Supporting Information

Revisiting AB_2 + A-R copolymerization: Direct access to *Janus* and peripherally *clickable* hyperbranched polymers

Runa Singla,[1] E. Bhoje Gowd[2] and S. Ramakrishnan[1]*
[1]Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore 560012 INDIA
[2]Materials Science and Technology Division
CSIR-National Institute for Interdisciplinary Science and Technology (CSIR-NIIST)
Trivandrum 695019 INDIA

*Email: raman@iisc.ac.in

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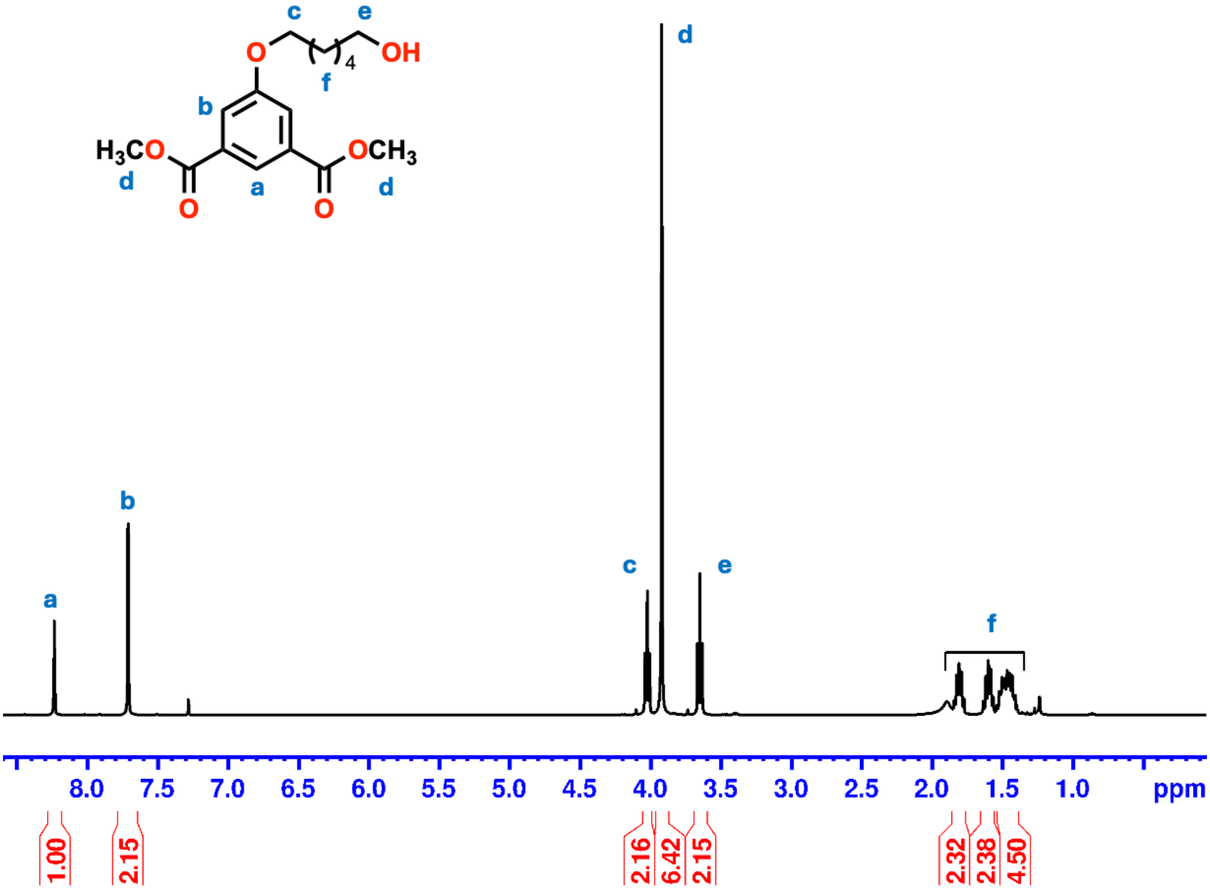

