Exploring the effects of polymer topologies on the properties of Poly(tert-Butyl acrylate)

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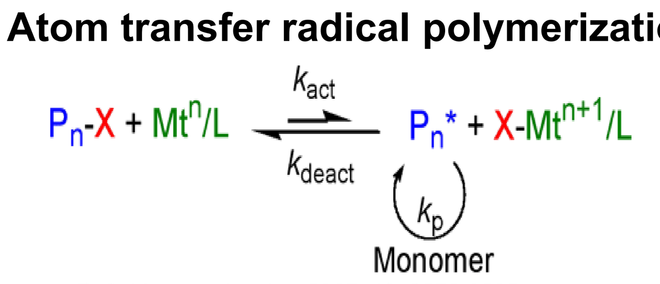
Abstract

Polymer topology plays a crucial role in physical properties and determines potential material applications. The shape and interconnectedness of polymer chains significantly influence their behavior, such as solution and thermal properties. We explored advanced polymer architectures including a cyclic and 8-shaped with precise molecular designs in addition to the conventional linear polymer. By studying these polymer architectures, material properties can be fine-tuned at the molecular level as advanced new possibilities in materials design. In this work, we synthesized poly(tert-butyl acrylate) with various shapes including linear, tetra-arm, cyclic, and 8-shaped polymers using ARGET-ATRP and click chemistry. This approach allowed us to control both the size and structure of the polymers. Comprehensive analysis using ^1H NMR, FT-IR, SEC, DSC, and MALDI-TOF mass spectrometry techniques confirmed the successful synthesis of these polymers. Our investigation revealed that the topologies significantly influenced the properties. Cyclic polymers exhibited higher glass transition temperatures compared to their linear precursors, attributing to their more compact rigid structures. Further, the intrinsic viscosity decreased with increasing structural compactness across different topologies. These findings demonstrate the profound impact of polymer topology on material properties, offering new avenues for fine-tuning polymer behavior in both solution and bulk states. This research covers the way for developing advanced materials with tailored properties, which can potentially revolutionize applications in fields such as drug delivery, smart coatings, and high-performance polymers.

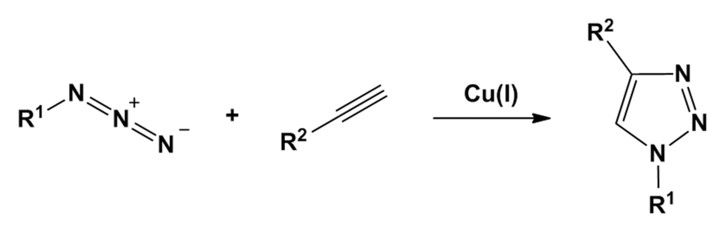
Introduction

- Atom transfer radical polymerization



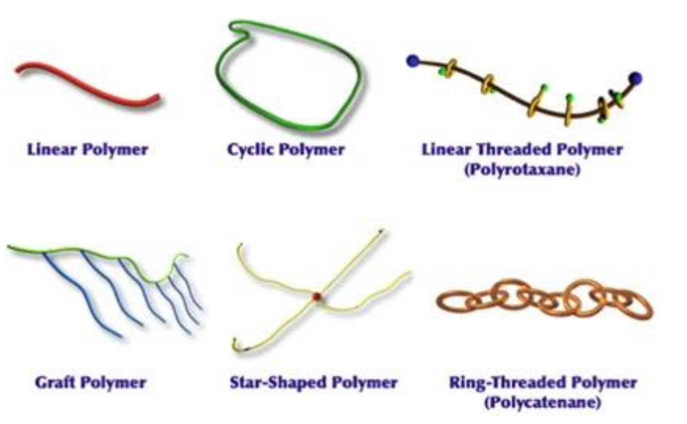
Ref: *Macromolecules* **2007**, 40, 8576-8585.

- CuAAC Click reaction



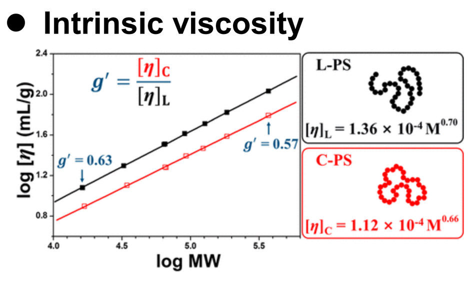
Ref: *Angew. Chem.* 40, **2001**, 11, 2004-2021.

