-wise in a ice cold 40% aqueous solution of dimethyl amine containing 11.8 g (0.105 mol) at 0°C under stirring condition for 3 h. After the addition stirring was continued for 2h at temperature 15 0°C. The product was extracted in chloroform. After removal of solvent, product was distilled out under vacuum as colourless liquid. Yield was 9.6 g (98%).

NMR (400 MHz, $CDCl_3$, δ ppm): 2.68 (t, 2H, NCC**H$_2$**CH_2), 2.55 (t, 2H, $NCCH_2$C**H$_2$**), 2.32 (t, 2H, N(C**H$_3$**)$_2$).

4-*N*,*N*-dimethylamino-1,8-naphthalic anhydride. 1 g (3.6 mmol) of 4-bromo-1,8-naphthalic anhydride and 1.5 g (15.3 mmol) 3-dimethylaminopropionitrile were taken in a RB along with 10 ml of isoamyl alcohol. The reaction mixture was heated at 132°C for overnight. Upon cooling orange precipitate separated out. Precipitate was filtered and washed with petroleum ether and dried. Product obtained as bright orange crystal. Yield was 0.58 g (76%).

NMR (400 MHz, $CDCl_3$, δ ppm): 8.58 (d, 1H, Ar-**H**), 8.48 (dd, 2H, Ar-**H**), 7.69 (t, 1H, Ar-**H**), 7.12 (d, 1H , Ar-**H**) 3.18 (s, 6H, N(C**H**$_3$)$_2$).



Scheme S3. Synthesis of 4-N,N-Dimethylamino-N-(2-azido-ethyl)-1,8-naphthalimide fluorescent dye.

2-Azido-ethylamine. 2 g (9.8 mmol) 2-bromoethylammonium bromide and 2.8 g (43 mmol) were taken together in 12 ml water. The reaction mixture was heated at 45°C for overnight. 5 ml $NaHCO_3$ was added to generate amine from the salt. Product was extracted in ethylacetate. After removal of solvent, product was obtained as light orange viscous liquid. Yield is 0.45 g (53%).

NMR (400 MHz, $CDCl_3$, δ ppm): 3.38 (t, 2H, N_3C**H**$_2CH_2$), 2.88 (t, 2H, N_3CH_2C**H**$_2$).

4-*N*,*N*-Dimethylamino-*N*-(2-azido-ethyl)-1,8-naphthalimide. 0.53 g (2.2 mmol) of 4-*N*,*N*-dimethylamino-1,8-naphthalic anhydridea was taken in a RB in 15 ml dry ethanol and 2-azido-ethylamine were dissolved in 15 ml ethanol and added dropwise under refluxing condition in nitrogen environment. After the completion of addition, reaction mixture was refluxed for 24 h under nitrogen atmosphere. Ethanol was removed under vacuum. Product was extracted in ethyl acetate as yellow solid. Yield is 0.46 g (67%).

NMR (400 MHz, $CDCl_3$, δ ppm): 8.6 (d, 1H, Ar-**H**), 8.48 (dd, 2H, Ar-**H**), 7.67 (t, 1H, Ar-**H**), 7.12 (d, 1H, Ar-**H**), 4.43 (t, 2H, $N_3C\mathbf{H_2}CH_2$), 3.65 (t, 2H, $N_3CH_2C\mathbf{H_2}$), 3.12 (s, 6H, $N(C\mathbf{H_3})_2$).

Thin film preparation

Thin films are prepared on glass slides and silicon wafer. Prior to thin film preparation all the glasses and the silicon wafers were cleaned using piranha solution and finally with distilled water. A 20 mg/ml solution of the polymer was prepared in 3:1 (v:v) THF and o-dichlorobenzene mixture of solvents. The solution was filtered via 0.2 μm syringe filter. All the thin films are prepared at 2000 rpm with an acceleration of 100 rpm and duration of 30 sec.

Photopatterning

All the photopatterning were done in clean room. EVG 620 double sided mask aligner was used for 365 nm UV irradiation. Typical exposure time was 5 minutes. After that silicon wafers or glass slides were dipped into isopropyl alcohol for 30 sec for developing. Finally washed with distilled water and dried with a stream of dry nitrogen gas.

Solution degradation

Clicking onto the micropatterns

The patterned glass slides were dipped into ethanol solution in a petri dish containing azide dye. 10 μl aqueous solution of 5 mol% $CuSO_4$, $5H_2O$ and 10 μl aqueous solution of 10 mol% Sodium Ascorbate were added to it. The reaction mixture was made homogeneous by gently shaking. It was kept for overnight. The glasses were rinsed thoroughly with ethanol solution to make sure that there were no residual unclicked dyes left. Finally those were washed with distilled water and dried with a slow stream of nitrogen gas.

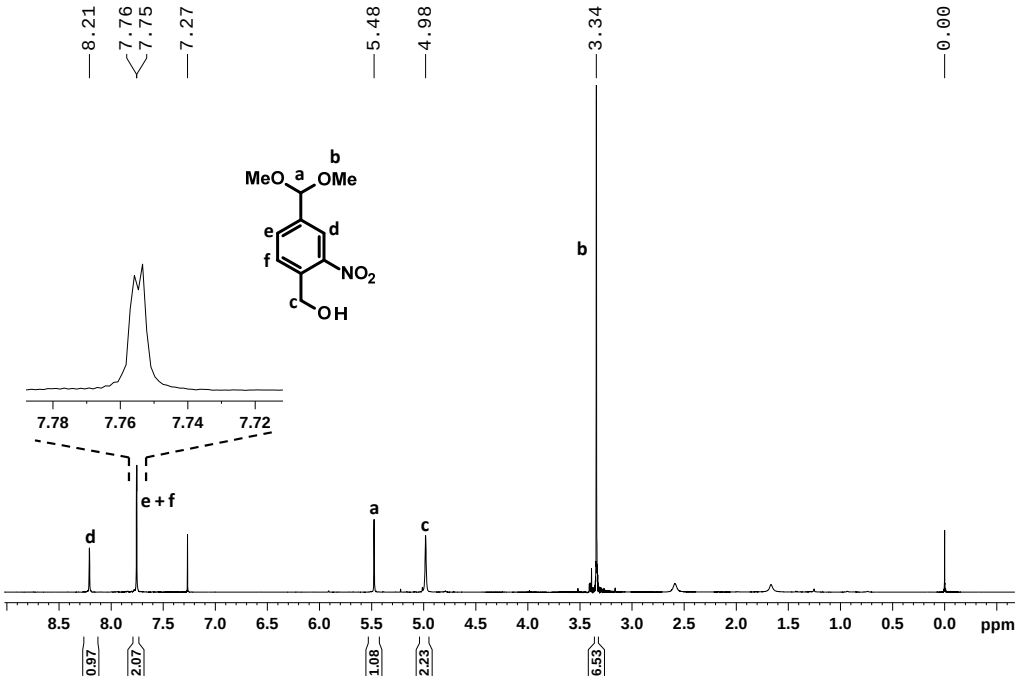


Figure S1a. ^{1}H NMR spectrum of the monomer.

