HYPERBRANCHED BASED POLYMER AMPHIPHILIC CROSSLINKED NETWORKS

Sunita Kumari Malla[1], Santosh Kumar Raut[2], Namrata Gundiah[2] and S. Ramakrishnan[1]*

[1]Department of Inorganic and Physical Chemistry, [2] Mechanical Engineering
Indian Institute of Science, Bangalore-560012, INDIA
E-mail: sunitamalla@iisc.ac.in

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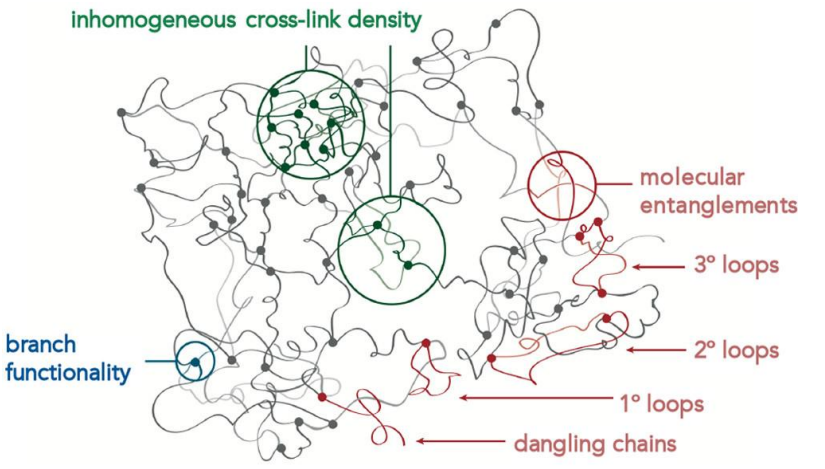
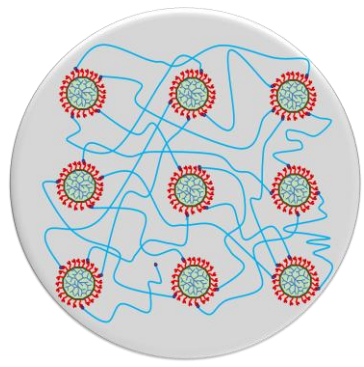
BACKGROUND

Polymer networks are an interesting class of materials, whose properties can be tailored by varying a wide range structural features at the molecular level, some of which are shown below.



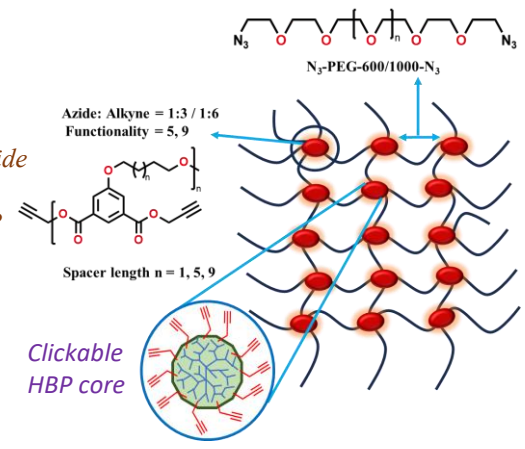
Scott P. O. Danielsen et al. *Chem. Rev,*121,5042-5092(**2021**)

OBJECTIVES OF THE STUDY



Key Parameters

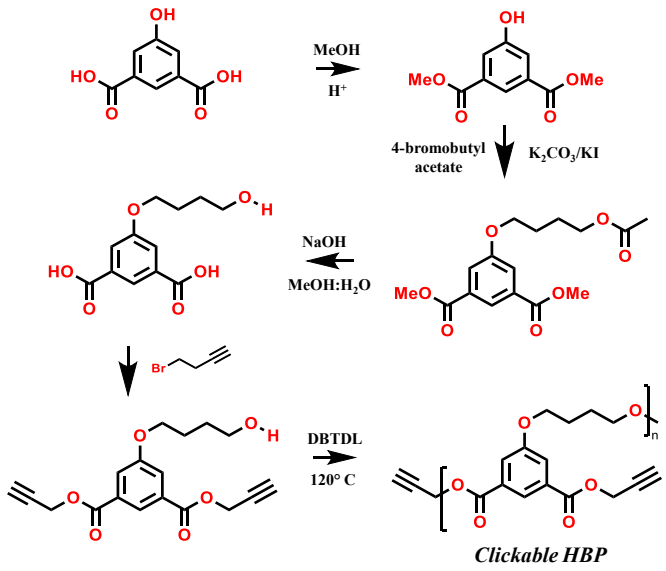
- *Mole ratio of propargyl:azide*
- *Length of the PEG-diazide.*
- *Spacer segment in the HBP*