- Topological polymers

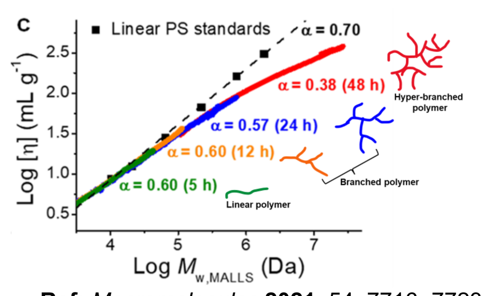


Ref: *Polymer Journal* **2018**, 50, 127–147.

- Topological effects on properties
  - Intrinsic viscosity

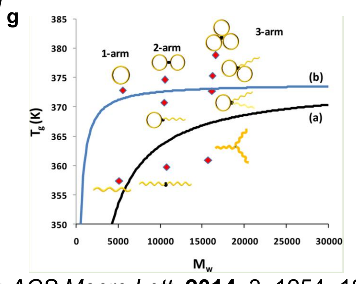


Ref: *Macromolecules* **2017**, 50, 7770–7776.



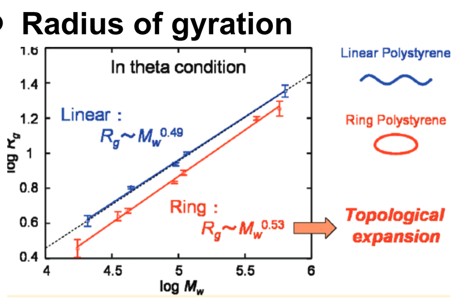
Ref: *Macromolecules* **2021**, 54, 7716−7723

  - T_g



Ref: *ACS Macro Lett.* **2014**, 3, 1254−1257.