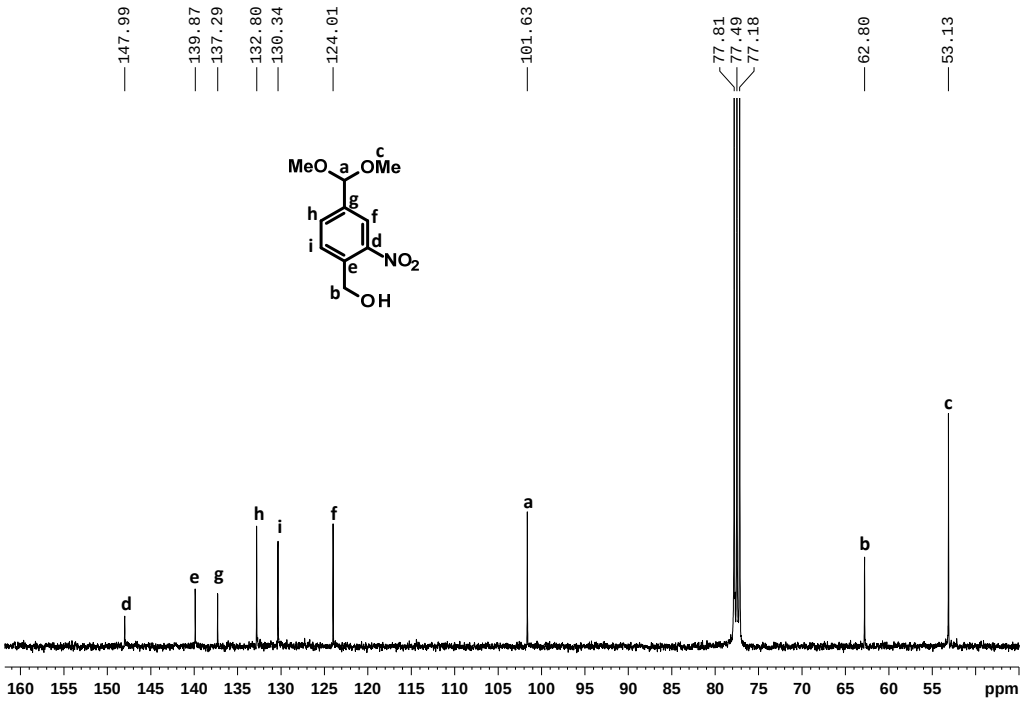


Figure S1b. ^{13}C NMR spectrum of the monomer.

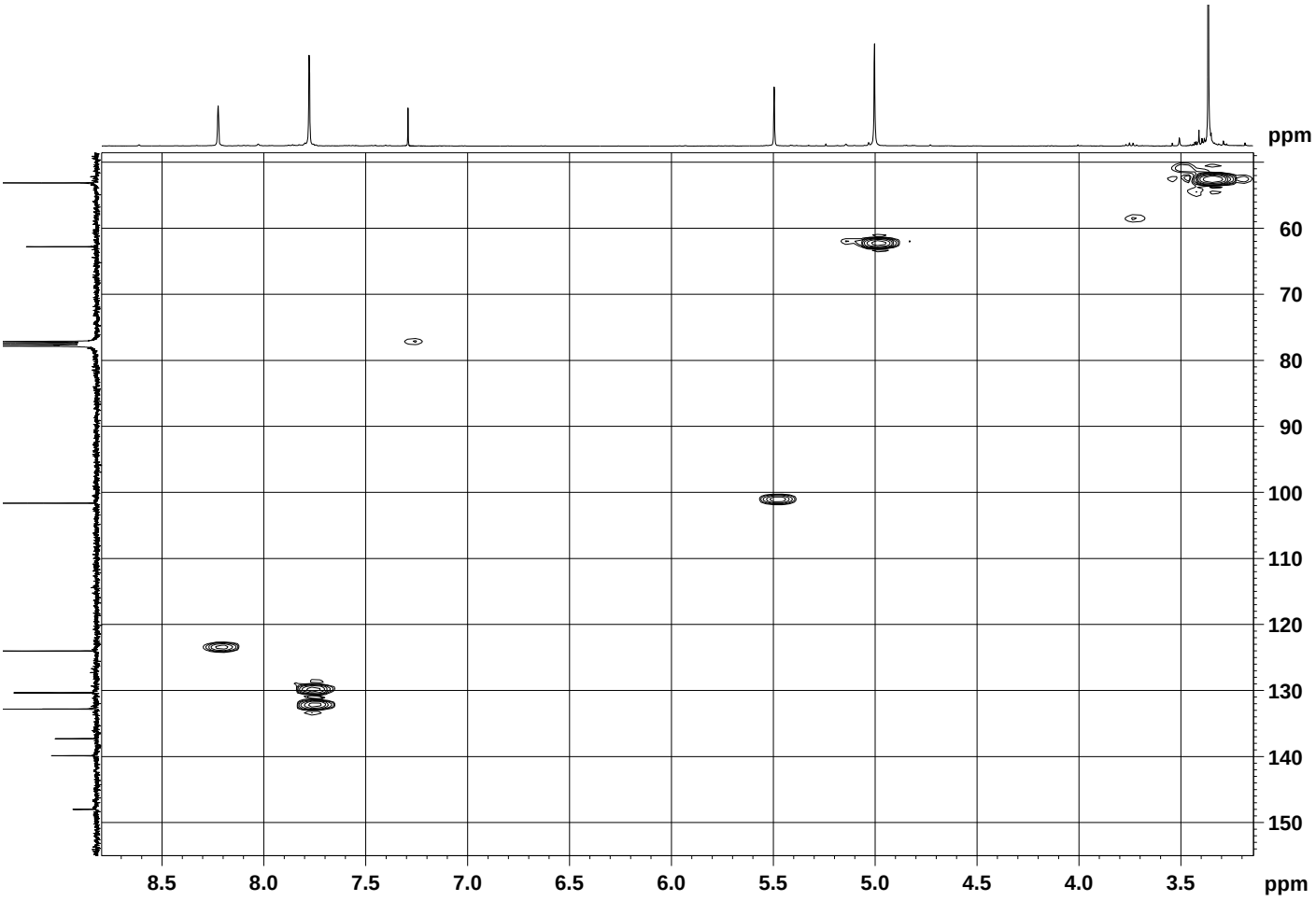


Figure S2. ^{1}H-^{13}C HSQC spectrum of the monomer.