Objectives

- Build amphiphilic networks using peripherally clickable hyperbranched polymers and polyethylene glycol (PEG) diazides by thermal alkyne-azide click reaction.
- Understand the influence of various structural elements, namely PEG segment length, average branch functionality and conformational flexibility of the HBP core, on their mechanical properties of the networks.

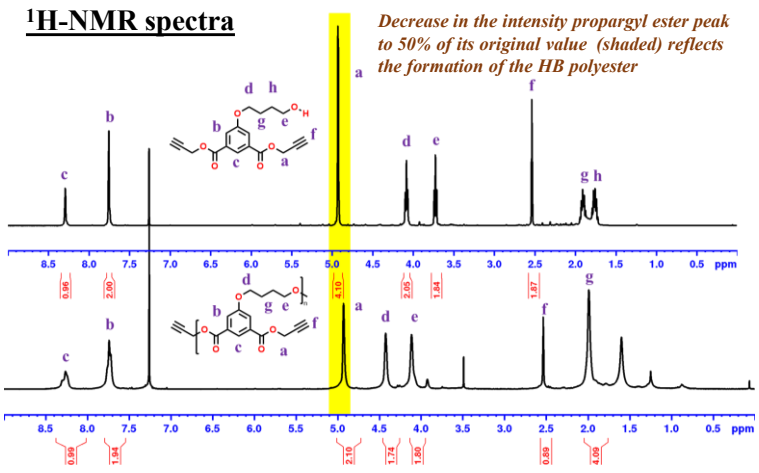
EXPERIMENTAL PLAN



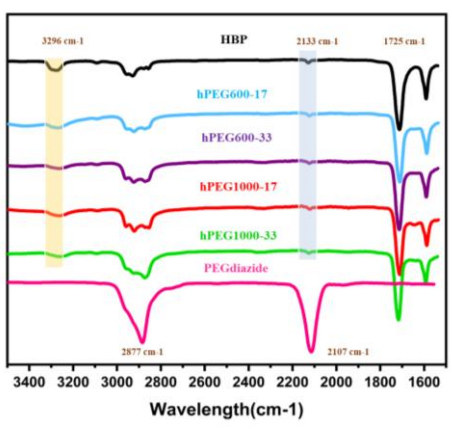
Clickable HBP

^{1}H-NMR spectra

Decrease in the intensity propargyl ester peak to 50% of its original value (shaded) reflects the formation of the HB polyester



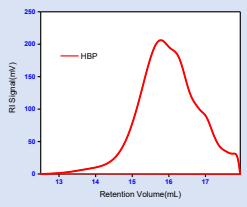
IR spectra of the crosslinked films



Near complete disappearance of the azide peak reflects the completion of the crosslinking

hPEG600-17 implies that 1 of 6 propargyl groups per HBP was utilized for crosslinking, while hPEG600-33 implies 1 of 3 are used, which implies a higher crosslink density

SIZE EXCLUSION CHROMATOGRAPHY



Mn(g/mol)	8100
Mw(g/mol)	34,700
Mw/Mn	4.29

The molecular weight (Mn) of the parent clickable hyperbranched polymer was estimated to be ~ 8100 g/mol, which implies that there are ~28 clickable propargyl groups, on average, per chain.