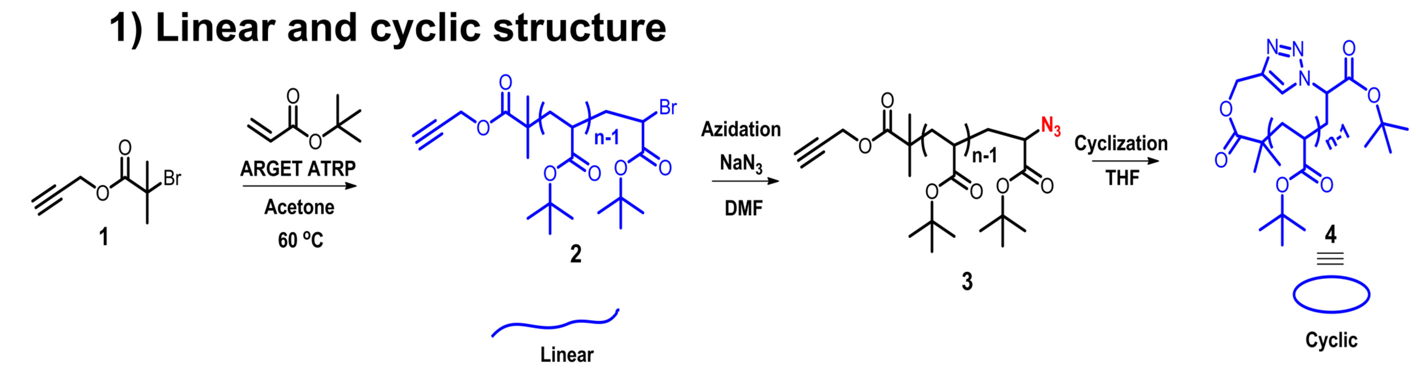
  - Radius of gyration



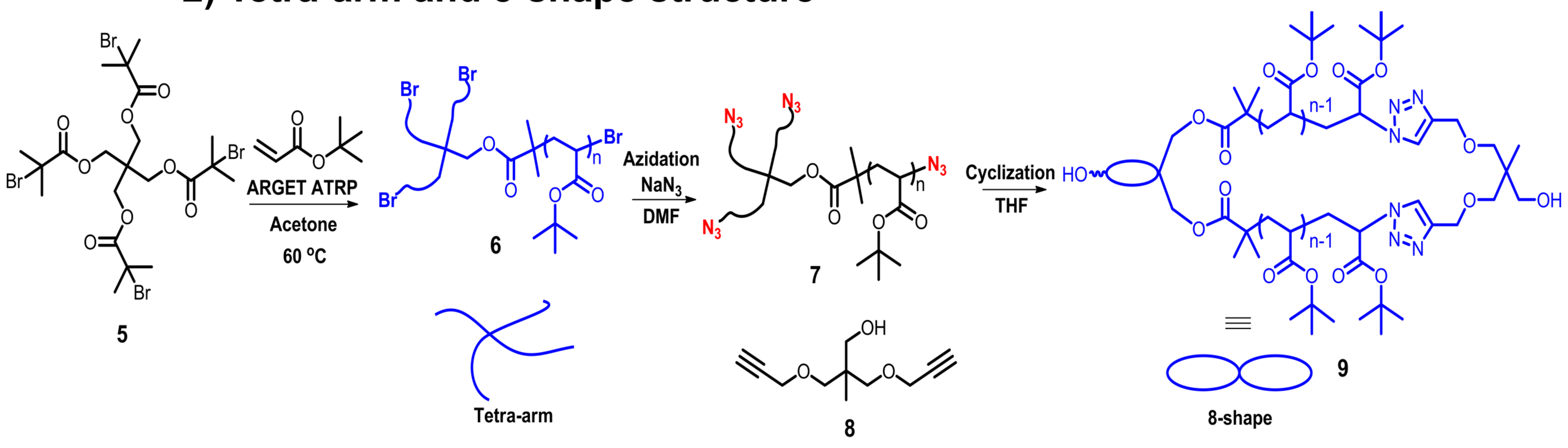
Ref: *Macromolecules* **2012**, 45, 369−373.

Research goal

1) Linear and cyclic structure



2) Tetra-arm and 8-shape structure



Scheme. Synthetic scheme of various topological poly(tert-butyl acrylate)s.

