Triethanolamine-Designed Dynamic Covalent Adaptable Network Template for Functional Composites

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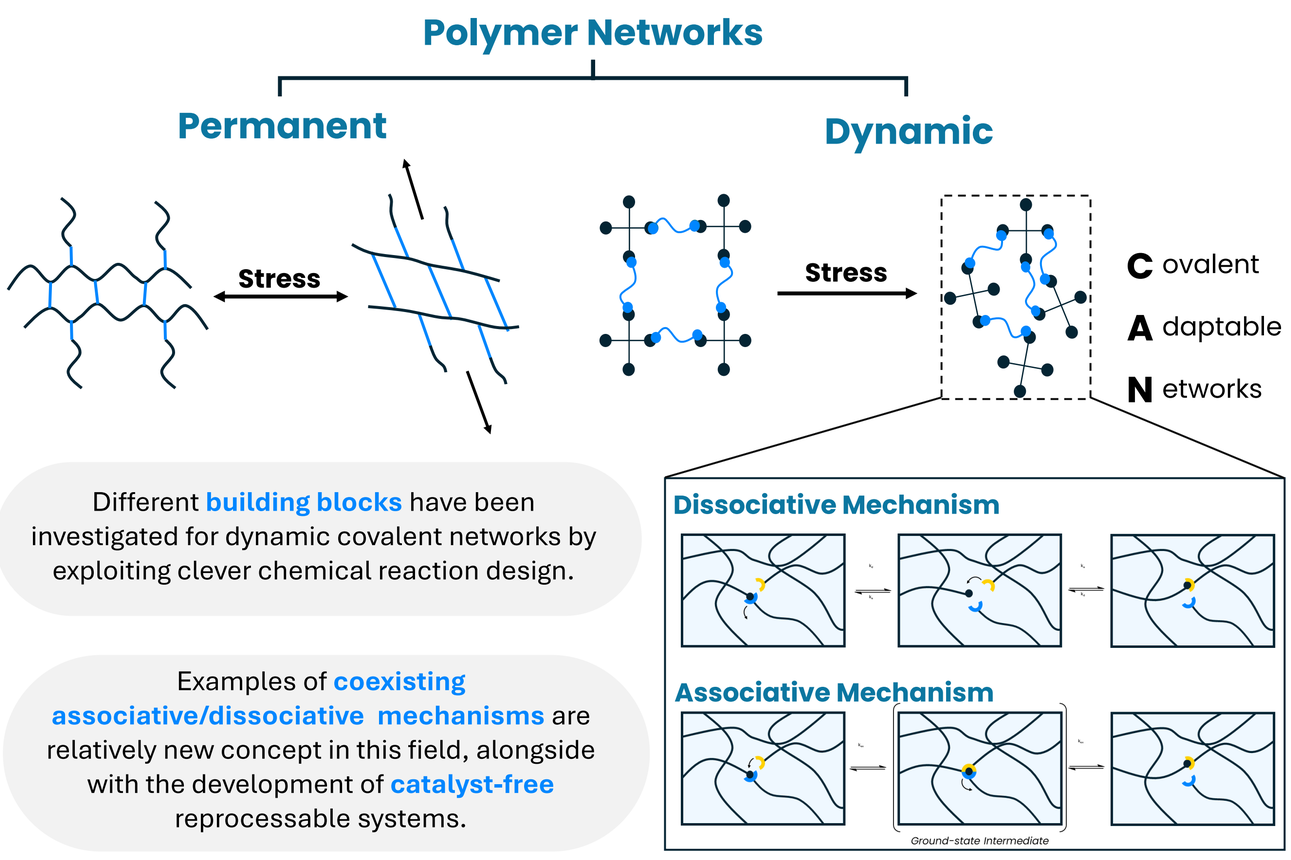
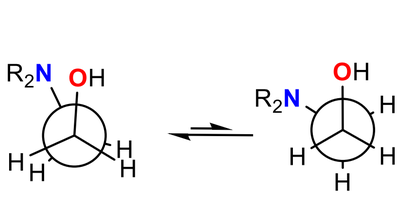
Introduction

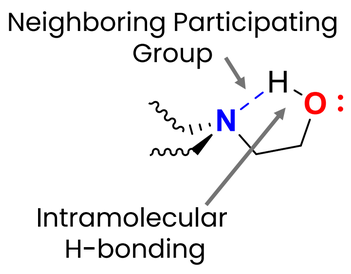
Polymer science is witnessing a shift in paradigm since the breakthrough of Covalent Adaptable Networks (**CAN**s), offering new insight on polymer networks.