CONCLUSIONS

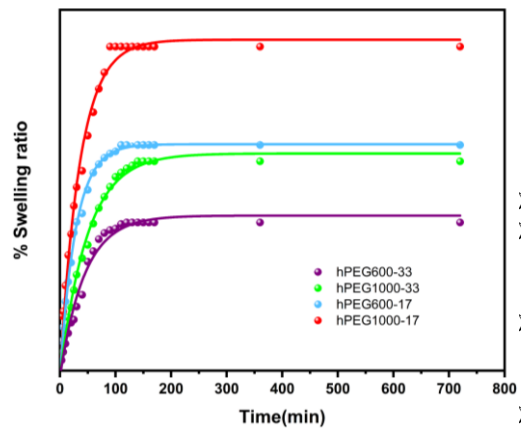
- Peripherally clickable HBPs serve as interesting multi-functional crosslinkers and can be used to generate amphiphilic networks under thermal azide-alkyne click reaction with PEG-diazides.
- Varying the length of the PEG-diazide and the relative ratio of alkyne:azide provides a simple handle to vary the crosslink density and functionality, respectively.
- Stress relaxation studies appear to reveal distinct features associated with the HBP and PEG segments; future work envisions increasing the spacer segment length (C4 to C12) to firmly establish this correlation.

ACKNOWLEDGEMENTS

We thank IISc for the instrument facilities and UGC-CSIR Fellowship.

RESULT AND DISCUSSION

Swelling studies in chloroform



[a] – Gayen et al. *Chem Asian J.*18, e202300143 (**2023**)

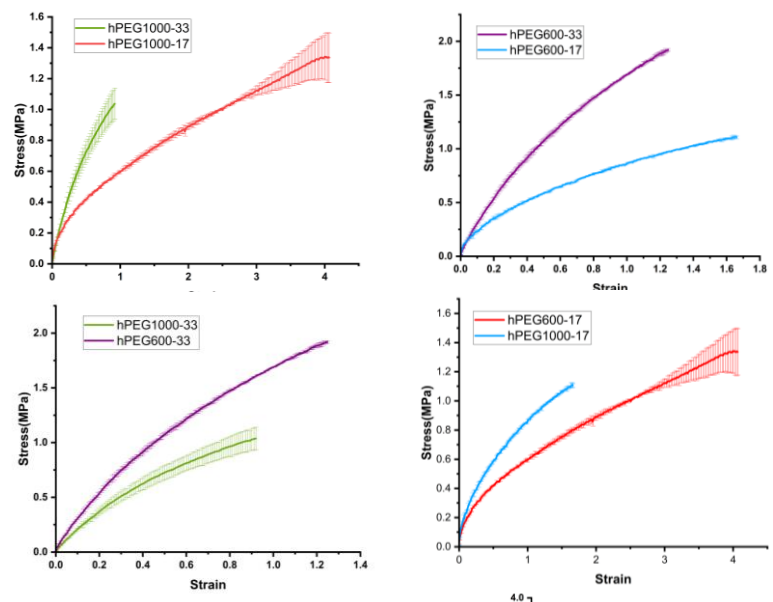
% Swelling

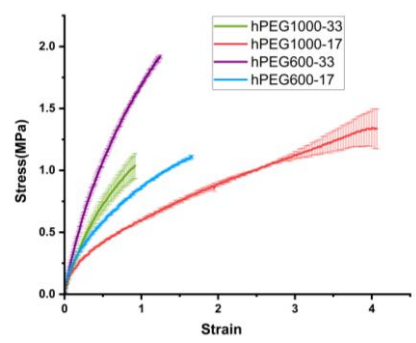
hPEG600-33 = 252%	hPEG600-17 = 379%
hPEG1000-33 = 352%	hPEG1000-17 = 539%

- Higher the branch functionality (33 *vs* 17), lower the swelling.
- Increase in PEG chain length from 600 to 1000 increases the average segment length between crosslinks (Mc) and reduces the crosslink density, causing increased swelling.
- Equilibrium swelling values of hPEG1000-33 and hPEG600-17 are almost comparable, suggesting that effect of increased branch functionality is compensated by the longer PEG chain length.
- Chloroform is a good solvent for both the HBP and PEG and therefore leads to complete solvation of both segments, unlike water that would lead to selective swelling of the PEG segments.[a]