Results and Discussion

SEC of linear and cyclic PtBA

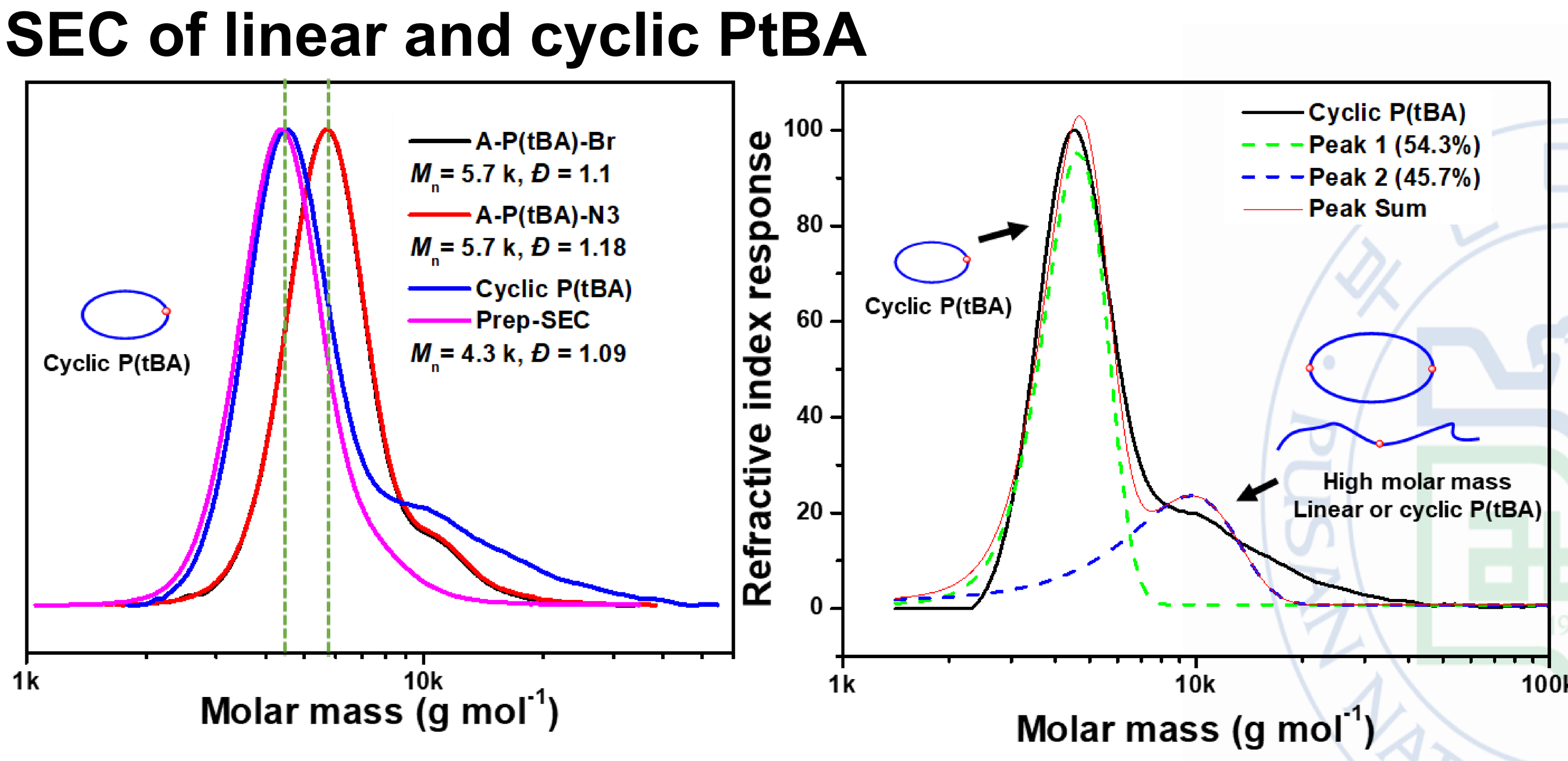


Figure 1. Molar mass in SEC with RI detector linear A-P(tBA)-Br, cyclic P(tBA), and SEC deconvolution of Cyclic P(tBA)