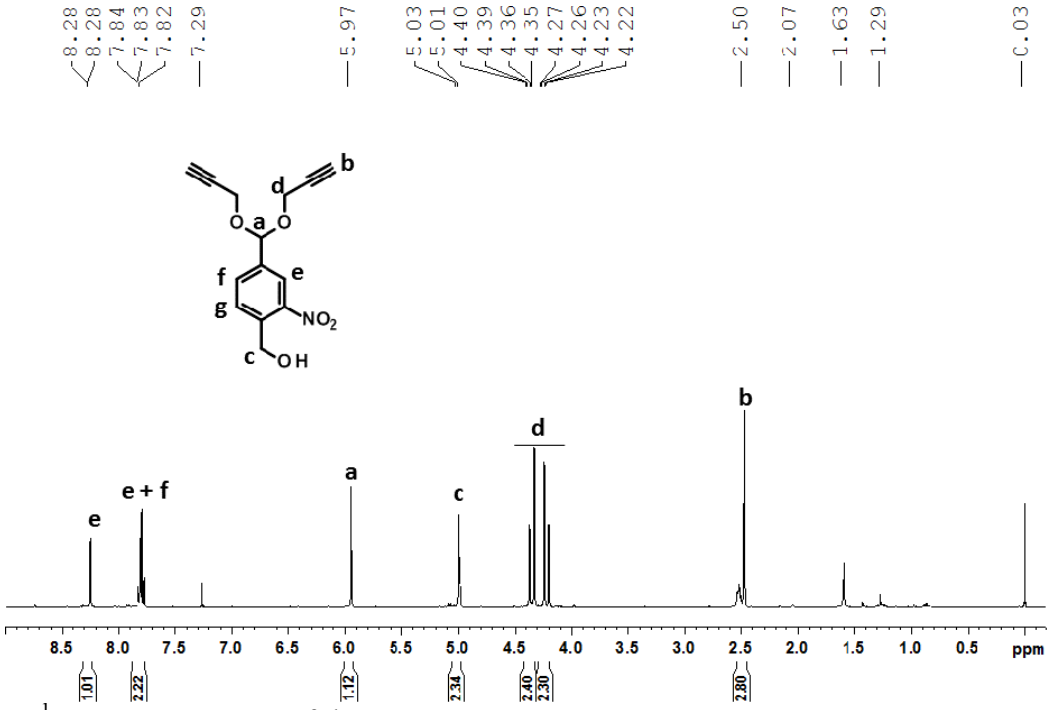


Figure S3a. ^{1}H NMR spectrum of the monomer.

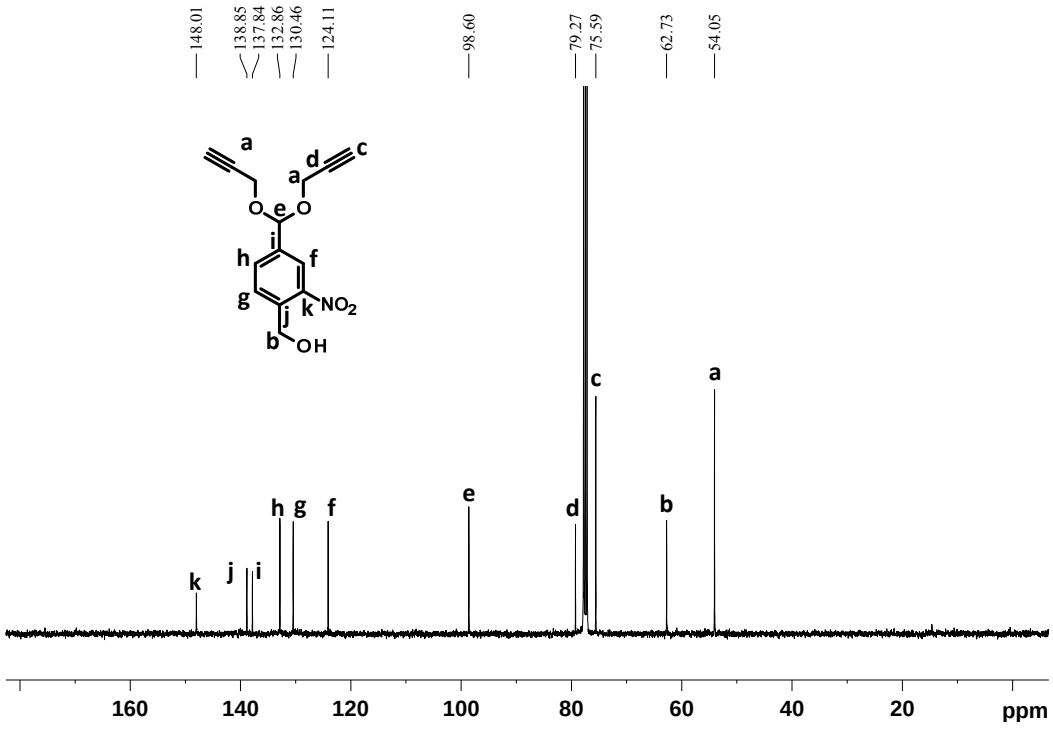


Figure S3b. ^{13}C NMR spectrum of the HBPA-nitro-P monomer.