Figure S1 : ^{1}H-NMR(CDCl$_3$) spectrum of DMHHI monomer

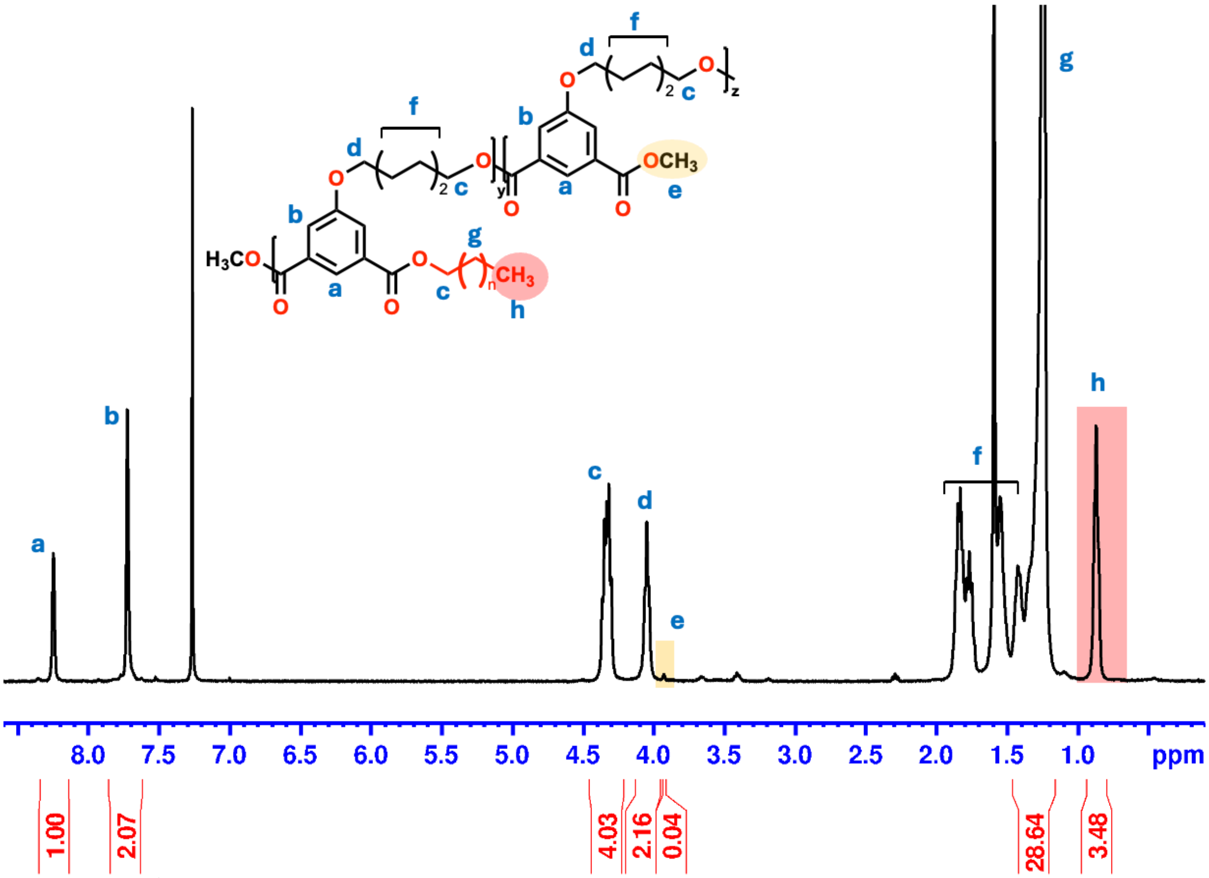

Figure S2: ^{1}H-NMR($CDCl_3$) spectrum of HBP C16 homopolymer

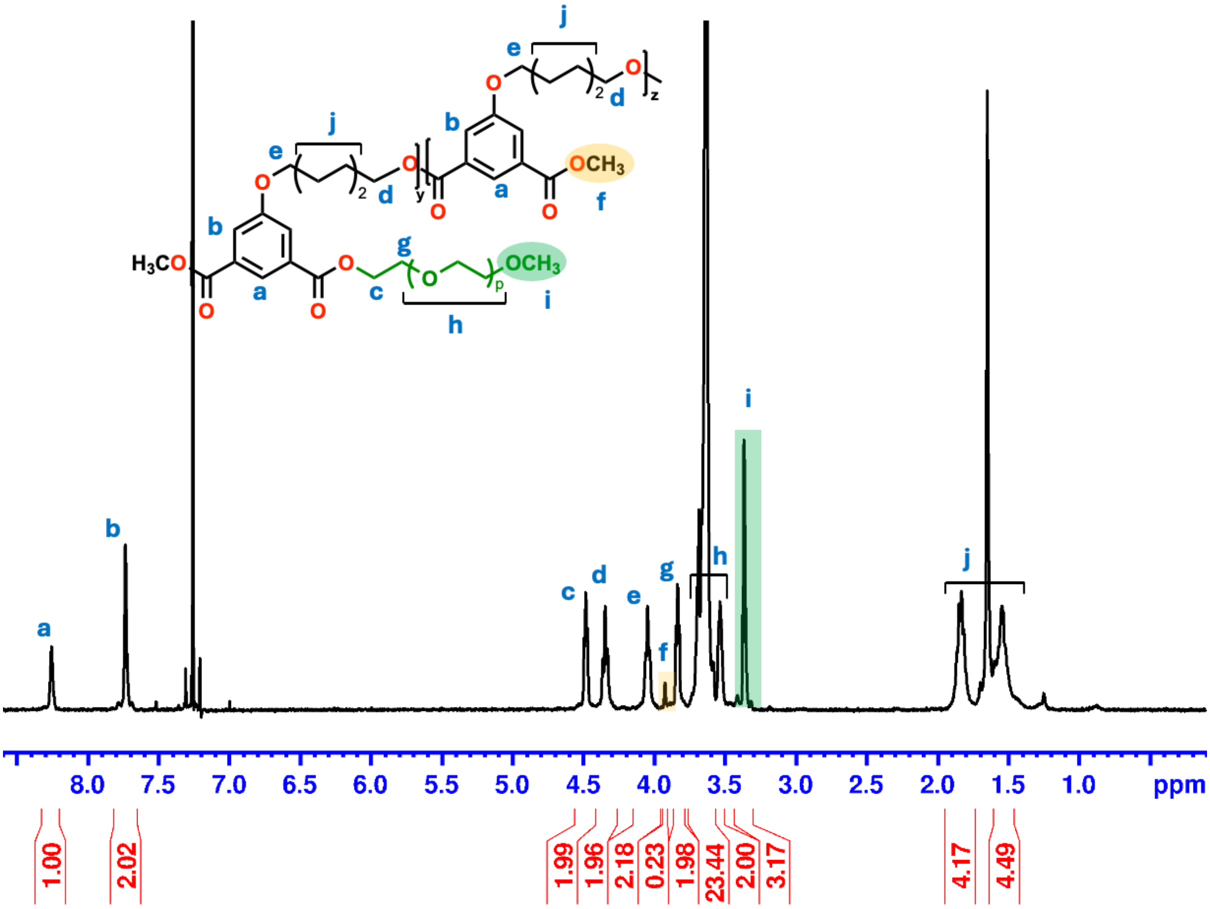

Figure S3 : ^{1}H-NMR($CDCl_3$) spectrum of HBP MPEG350 homopolymer

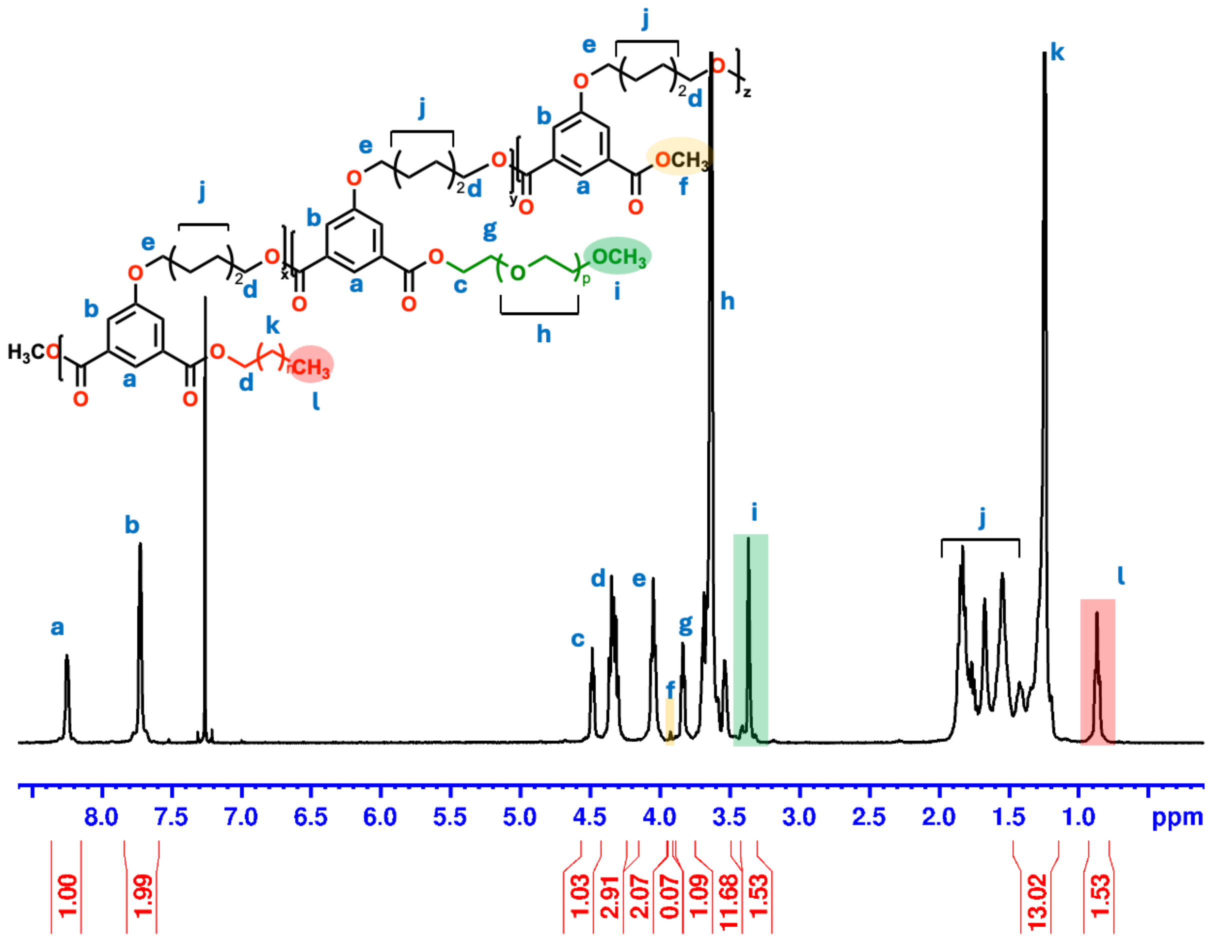

Figure S4 : ^{1}H-NMR($CDCl_3$) spectrum of HBP C16: MPEG350

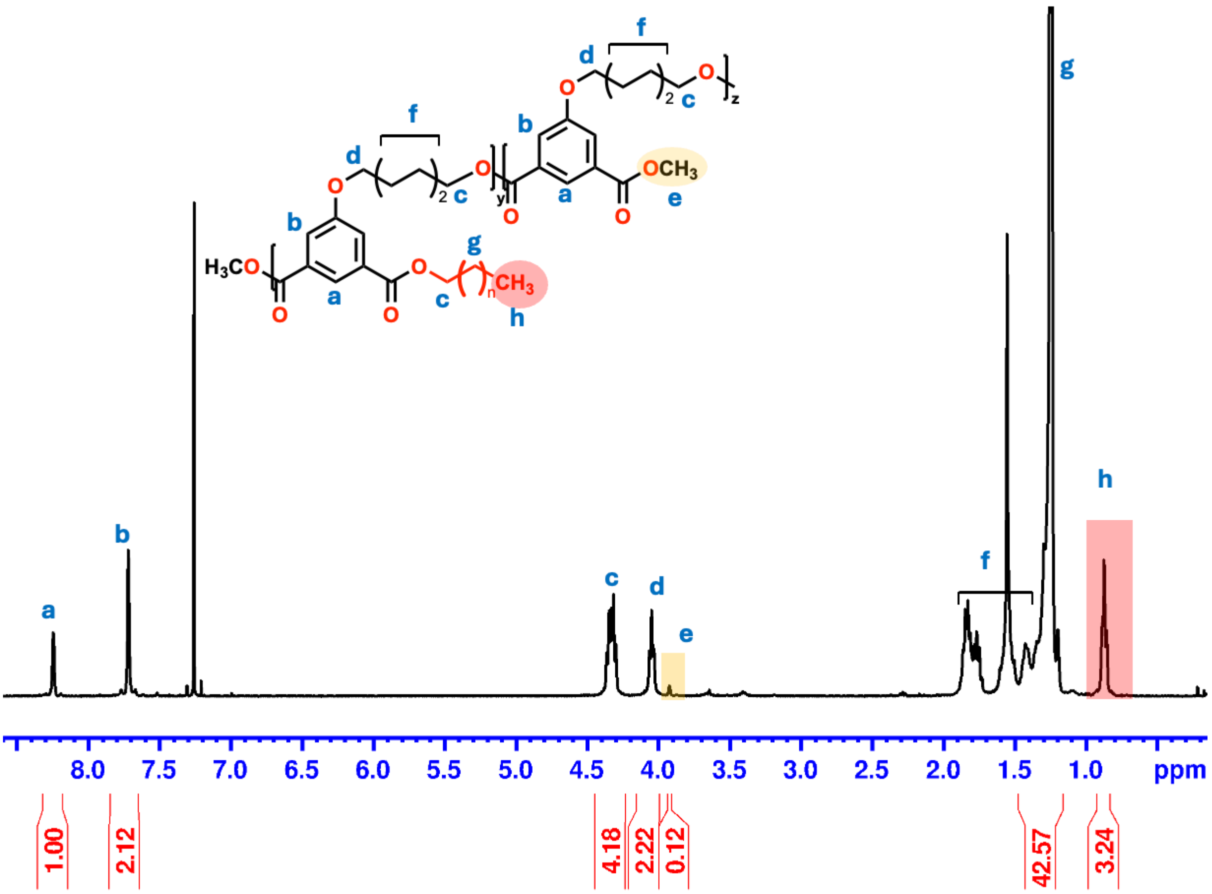

Figure S5: ^{1}H-NMR($CDCl_3$) spectrum of HBP C22 homopolymer

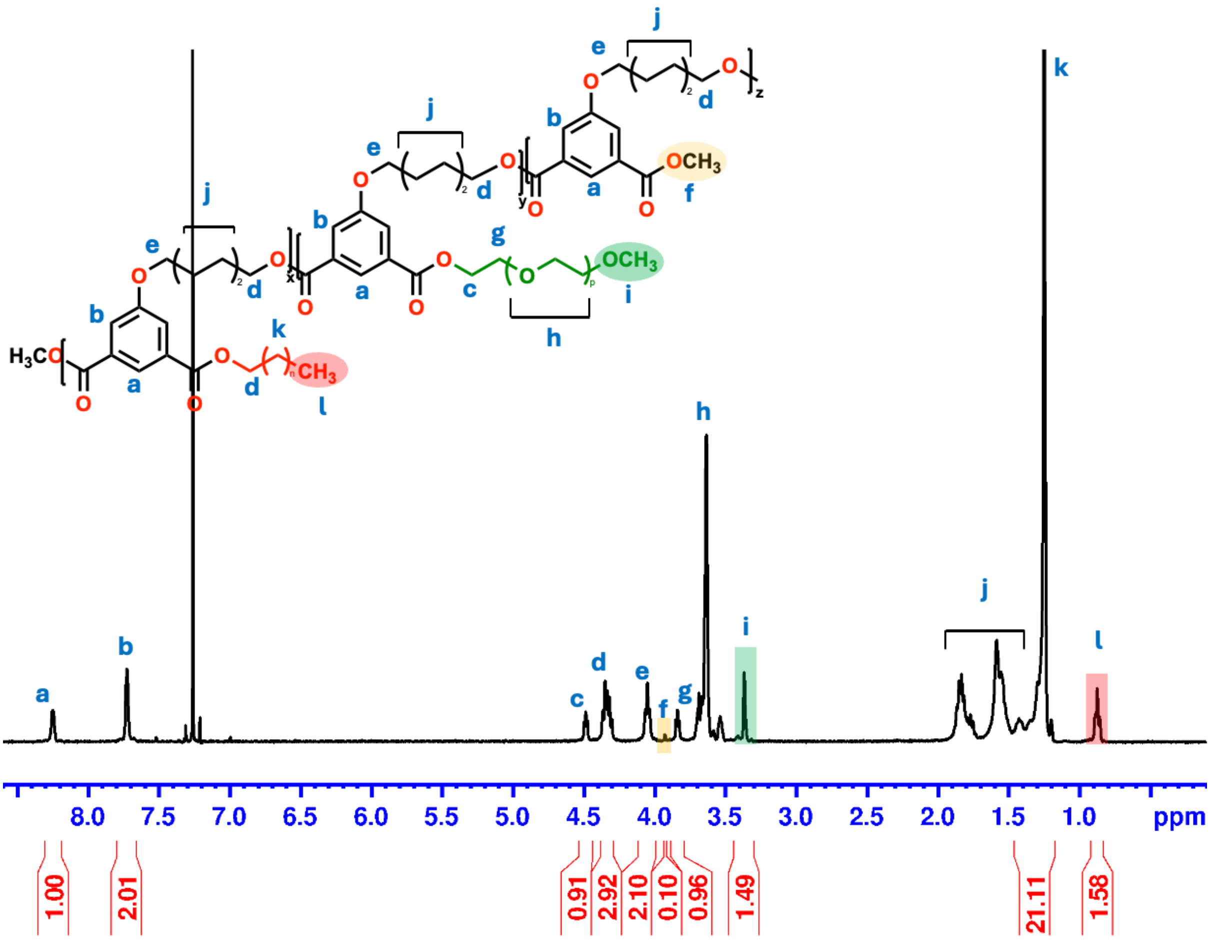

Figure S6 : ^{1}H-NMR($CDCl_3$) spectrum of HBP C22: MPEG350