SEC of tetra-arm and 8-shape PtBA

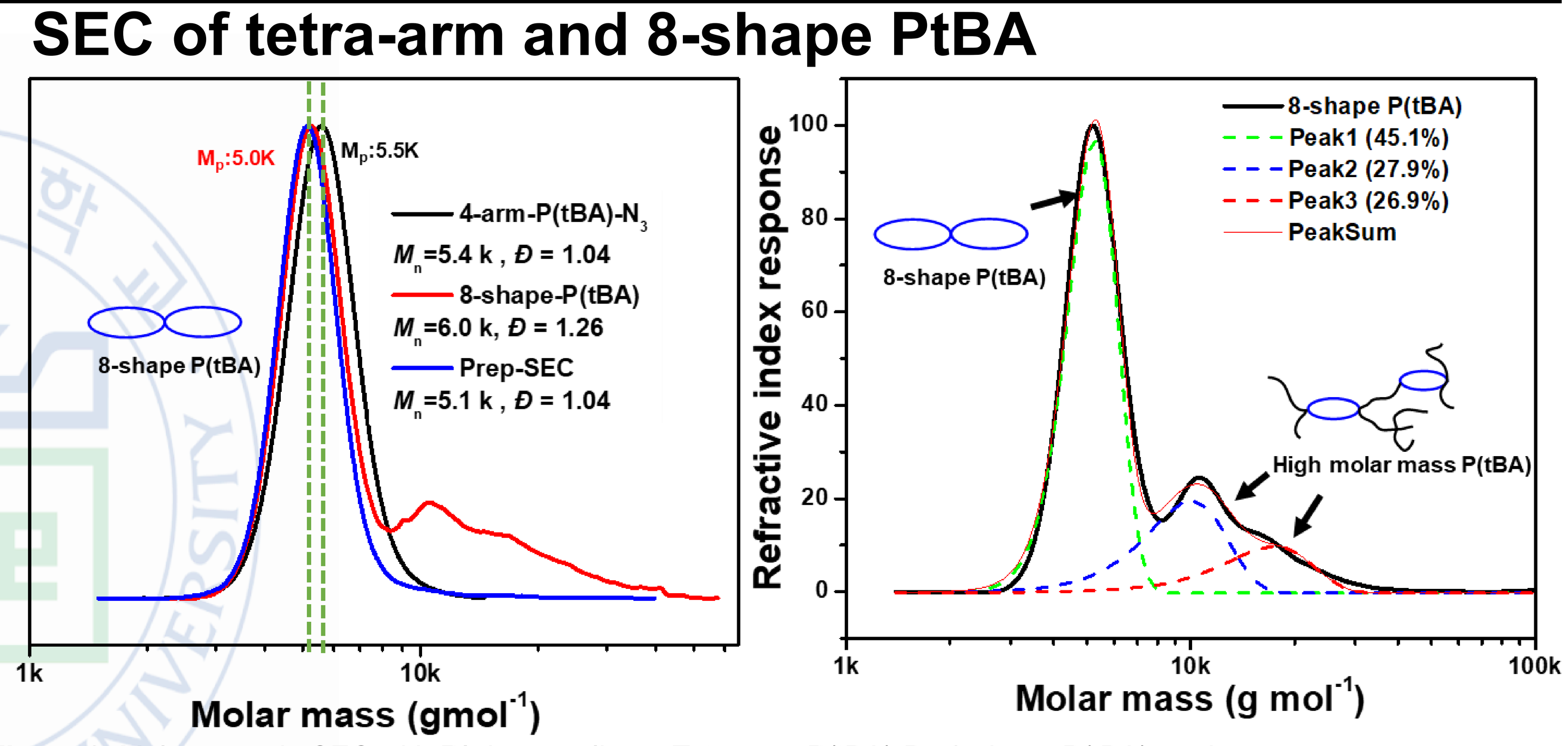


Figure 2. Molar mass in SEC with RI detector linear Tetra-arm P(tBA)-Br, 8-shape P(tBA), and SEC deconvolution of 8-shape P(tBA