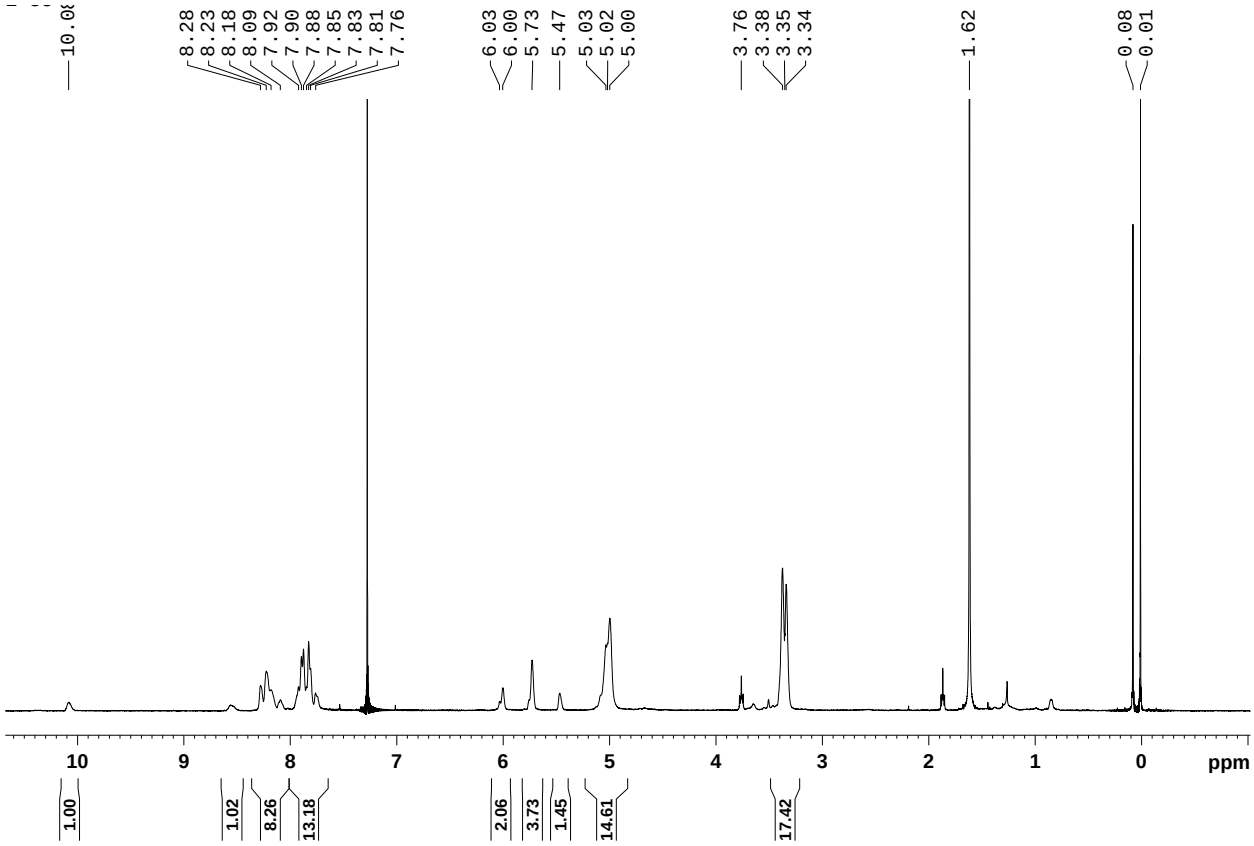
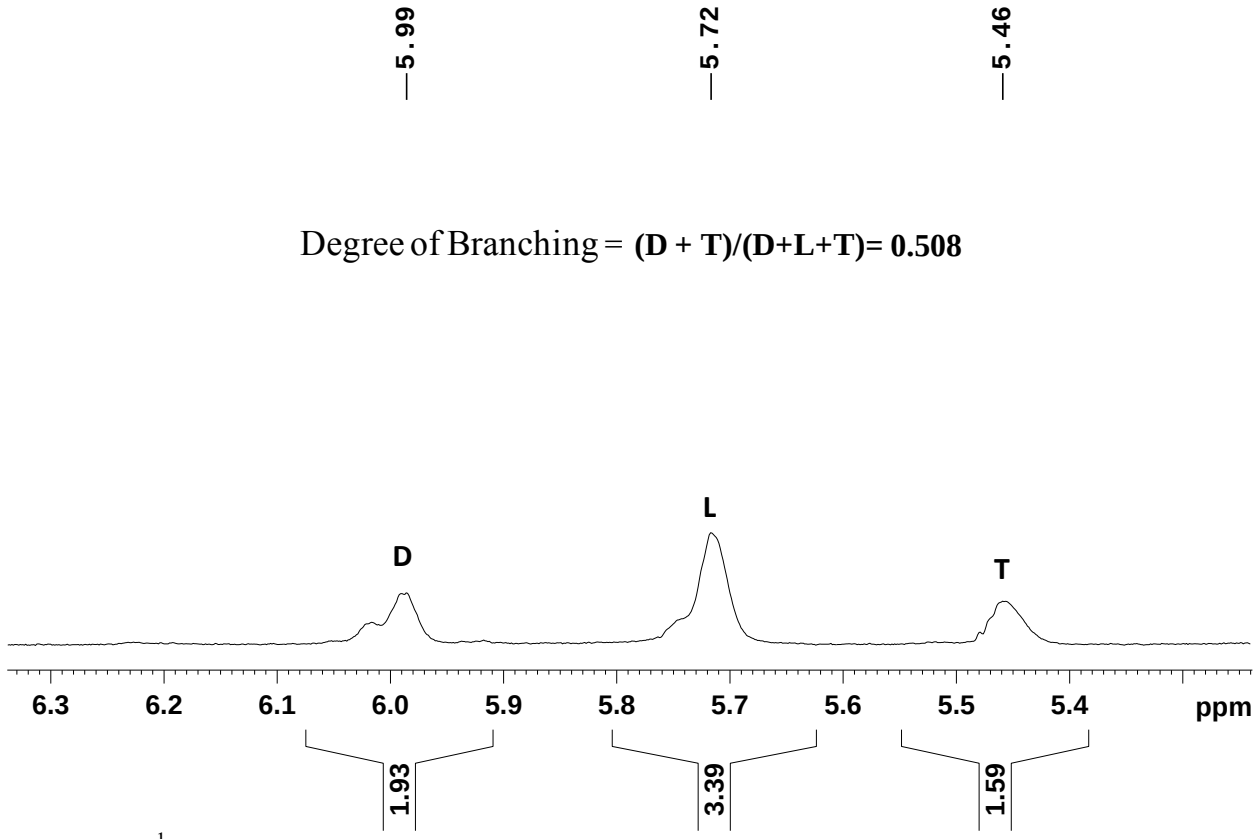


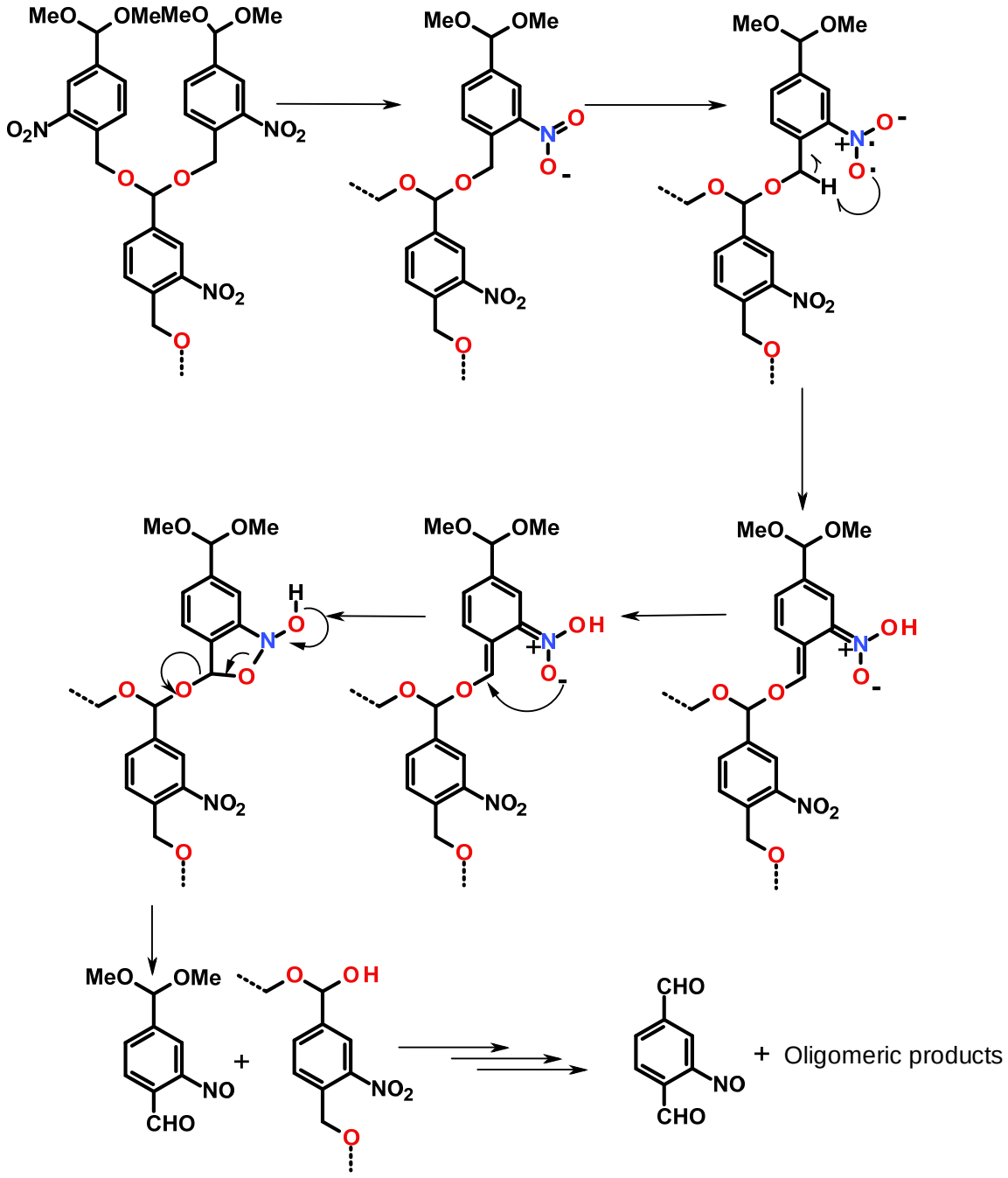
Figure S4. ^{1}H-NMR spectrum of the **Nitro-HBPA**. The extent of hydrolysis can be calculated by comparing the integral intensity of the peak at ~10.1 ppm with those of the three methine protons in the region 5.5 -6.1 ppm. Thus, Percentage hydrolysis = 1.00/(2.06 + 3.73 + 1.45 + 1) = 12.13 %.