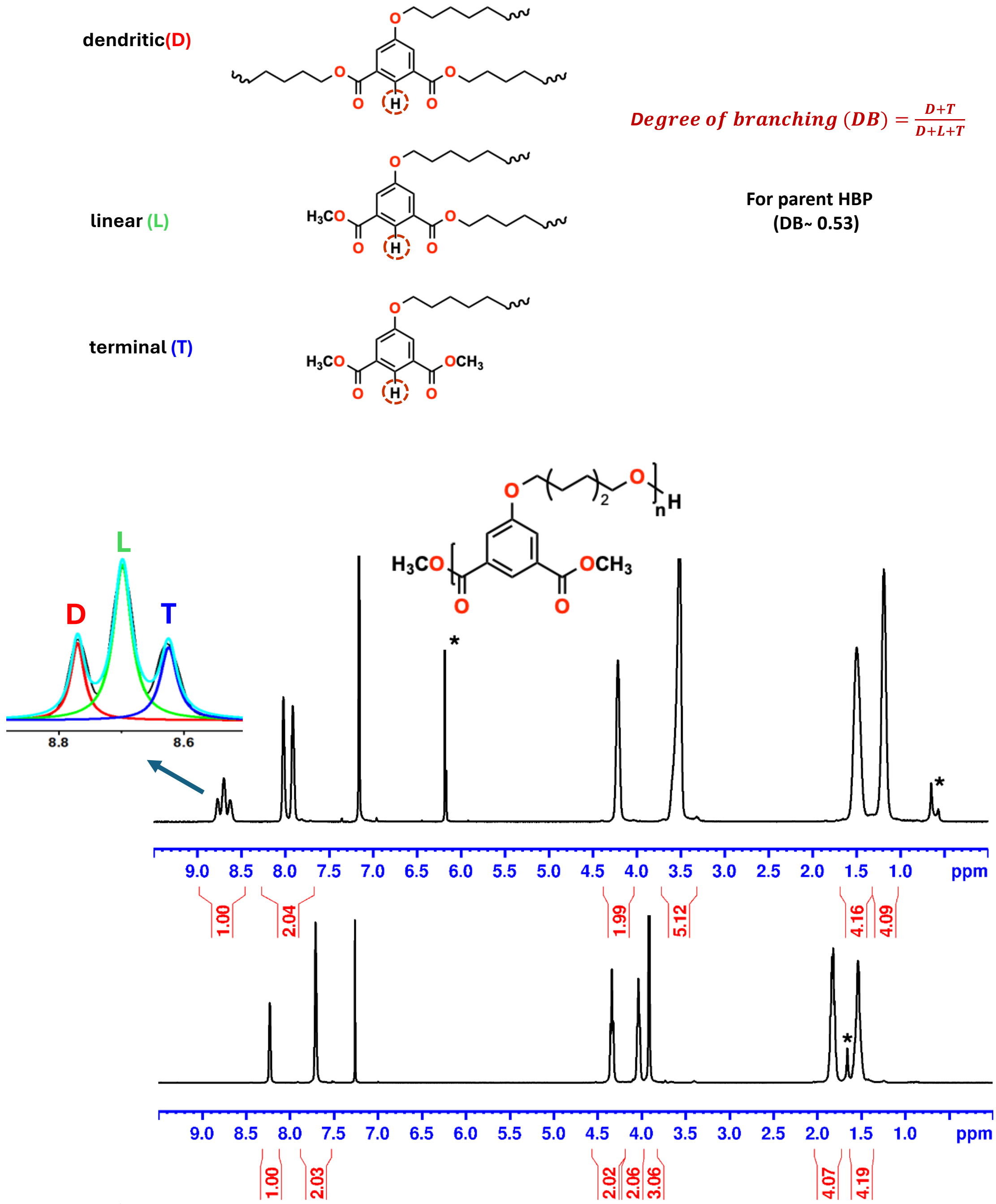

Figure S7: ^{1}H-NMR bottom ($CDCl_3$) and top (C_6D_6) spectrum of parent HBP carrying terminal methyl ester groups (peaks marked by * are due to solvent/water); as evident the peak due to the most downfield aromatic proton resolves into three in C_6D_6 due to Aromatic Solvent Induced Shift (ASIS). The peaks corresponding to the D, T and L were assigned by comparison of this spectra with that of the monomer, where this aromatic proton will appear at chemical shift close to the terminal (T) unit peak; the other two we assigned based on the expectation that the peak will sequentially shift down-field as the methyl ester is displaced with an alkyl/PEG ester. Furthermore, it is known that for high molecular weight HBPs, the D and T units will be present in equal amounts; thus, the peak intensities corresponding to the D and T units is expected to be equal, as seen in this case; this further helps reconfirm the peak assignment. The peak was deconvoluted employing 3 Lorentzian peaks, using Origin software, and their relative areas were estimated and used to calculate the DB.