^1H NMR

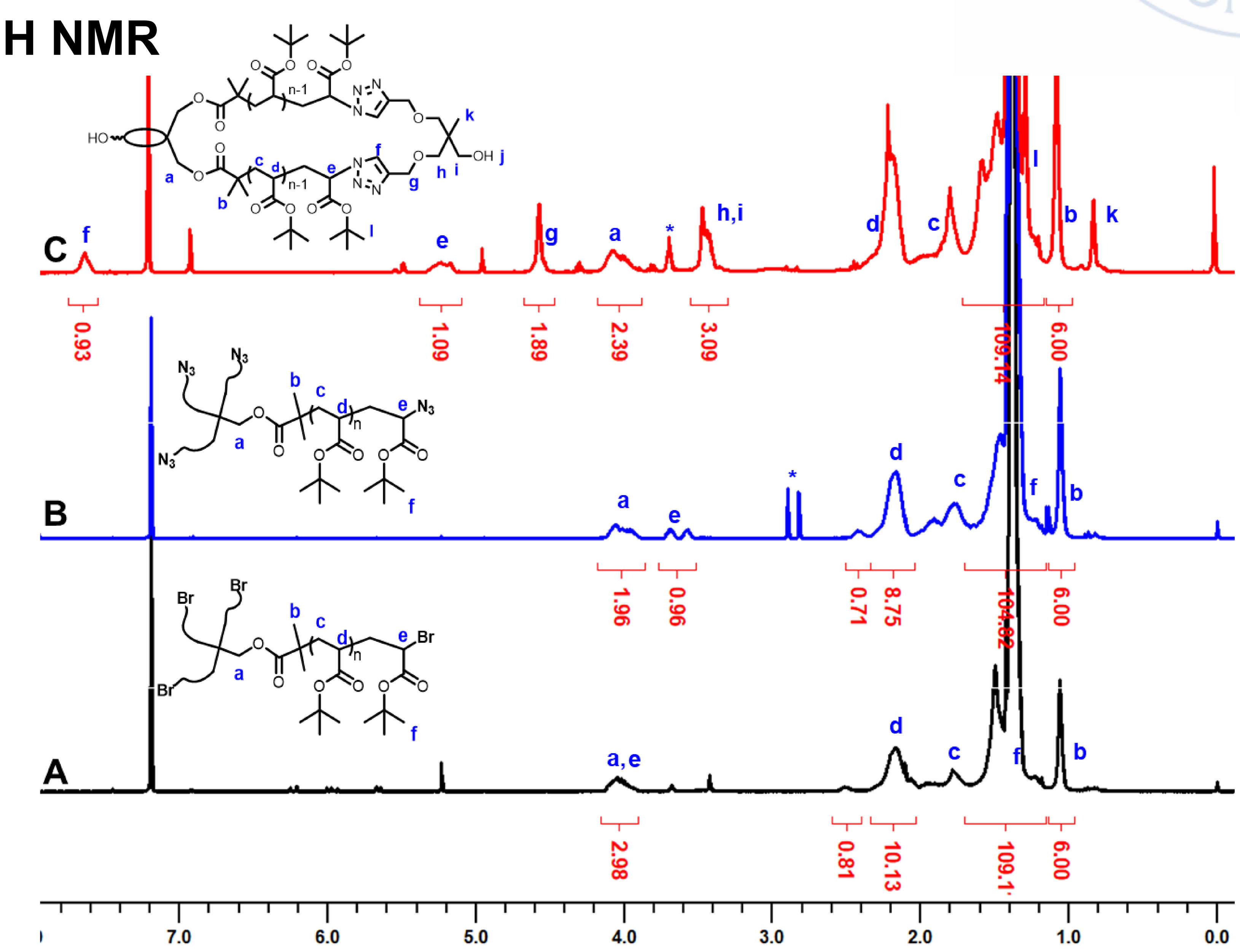
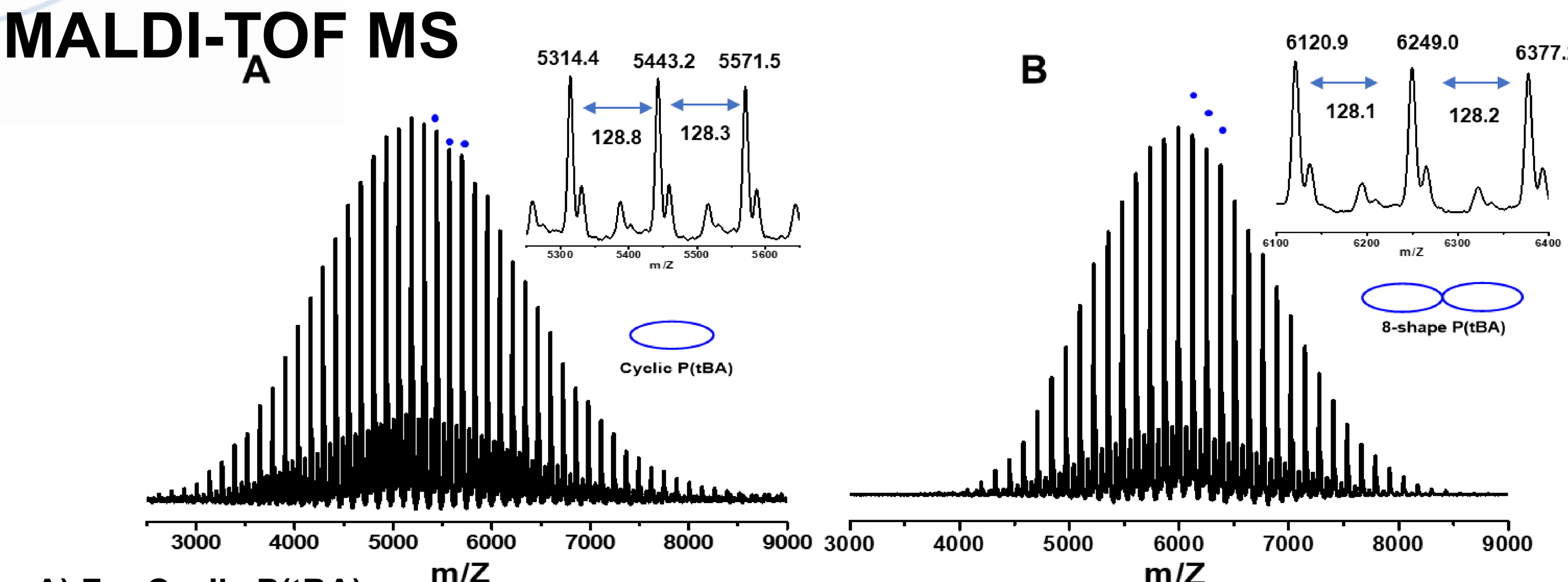


Figure 3: ^1H NMR of A) Tetra-arm P(tBA)-Br, B) Tetra arm P(tBA)N3,and C) 8 shape P(tBA).