Degree of Branching = **(D + T)/(D+L+T)= 0.508**

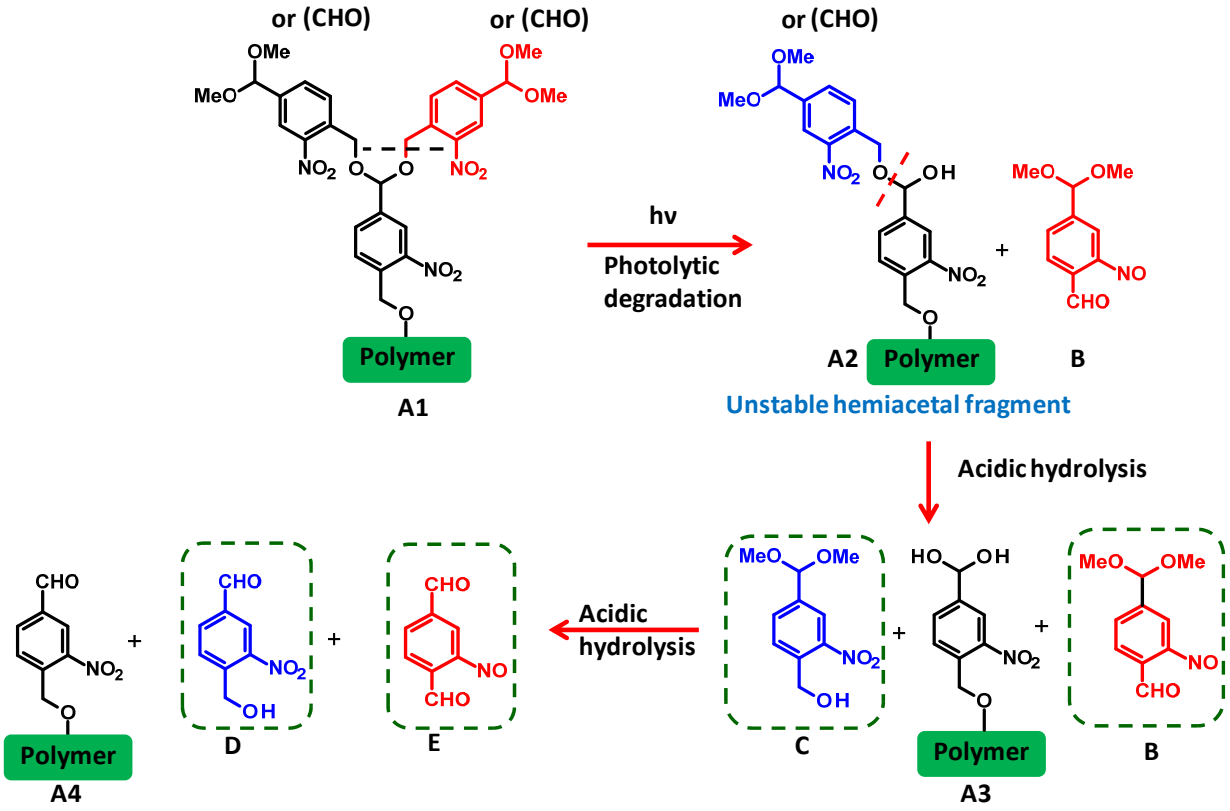
Figure S5. [1]H NMR spectra of the expanded methine region of Nitro-HBPA polymer showing Dendritic(**D**), Linear(**L**) and Terminal(**T**) unit protons. The DB of the HBP polymer was calculated using formula defined by Frechet et al.[5]

Postulated Mechanism for photodegradation



Scheme S4: Plausible mechanism for the formation of nitrosoterepthaladehyde as photodegradation product from **Nitro-HBPA** under UV irradiation. The above mechanism is based on earlier proposed mechanism[6-8] for the photodegradation of 2-nitrobenzyloxy units.

Possible degradation products



Scheme S5: Plausible degradation pathway of hyperbranched polymer (**Nitro-HBPA)** under UV irradiation resulting D and E as major degradation product along with several other products.