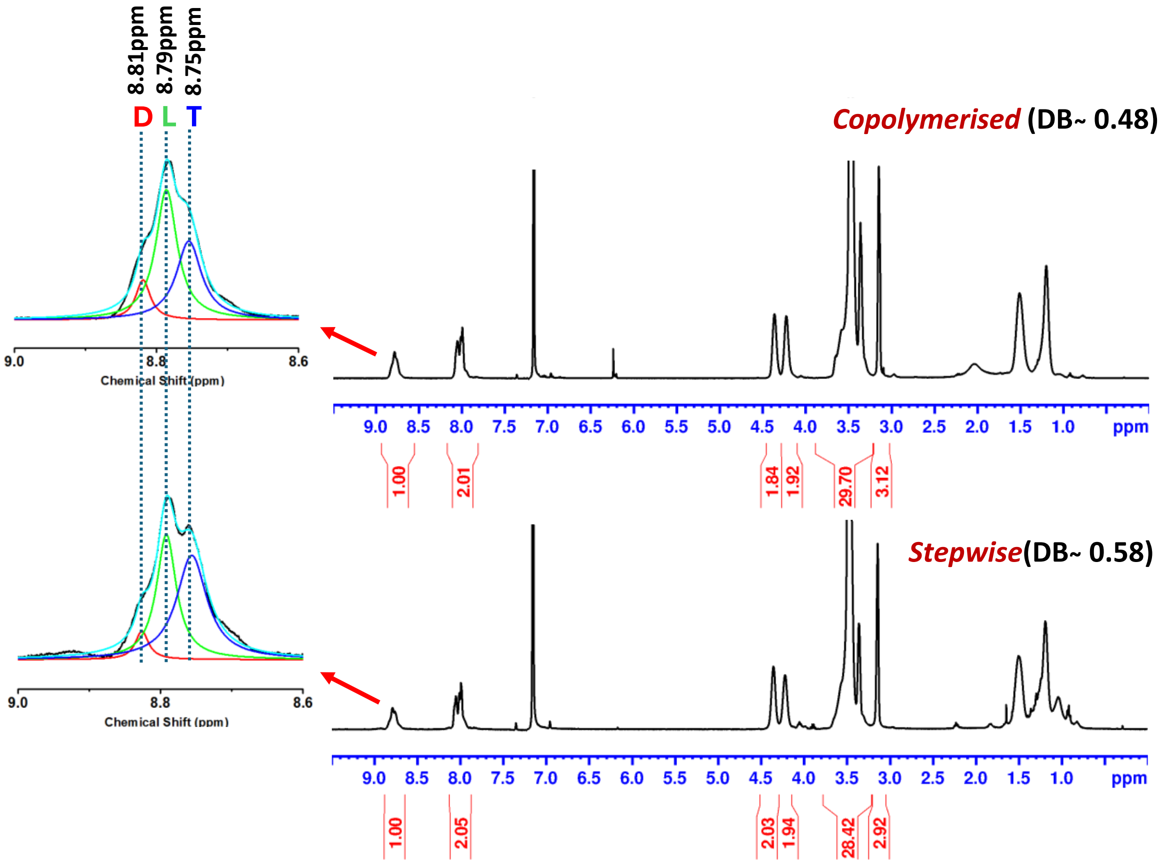

Figure S8: ^{1}H-NMR (in C_6D_6) spectrum of HBP-MPEG350, prepared directly using AB_2 + A-R copolymerization (top) and using a two-step process by reacting the parent HB polyester with MPEG350-OH (bottom), under melt transesterification conditions, using DBTDL catalyst 150°C. Unlike in the parent HB polyester, here the aromatic peak was not well resolved. The reason evidently is that change from methyl ester to any other longer chain ester brought about a significant change in the chemical shift of the aromatic proton; however, the difference between having two different long-chain alkyl esters, like between the D unit and the PEG/alkyl ester or two PEGs, as in the L and T units, respectively, is not very significant. Furthermore, the peak assignment here was based on the assignment in the parent HB polyester and not by direct comparison with a model. Hence, the estimation of DB from these spectra are not very robust; this is also evident from the fact that the peaks assigned to D and T were not of equal intensity, clearly revealing a deficiency in this approach. Hence, the values of DB obtained using this deconvolution may only provide a very rough estimate and not an accurate one.

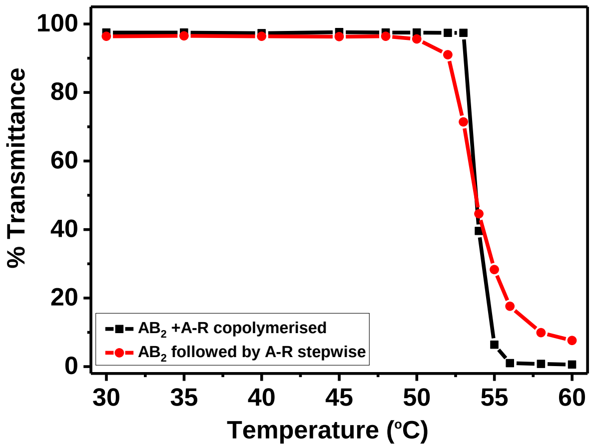

Figure S9: LCST plots (λ=600nm) of HBP MPEG350 copolymerised in one pot (black) and stepwise(red) wherein AB2 monomer was polymerised first, followed by addition of MPEG-OH (350)

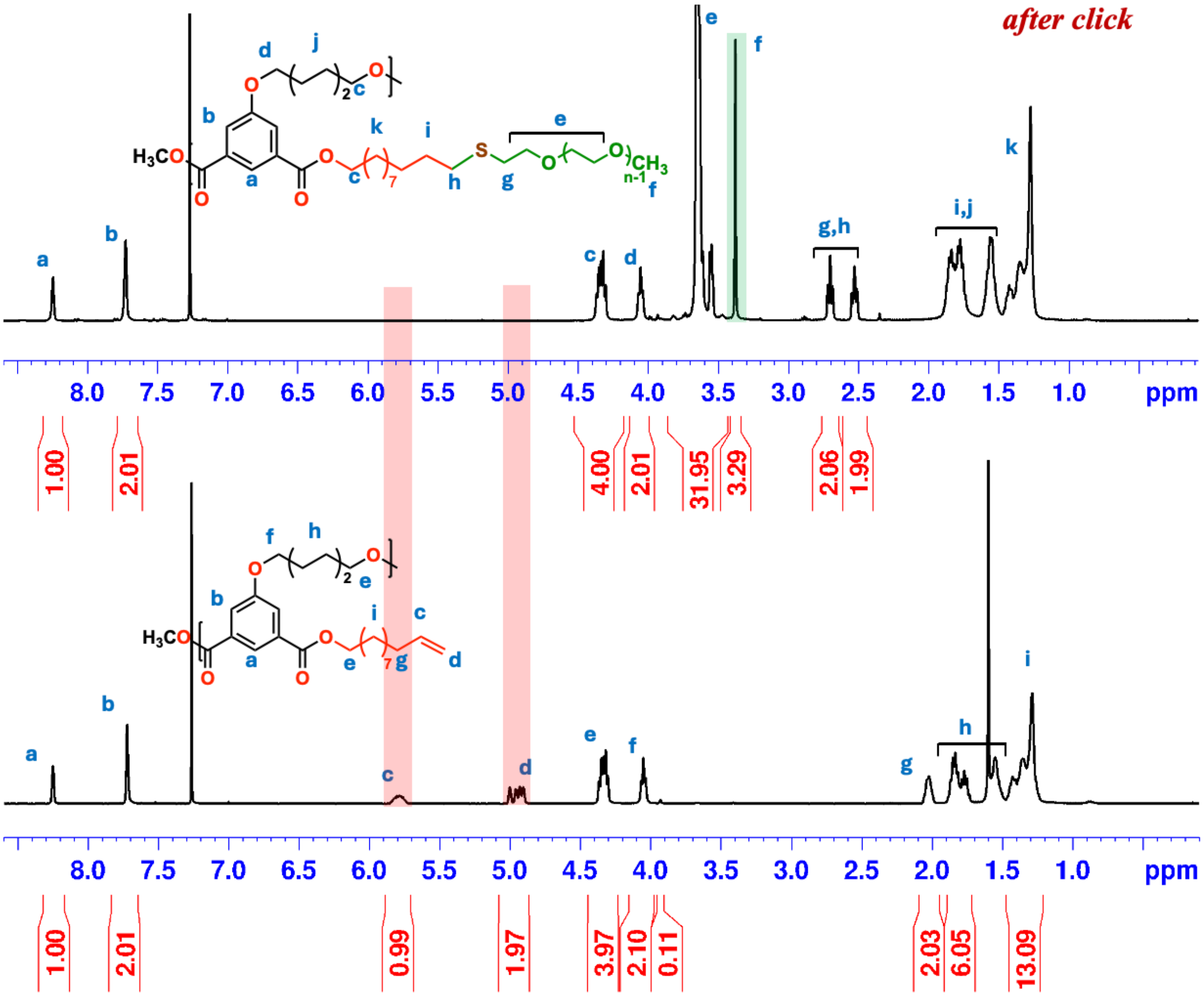

Figure S10: ^{1}H-NMR($CDCl_3$) spectrum of HBP C11 (undecene) and after click HBP C11 (MPEG 350)