Different **building blocks** have been investigated for dynamic covalent networks by exploiting clever chemical reaction design.

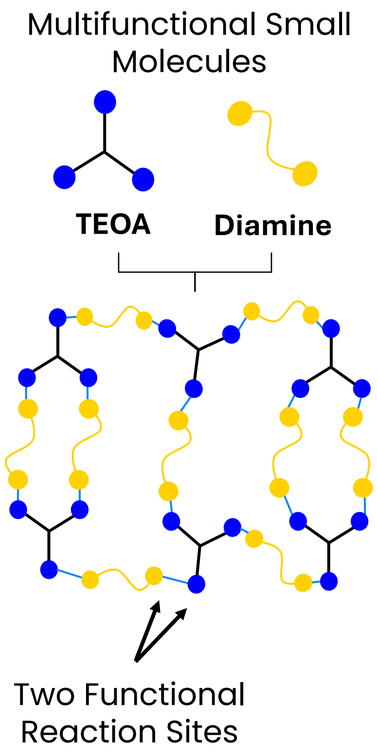
Examples of **coexisting associative/dissociative mechanisms** are relatively new concept in this field, alongside with the development of **catalyst-free** reprocessable systems.



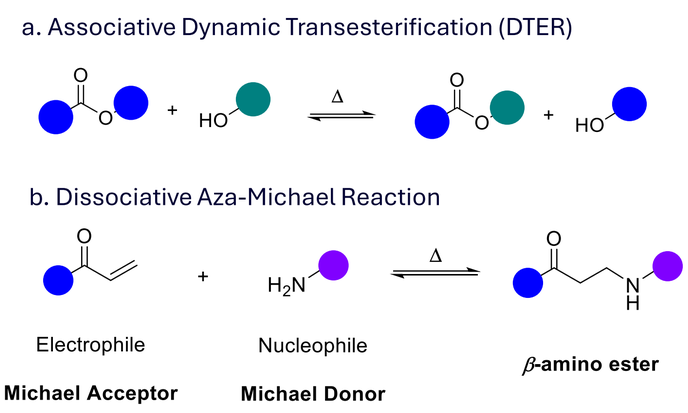


This study will try to give some insight on the applicability of **triethanolamine (TEOA)** as building block with a pre-existent participating neighboring group (NPG).

Goal

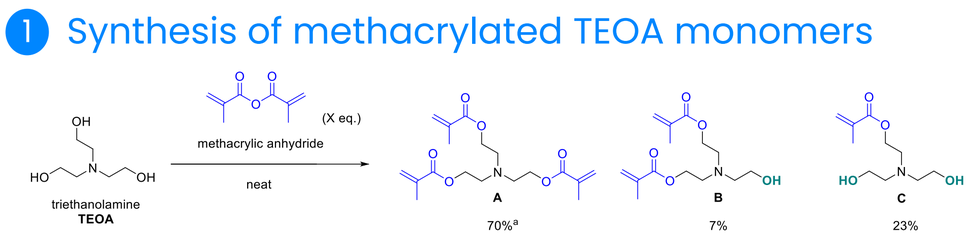


Developing CANs based on triethanolamine and diamine as functional monomers with the following characteristic mechanisms

