

Novel Elastomeric Polystyrene via Photopolymerization and Post-Functionalization of Durable Ultra-High Molecular Weight Perfluorostyrene Copolymers

Introduction

Plastics are incredibly important to our daily lives; however, our reliance on plastics has also led to concerns over pollution and plastic waste. Crosslinked plastics known as thermosets (e.g., car tires), are a particular issue, as their irreversible covalent crosslinks grant them exceptional strength and durability but also prevent recycling.

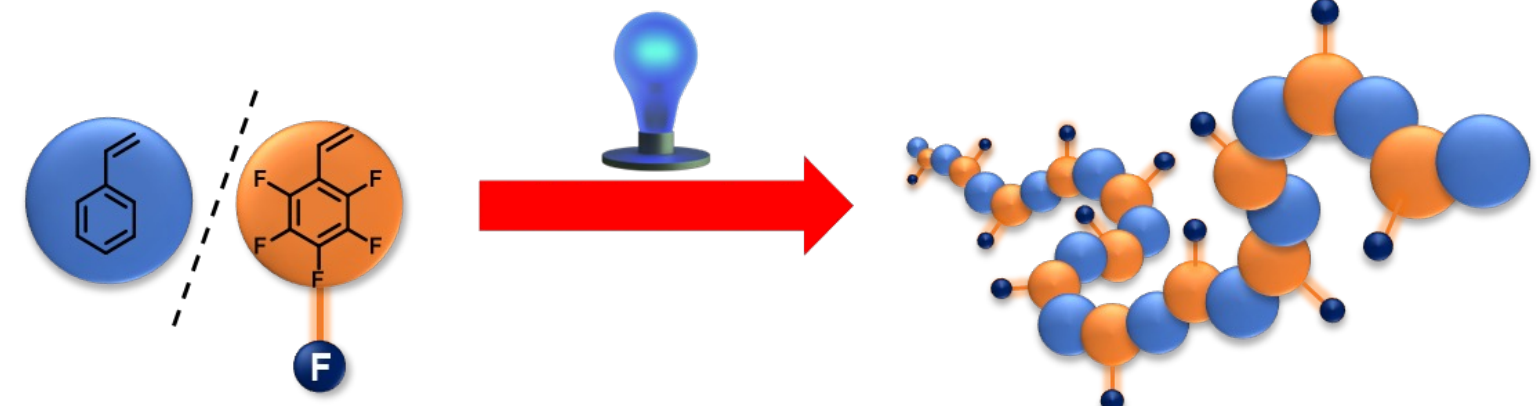
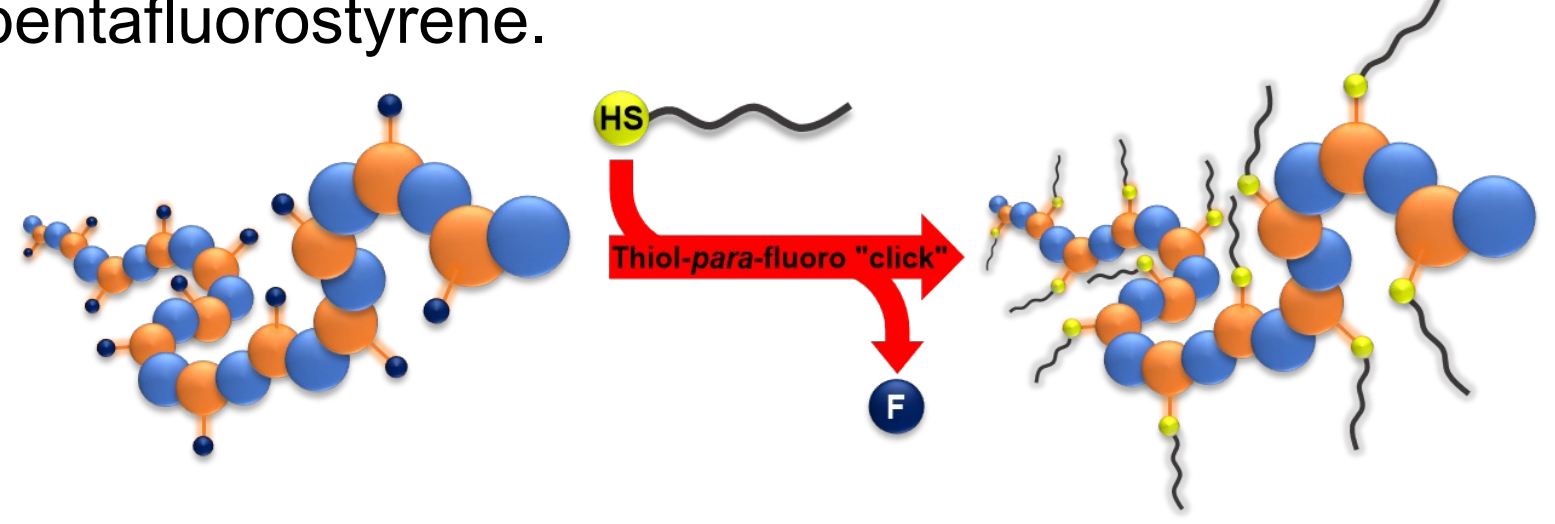
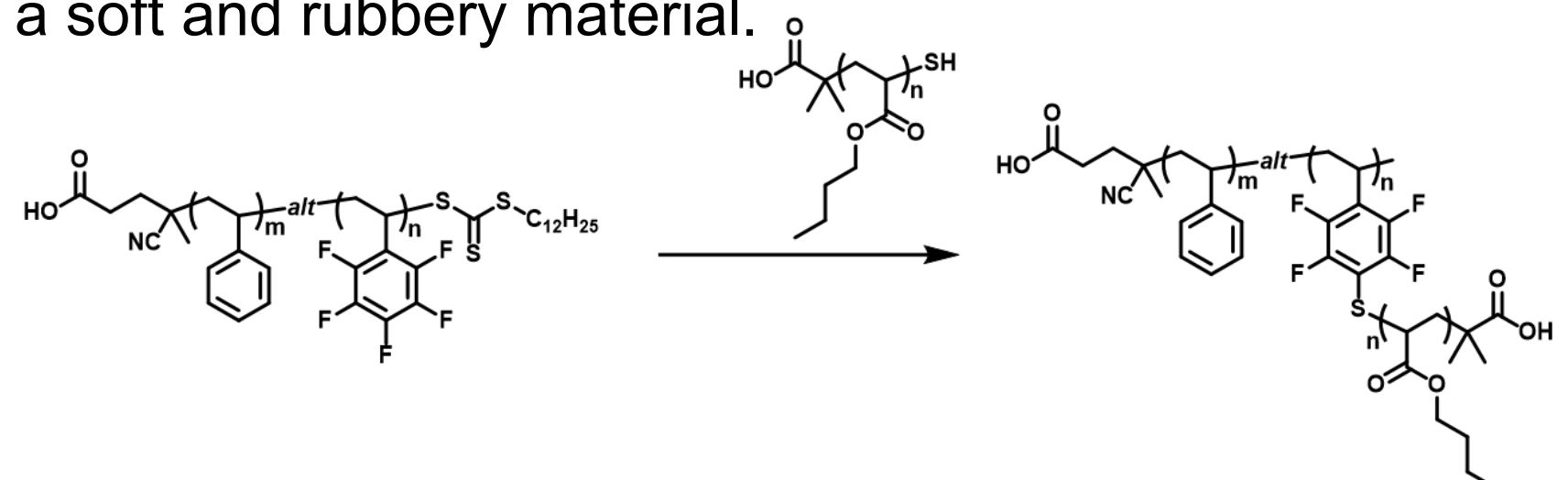
Ultrahigh molecular weight (UHMW) polymers may offer a solution due to the extreme strength granted by high chain lengths.

However, for some plastics such as polystyrene, existing methods to synthesize polymers of UHMW are limited and often require harsh conditions.

By using the tendency for styrene to alternate when polymerized with pentafluorostyrene, we can easily access UHMW polystyrenes.