MECHANICAL PROPERTIES

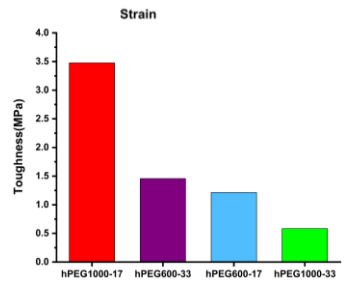
Uniaxial Tensile tests

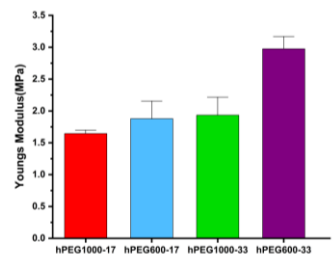




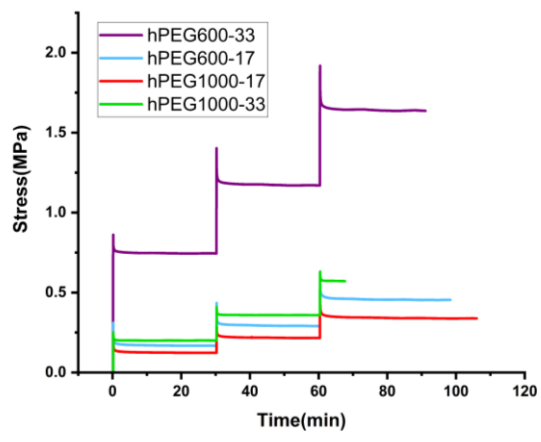
- The expected increase in modulus is noticed with increase crosslink density
- hPEG600-33 is the stiffest and hPEG1000-17 the softest of the samples and is most extendable.

- Interestingly, hPEG1000-33 and hPEG600-17 have comparable moduli; this is consistent with their similar swelling characteristics.
- hPEG1000-17 exhibits the highest toughness as evident from the plot on the right.



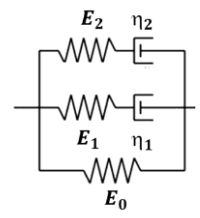


Stress Relaxation Studies



Crosslinked Networks	Weichert Model		
	τ_1	τ_2	R^2
hPeg600-17	4.8	250.9	0.96
	6.4	414.94	0.95
	15.21	416	0.96
hPeg600-33	6.3	226.6	0.96
	7.4	344.5	0.96
	6.9	235.8	0.96
hPeg1000-17	6.04	237.5	0.97
	7.5	314.3	0.96
	16.7	590.9	0.97
hPeg1000-33	3.05	44.64	0.98
	5.26	72.46	0.97
	3.19	28.98	0.98

Weichert Model

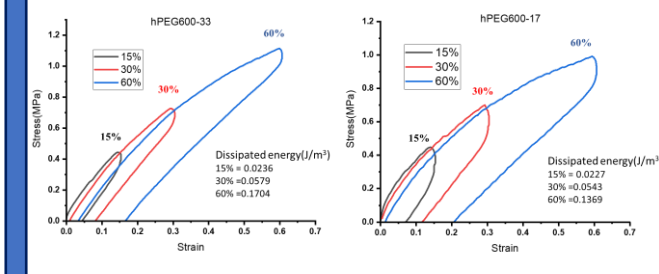


$$\tau_1 = \frac{\eta_1}{E_1}$$

$$\tau_2 = \frac{\eta_2}{E_2}$$

$$\sigma = E_0\varepsilon_0 + E_1\varepsilon_0 e^{(-t/\tau_1)} + E_2\varepsilon_0 e^{(-t/\tau_2)}$$

Hysteresis



- Hysteresis at 15 % extension is lower than those at 30 % and 60 % stretch, in both PEG600 samples, as expected; indicating lower energy dissipation at lower strain.
- hPEG600-17 clearly reveals larger hysteresis reflecting its lower crosslink density.

- The stress relaxation studies show interesting features that reveal two distinct components to the relaxation process; one rapid and the other a relatively slow one.
- Since the networks carry two components, namely the HBP that serves as a multi-point crosslink and the PEG segments, the two time-constants probably reflect the relaxation associated with the relatively stiffer HBP and the more flexible PEG segments.
- hPEG600-33 and hPEG1000-17 appear to exhibit somewhat similar stress relaxation behavior; the roughly similar values of τ_2 suggesting that the relaxation process of the PEG segments become independent of length beyond a threshold length.
- hPEG1000-33 exhibited unusual stress relaxation behviour; presently we do not fully understand the exact reason for this. Further experiments are required to ascertain if this is an anomaly.