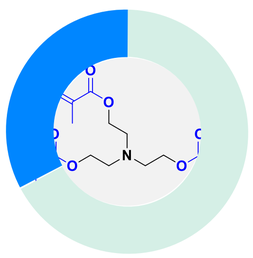


Methodology

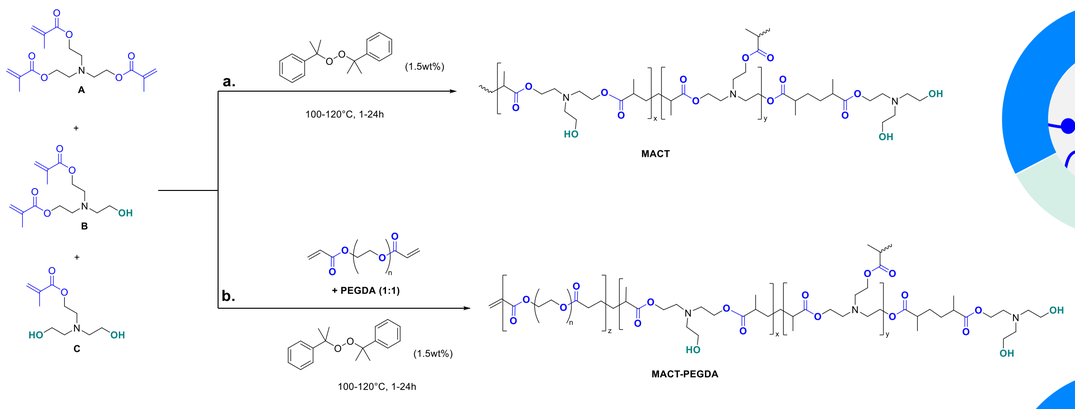
1 Synthesis of methacrylated TEOA monomers

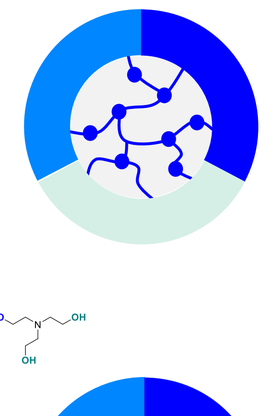


a) Ratio calculated by ^{1}H NMR peak integration

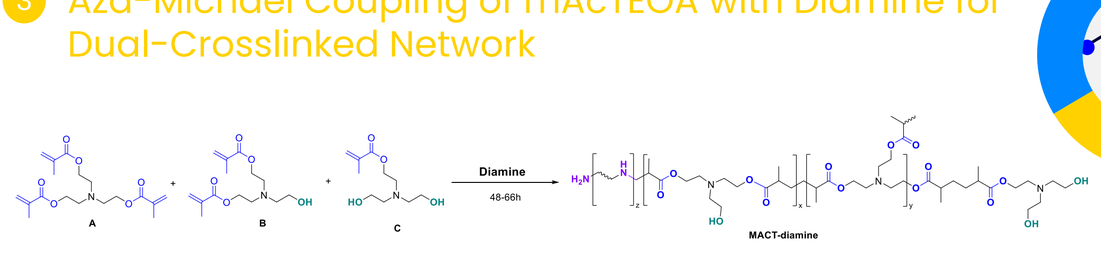


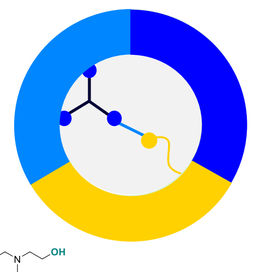
2 Polymerization of mAcTEOA for DTER-based Networks





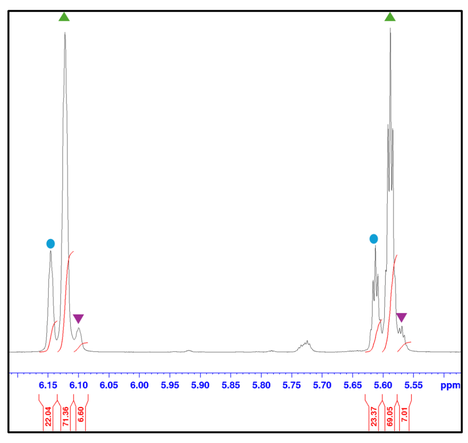
3 Aza-Michael Coupling of mAcTEOA with Diamine for Dual-Crosslinked Network

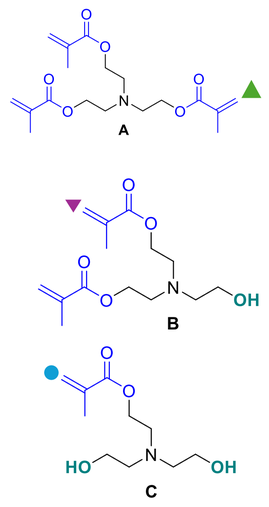




Results

1 ^{1}H NMR studies helped clarifying the methacrylation condition suitable for installing methacrylic moieties and keeping free hydroxy groups at some extents at the same time.