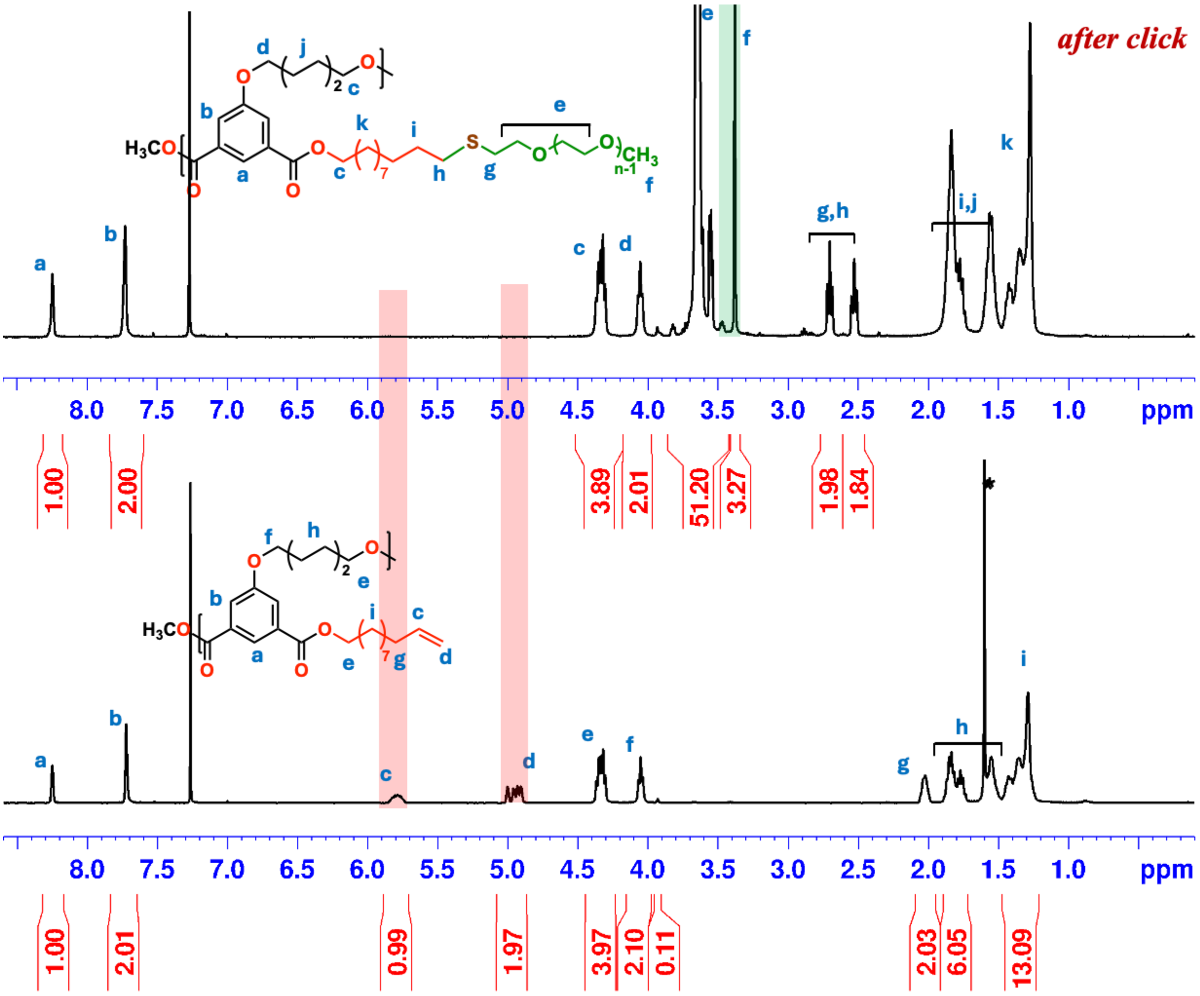

Figure S11: ^{1}H-NMR($CDCl_3$) spectrum of HBP C11 (undecene) and after click HBP C11 (MPEG 550)

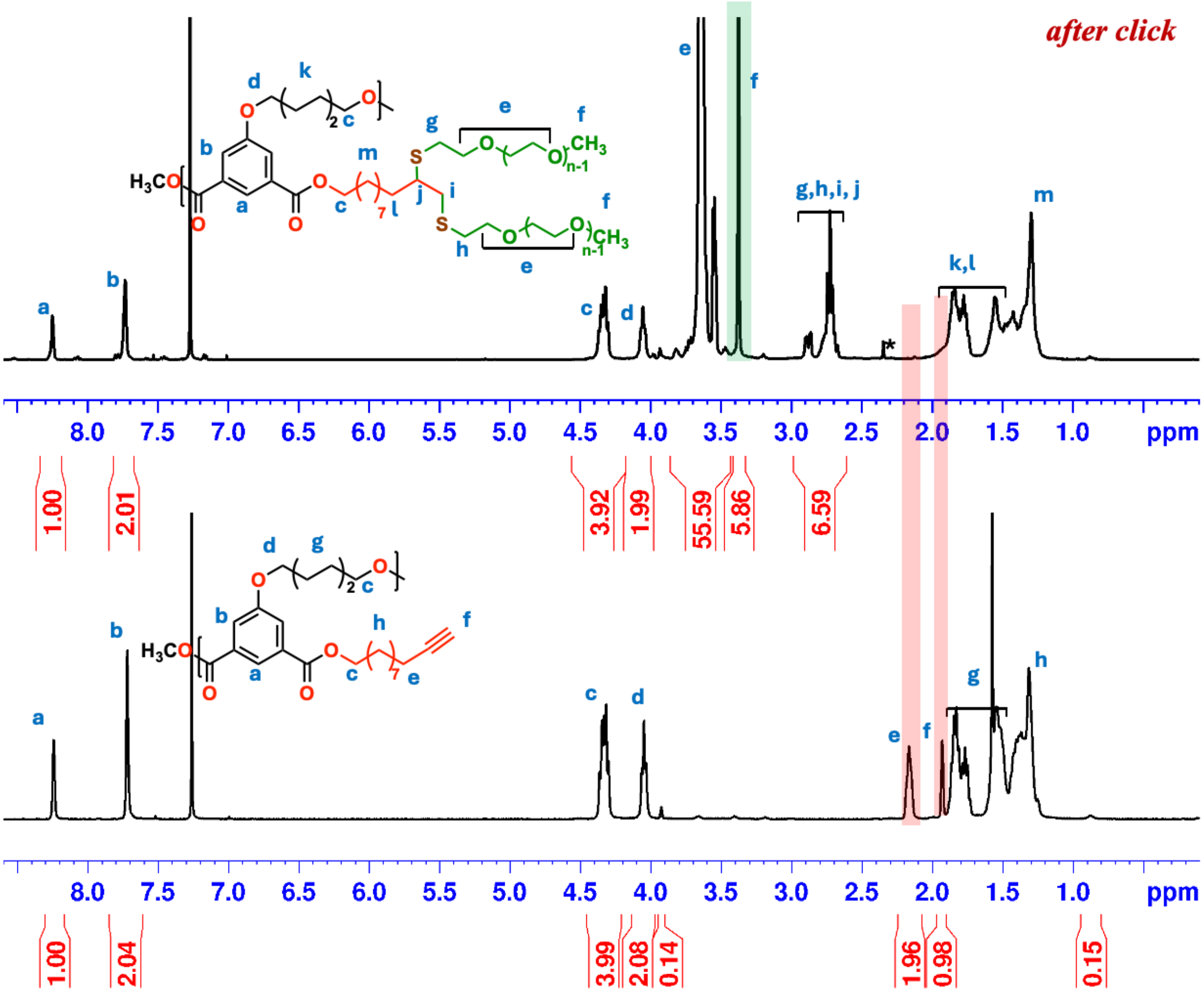

Figure S12: ^{1}H-NMR(CDCl$_3$) spectrum of HBP C11 (undecyne) and after click HBP C11 (MPEG 350)$_2$