Variation of ^{1}H-NMR spectra as a function of irradiation time

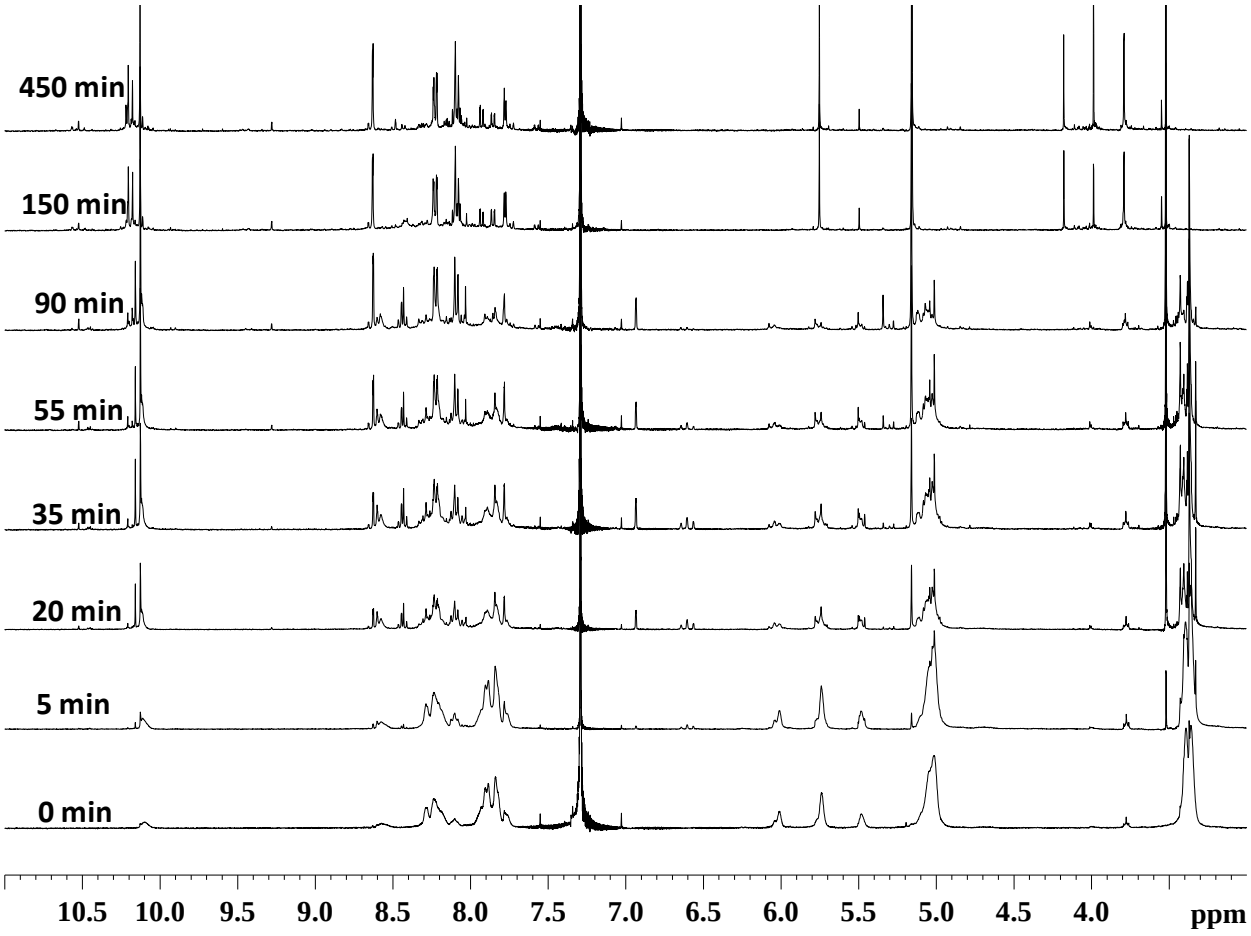


Figure S6: Stack plot of the proton NMR spectra of a solution of the polymer **Nitro-HBPA** in $CDCl_3$ as function of irradiation. The solution was taken in a quartz tube and irradiated with a 150 W Hg vapour lamp. Aliquots were taken out after various times and their spectrum was recorded. The solution was first degassed by bubbling dry N_2 gas at the beginning of the experiment to minimize oxidation. The times on the left indicate irradiation times. It is evident that the broad peaks typically associated with spectra of polymers transform into very sharp ones after prolonged irradiation indicative of the formation of low molecular weight compounds. Furthermore, all the three methine protons (D, T, & L) completely disappear leaving behind, primarily, a single peak in this region; on the other hand, the aldehyde region has three peaks suggesting the presence of several compounds. The final spectrum is compared with one possible product, namely 4-hydroxymethyl, 3-nitrobenzaldehyde, in the Figure S7.

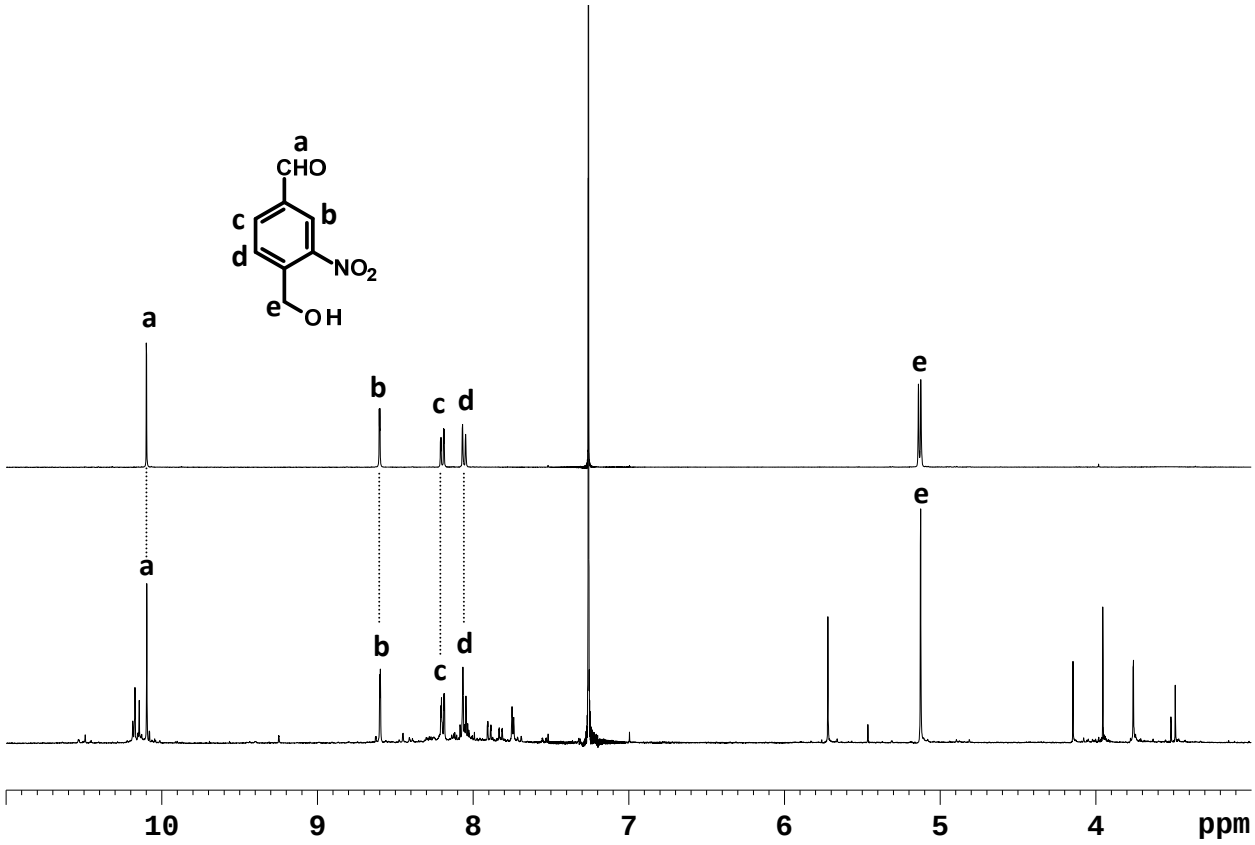


Figure S7: Stack plot of a selected region of the proton NMR spectra of **Nitro-HBPA** after prolonged irradiation, along with that of 4-hydroxymethyl, 3-nitrobenzaldehyde; the dotted lines clearly reveal that this is one of the major products, that is likely to be formed by the hydrolysis of an intermediate hemiacetal, as shown in Figure S6. This occurs due to the presence of water in $CDCl_3$ and the possible presence of some acid impurity, possibly generated by the irradiation of $CDCl_3$. Other products formed are not readily identifiable.