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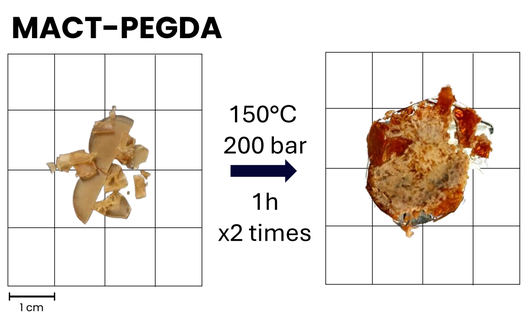
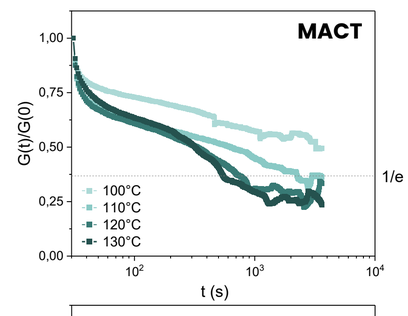
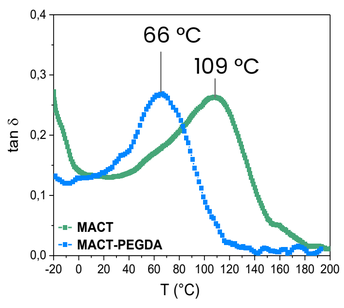
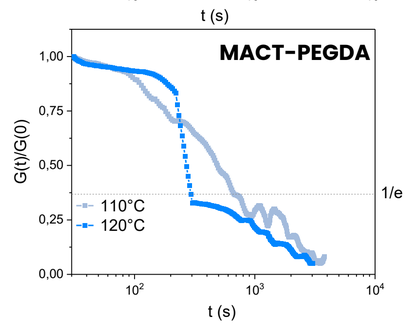




TEOA was then polymerized in thermal conditions to first investigate the transesterification behavior of such networks, for which stress-relaxation curves are reported here.





The mix of TEOA monomers was also used in combination with poly(ethylene glycol) diacrylate as comonomer, attempting to increase the network mobility to facilitate DTER; however, practical reprocessing at 150 °C were unsuccessful despite the lower characteristic relaxation time associated.

3

Lastly, mAcTEOA mix was reacted in presence of diamines. Herein we are reporting two examples with Priamine 1071, a bio-resourced diamine, and hexamethylenediamine, a common monomer for Nylon-6,6 synthesis. These represents the very first example of Aza-Michael CANs based on TEOA with coexisting associative/dissociative mechanism.

Conclusions

Methacrylated TEOA is an unprecedented building block to structure CANs and its employment has to be characterized further to fully understand its applicability.

MACT polymers showed promising stress-relaxation properties as DTER network, even tough reprocessing in hot press was unsatisfactory and requires further investigation.

Aza-Michael coupling is a useful tool in building CANs architecture as for its ease of applicability to acrylic and methacrylic monomers. Followingly, efforts are going to be made on the characterization of their mechanical and rheological properties

[1] Zhang, V., Kang, B., Accardo, J. v., & Kalow, J. A. (2022). Structure–Reactivity–Property Relationships in Covalent Adaptable Networks. *Journal of the American Chemical Society*, *144*(49), 22358–22377.

[2] Yu. Rulev, A. (2023). Aza-Michael Reaction: A Decade Later – Is the Research Over? *European Journal of Organic Chemistry*, *26*(26)

[3] Taplan, C., Guerre, M., & du Prez, F. E. (2021). Covalent Adaptable Networks Using β-Amino Esters as Thermally Reversible Building Blocks. *Journal of the American Chemical Society*, *143*(24), 9140–9150.

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