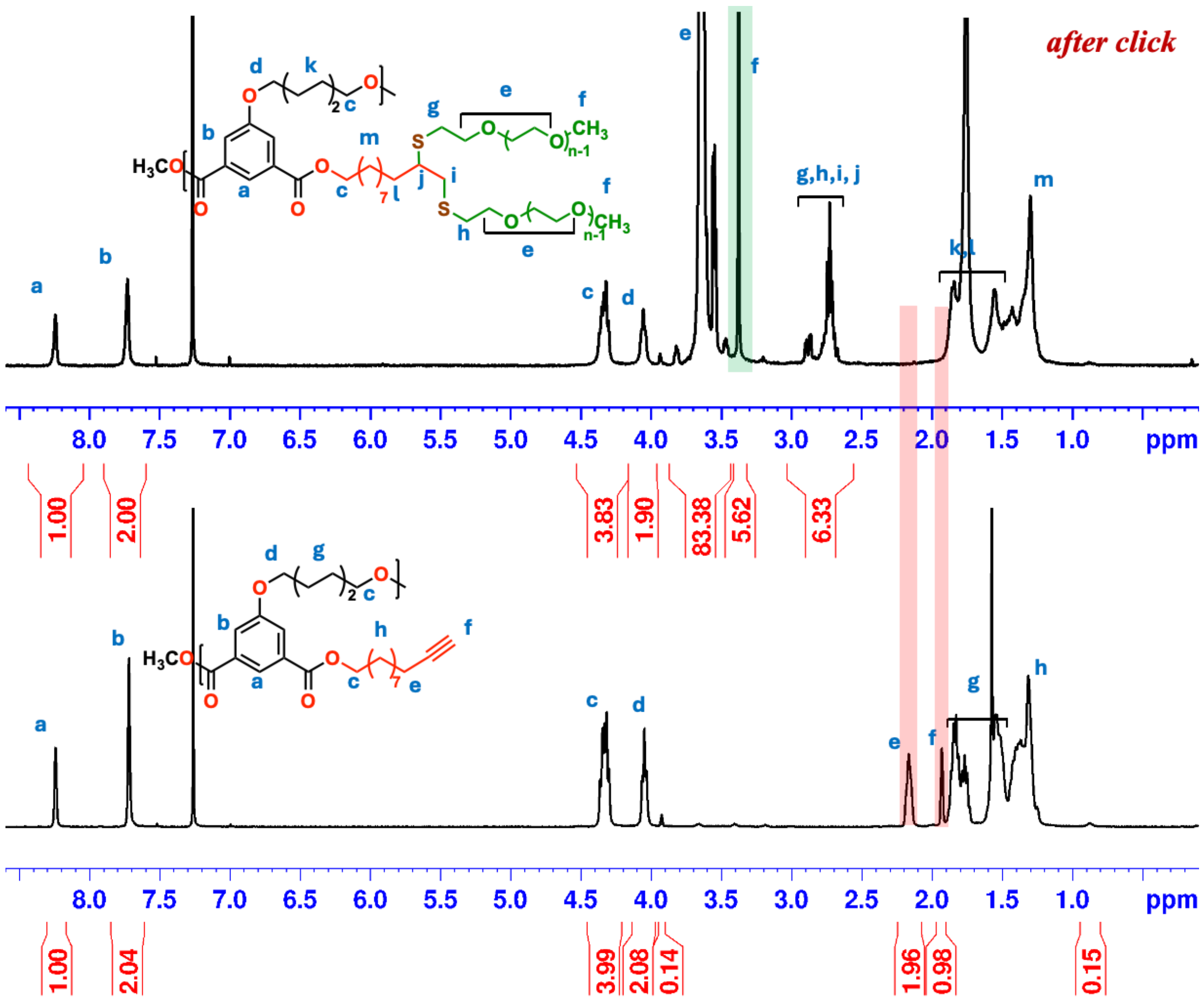

Figure S13: ^{1}H-NMR($CDCl_3$) spectrum of HBP C11 (undecyne) and after click HBP C11 (MPEG 550)$_2$

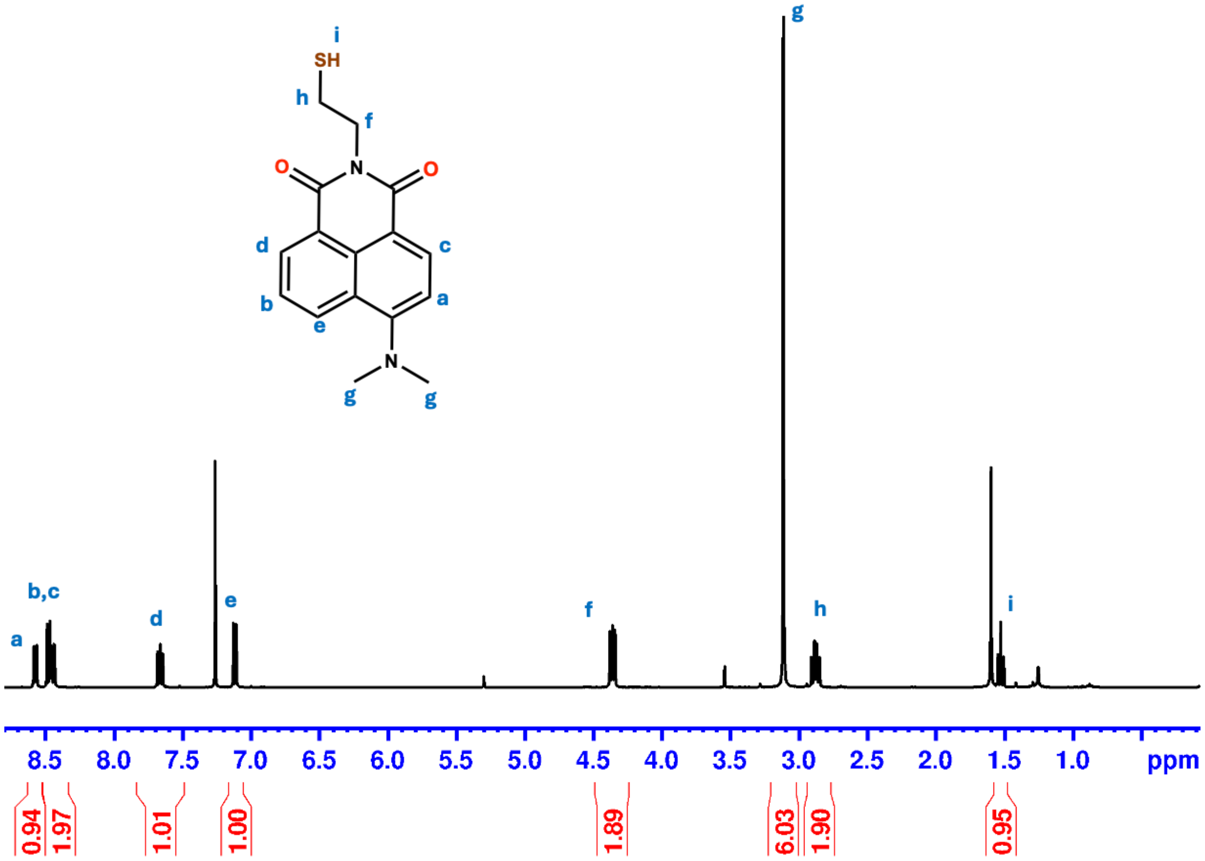

Figure S14: ^{1}H-NMR(CDCl$_3$) spectrum of NADSH fluorophore

Synthesis of HBP C11-yne clicked with MPEG 350 (~95%) and NADSH fluorophore (~5%):