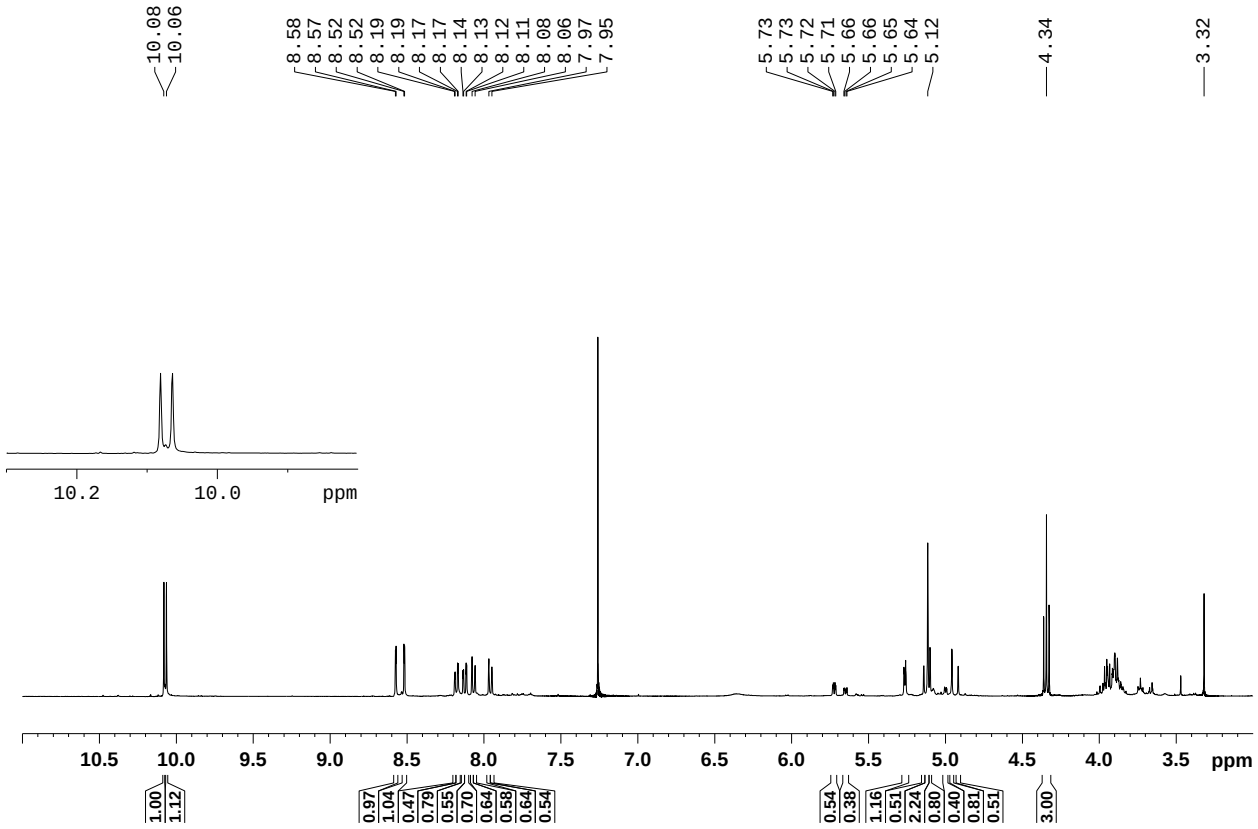


Figure S8. Proton NMR spectrum of the sample formed after irradiation of a thin film of the **Nitro-HBPA** after prolonged irradiation (3 h) using a 150W Hg vapour lamp. A solution of the polymer was taken in a quartz tube and evaporated using a rotary evaporator to generate a thin film on the inside wall of the quartz tube; the tube was flushed with dry N_2, sealed and irradiated; the products formed was dissolved in $CDCl_3$ and its spectrum recorded.

Summary of degradation studies

The photodegradation process is evidently far more complex than was initially presumed. The irradiation of chloroform solution of the polymer clearly reveals the formation of a product that arises presumably by the hydrolysis of an intermediate hemiacetal; while this is possibly one of the major products, several other products are also evidently formed as seen from the spectra. However, an alternate experiment done by prolonged irradiation (3 h) of thin films coated on the inner walls of a quartz tube, confirms that in the absence of hydrolysis alternate product(s) are formed, the exact nature of which is unclear, as of now. Further studies are required to establish the identity of the products, that is clearly beyond the scope of this preliminary communication.

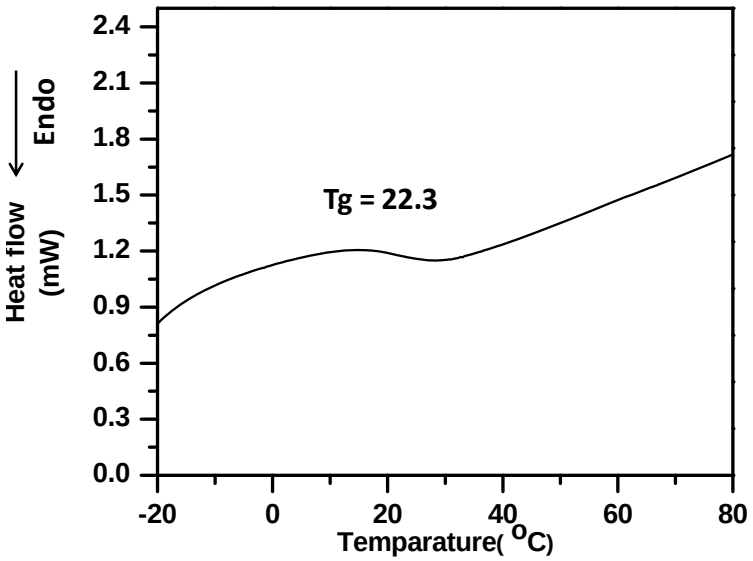


Figure S9. DSC thermogram of **Nitro-HPBA**.

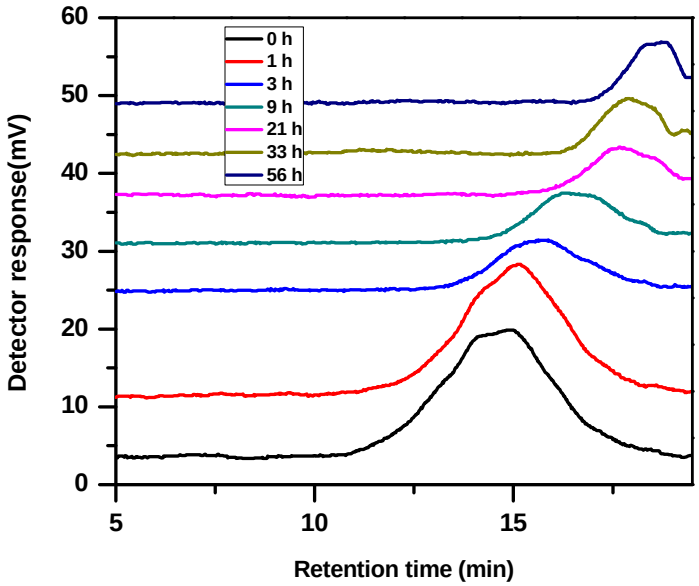


Figure S10. GPC chromatograms of aliquots of **Nitro-HPBA** solution (in chloroform) taken after different times of exposure (indicated in the legend) to Hg-vapor lamp.