MALDI-TOF MS



A) For Cyclic P(tBA)
M+H calculated: 4917.7
M+H observed: 4918.9

B) For 8-shape P(tBA)
M+H calculated: 6097.2
M+H observed: 6097.4

Figure 4: MALDI-TOF of A) Cyclic P(tBA), and B) 8-shape P(tBA).

Table1: Summarized data of all topological polymers.

Sample	aMn,RI SEC	bMw,LS, SEC	aĐ	η	Tg	Rh(nm)
A-P(tBA)-Br	5.7K	5.0K	1.10	0.056	32	1.63
Cyclic P(tBA)	4.3K	5.0K	1.21	0.036	39	1.40
Tetra-arm P(tBA)-Br	5.4K	5.6K	1.04	0.042	31	1.55
8-shape P(tBA)	5.0K	6.6K	1.04	0.034	52	1.52

a- Refractive index (RI) detector response in Size exclusion chromatography.
b- Light scattering detector(LS) response in multi responsive size exclusion chromatography

Intrinsic Viscosity

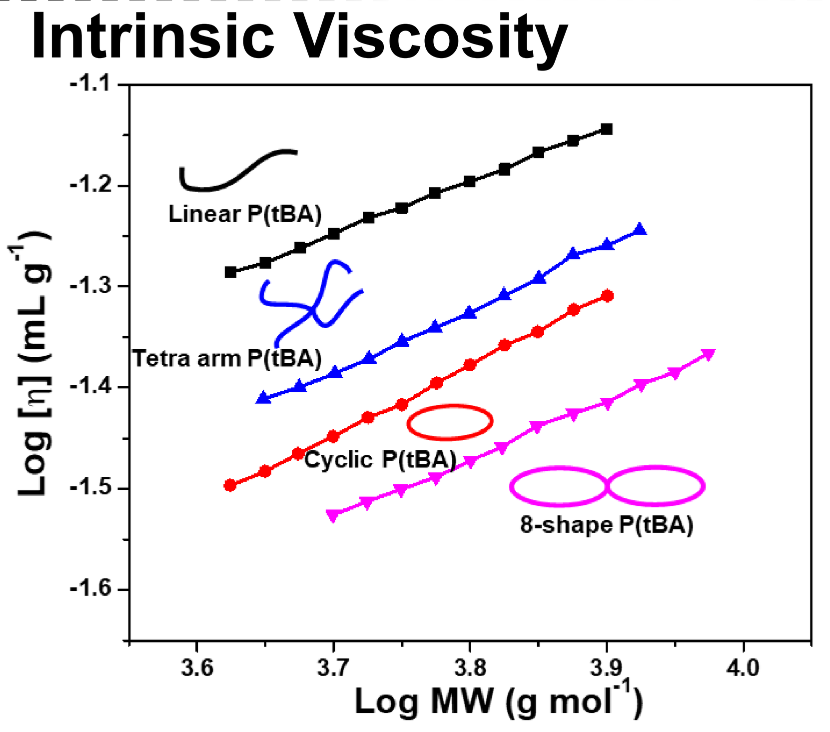


Figure 5: Intrinsic viscosity [η] of all topological polymers were measured using multi-angle laser light scattering detector-equipped SEC, plotted as Intrinsic viscosity Vs Log MW and Cover image of MRC .