In step1, HBP C11-yne polymer is taken with 0.1eq. NADSH and 0.1 eq. MPEG350 thiol in presence of 0.05 eq. of DMPA. After 8 hours of irradiation at 365nm, added another 5 eq. of MPEG 350 thiol and 0.18 eq. of DMPA to same solution which was degassed again and carried out click reaction for another 8 hours. After 8 hours, added BHT (a radical scavenger) to quench the radical reaction and clicked polymer was purified by repeated cycles of dissolution and precipitation in CHCl$_3$ and Pet Ether to get rid of unreacted thiols/ catalyst and BHT. The polymer was dried under reduced pressure and characterised by ^{1}H-NMR as shown below

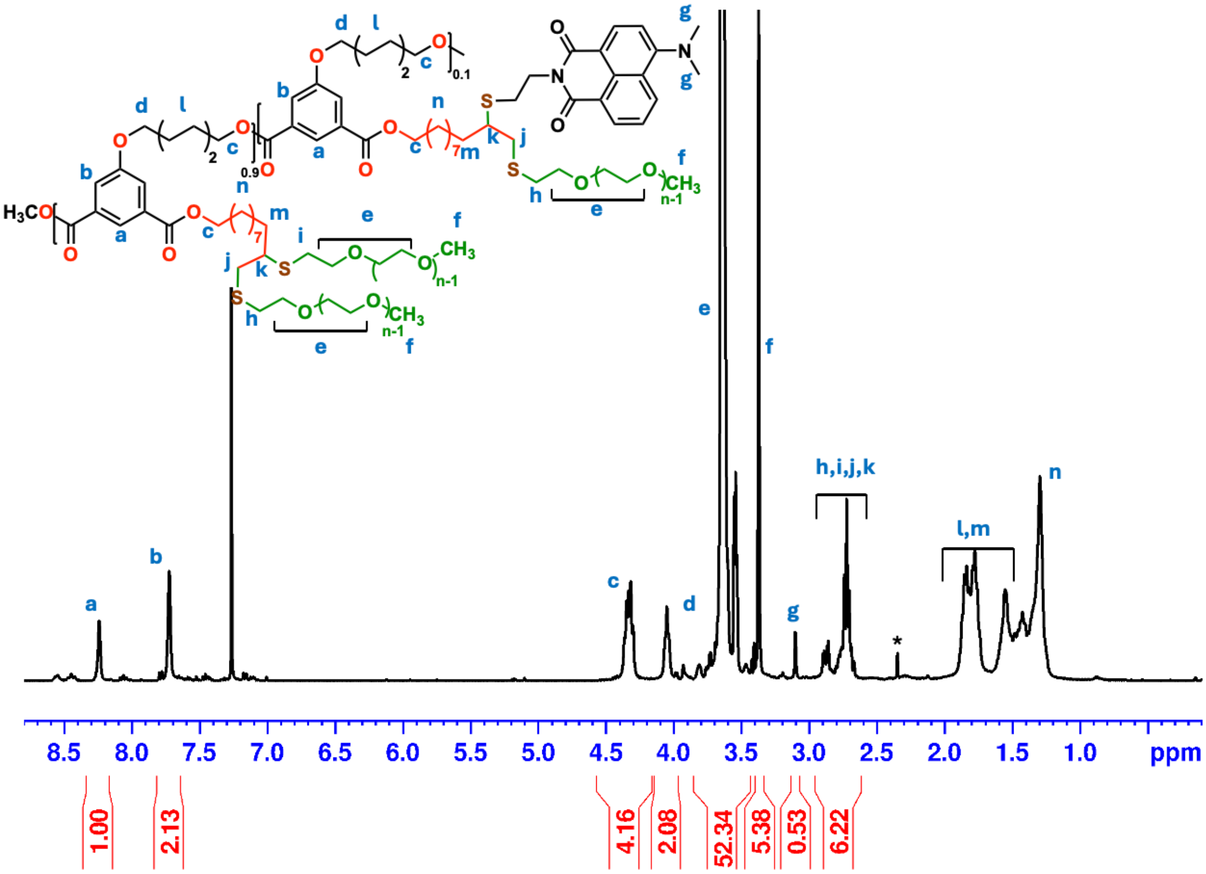

Figure S15: ^{1}H-NMR($CDCl_3$) spectrum of HBP C11-yne clicked with MPEG 350 (~95%) and NADSH fluorophore (~5%)

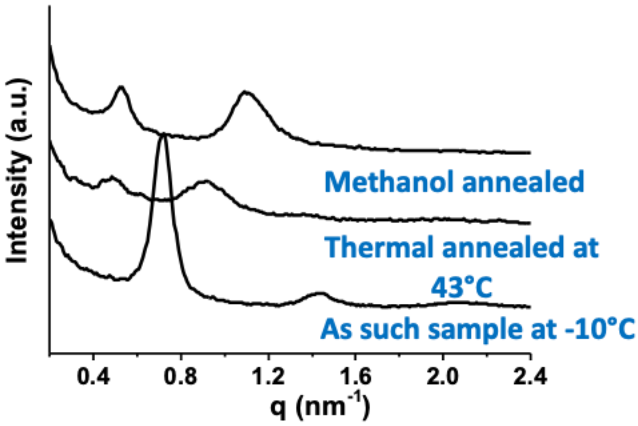

Figure S16: SAXS profile for HBP C22:MPEG350 after thermal annealing and MeOH vapour annealing.

Table S1: GPC table of HBPs systems

HBP system	**M_n**	**M_w**	**M-H constant log K (dL/g)**	**M-H exponent *a***
HBP C16 homopolymer	12800	47300	-2.5	0.351
HBP C22 homopolymer	12900	61500	-2.3	0.307
HBP MPEG 350 homopolymer	76900	89500	-4.5	0.719
C16:MPEG 350 (1:1)	27500	276000	-3.6	0.540
C22:MPEG 350 (1:1)	32200	115600	-3.0	0.441
HBP C11 (Undecene) homopolymer	12800	51600	-2.5	0.384
HBP C11 (MPEG 350)	69900	101200	-3.1	0.476
HBP C11 (MPEG 550)	83200	93700	-2.9	0.402
HBP C11 (Undecyne) homopolymer	36500	80600	-3.4	0.525
HBP C11 $(\text{MPEG 350})_2$	99400	110000	-4.9	0.770
HBP C11 $(\text{MPEG 550})_2$	125000	151400	-5.6	0.830
HBP C11 $(\text{0.95 MPEG 350+ 0.05 NADSH})_2$	88300	92500	-5.3	0.839

The GPC data reveal that the HBPs are of moderate molecular weights; the homo-terminated HBPs carrying long chain alkyl segments (C16 an C22) on their periphery exhibit very compact conformation, as revealed by the low M-H exponent, *a* (entries 1 and 2), whereas those carrying MPEG segments exhibit higher values. Likewise, the core-shell amphiphilic HBPs with MPEG segments on their periphery (last three entries) also exhibit high *a* value, whereas the Janus-type amphiphilic HBPs exhibit that lie in between, in the range 0.4-0.6.