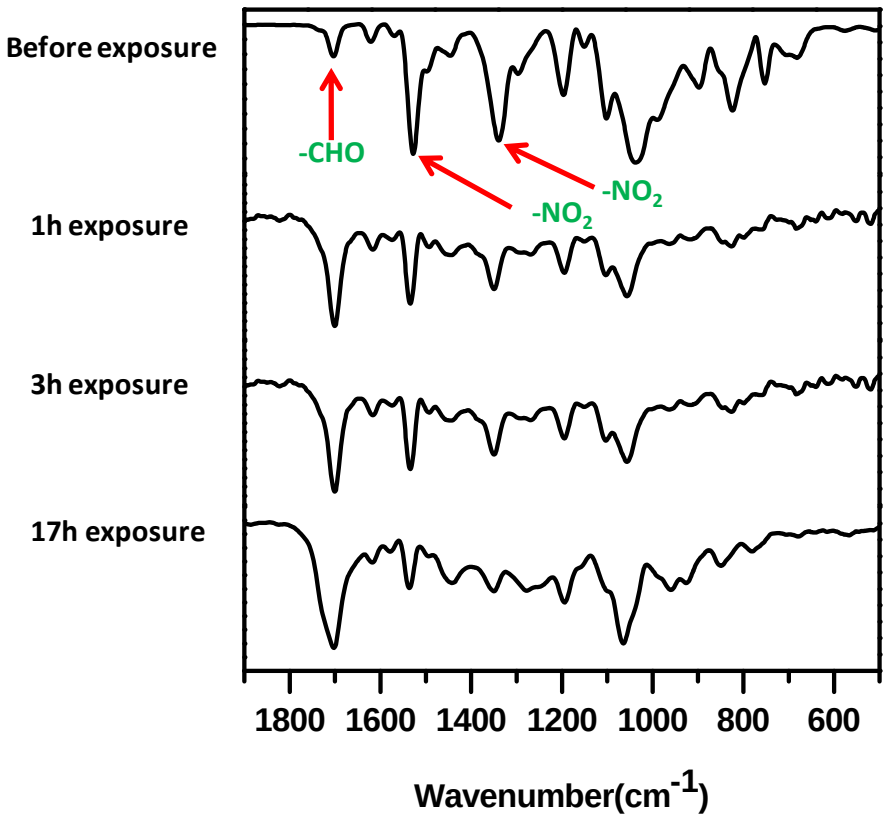


Figure S11. Stack plot of IR spectra of **Nitro-HBPA** as a function of irradiation time; a continuous decrease in the intensity of the bands due to the nitro-group with the concomitant increase in the peak due to aldehyde provides evidence for the postulated mechanism for photo-degradation.

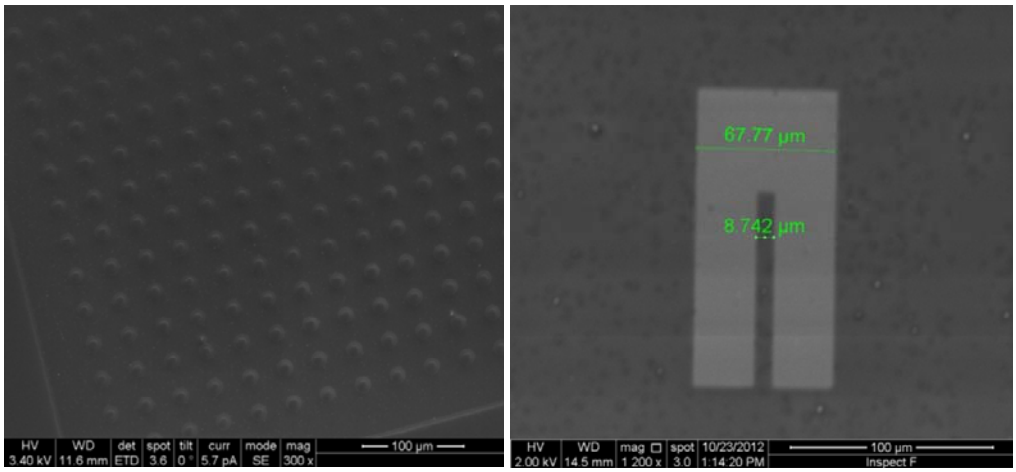


Figure S12. Scanning electron micrographs of the positive micro-pattern obtained using **Nitro-HBPA**. Left: microdot patterns and right: a higher magnification image of the cantilever showing the dimensions.

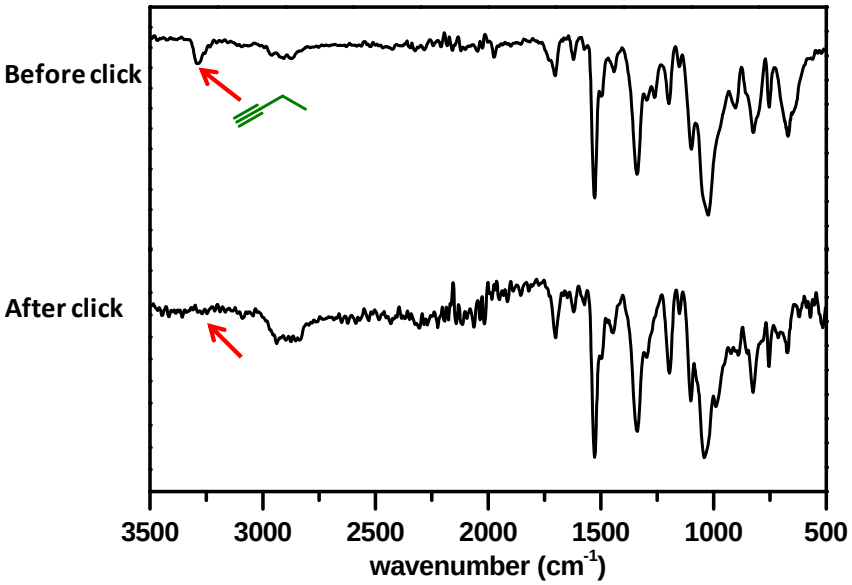


Figure S13. Stack plot of IR spectra of the parent **Nitro-HBPA-P** and that after heterogeneous clicking with the fluorescent dye. The patterned thin film was dissolved in a few drops of THF and directly cast onto the ATR window of a Bruker Alpha spectrometer for recording its IR spectrum.

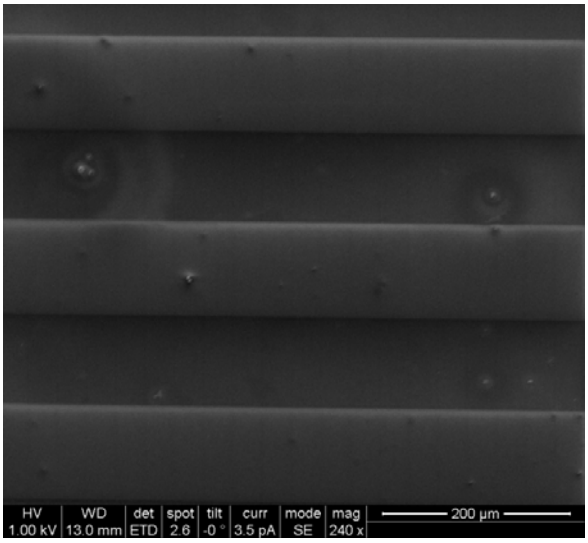


Figure S14. Scanning electron micrograph of the positive micropattern obtained using **Nitro-HBPA-P**, which carries the clickable terminal groups. Fluorescence microscope image of the film heterogeneously clicked with a fluorescent dye is shown in the figure 3 of the main text.

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