Hydrodynamic volume

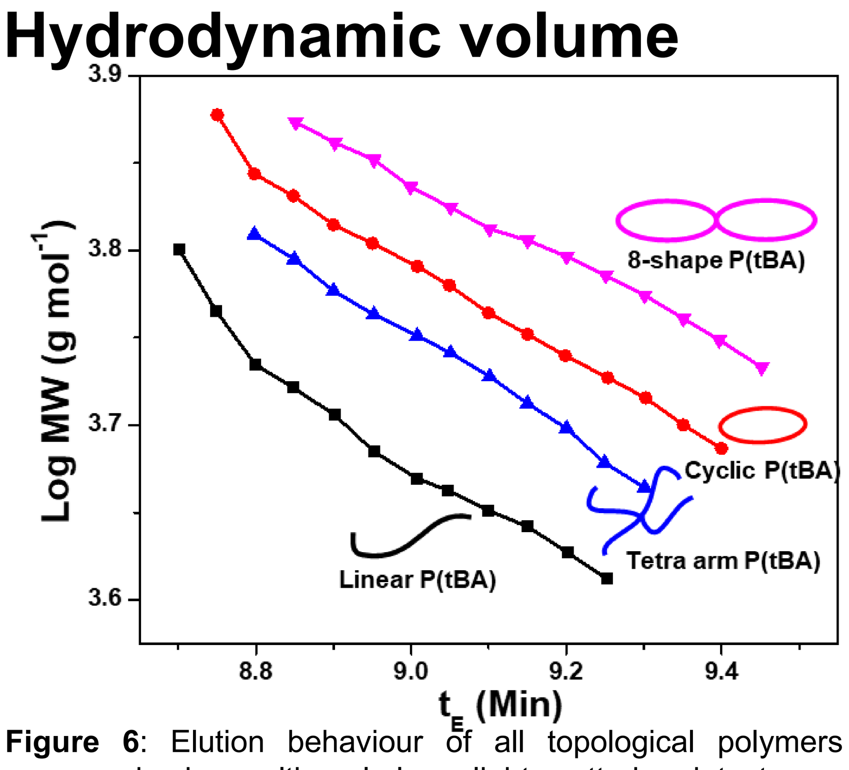


Figure 6: Elution behaviour of all topological polymers were measured using multi-angle laser light scattering detector-equipped SEC, plotted as Log MW Vs elution time.

DSC

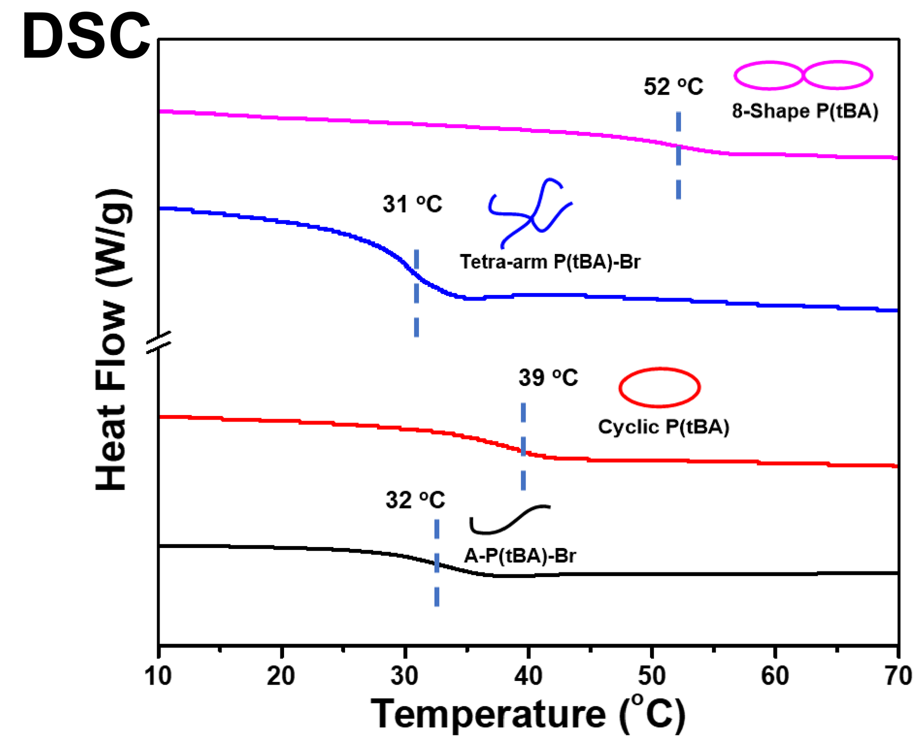


Figure 7: Glass transition temperature of A-P(tBA)-Br, Cyclic-P(tBA), 4-arm-P(tBA)-Br, and 8-shape-P(tBA).

Conclusion

- Polymer topology significantly affects on **Intrinsic viscosity**: linear > tetra-arm > cyclic > 8-shape, **Glass transition influence**: 8-shape > cyclic > linear > tetra-arm
- Compactness and the number of free chain ends, governed by polymer topology, play a crucial role in determining solution behavior and thermal transitions, offering new strategies for designing materials for applications like drug delivery and nanotechnology.
- Aswale S.; et al. Various topological poly(tert-Butyl acrylates)s and their impacts on thermal and solution properties. *Macromo. Rapid Commun.* **2025**, 2401043.

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