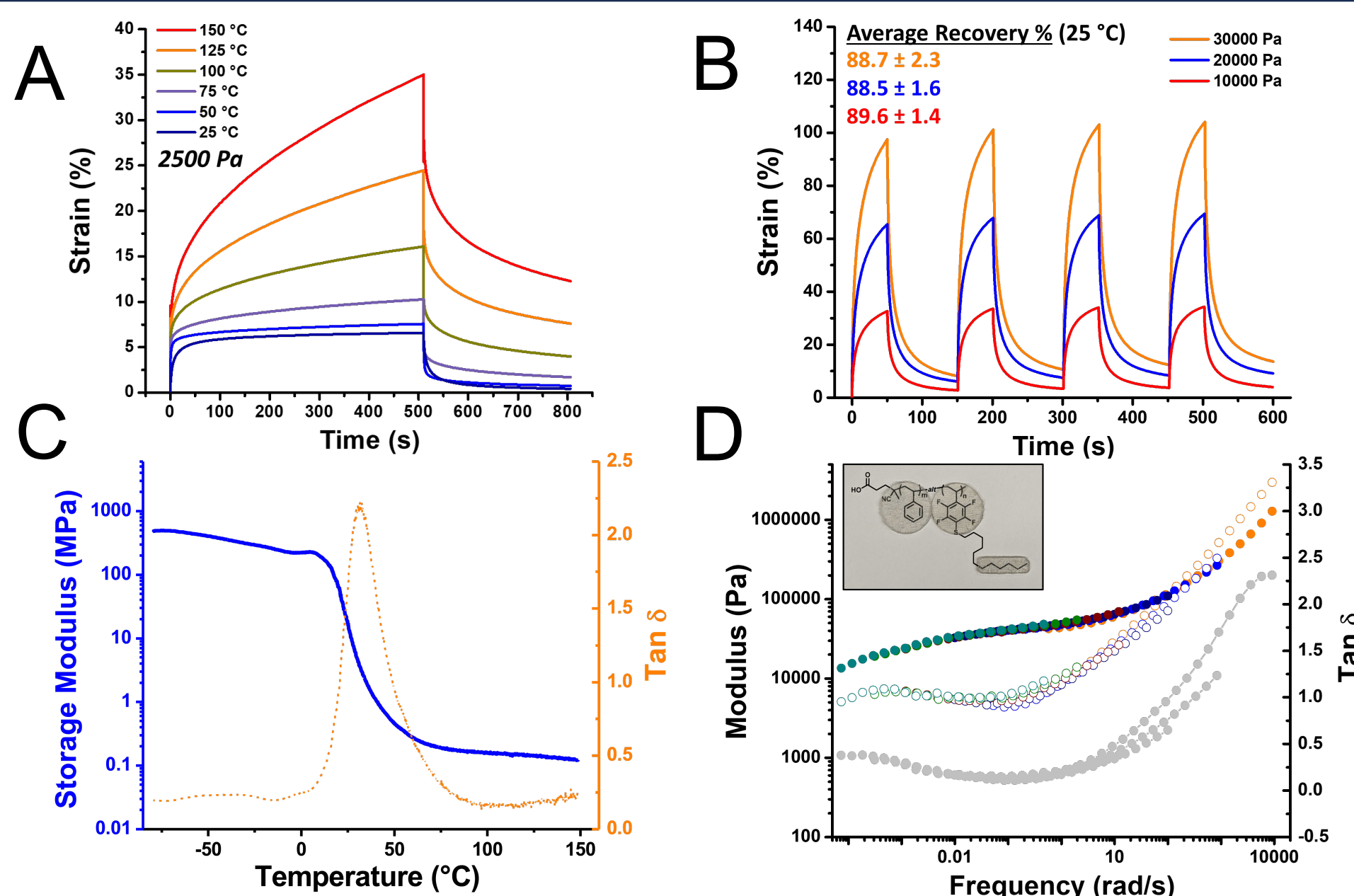
The use of pentafluorostyrene also gives us a way to efficiently modify the polymer, allowing us to beneficially tune its material properties.

Polymerization and Functionalization

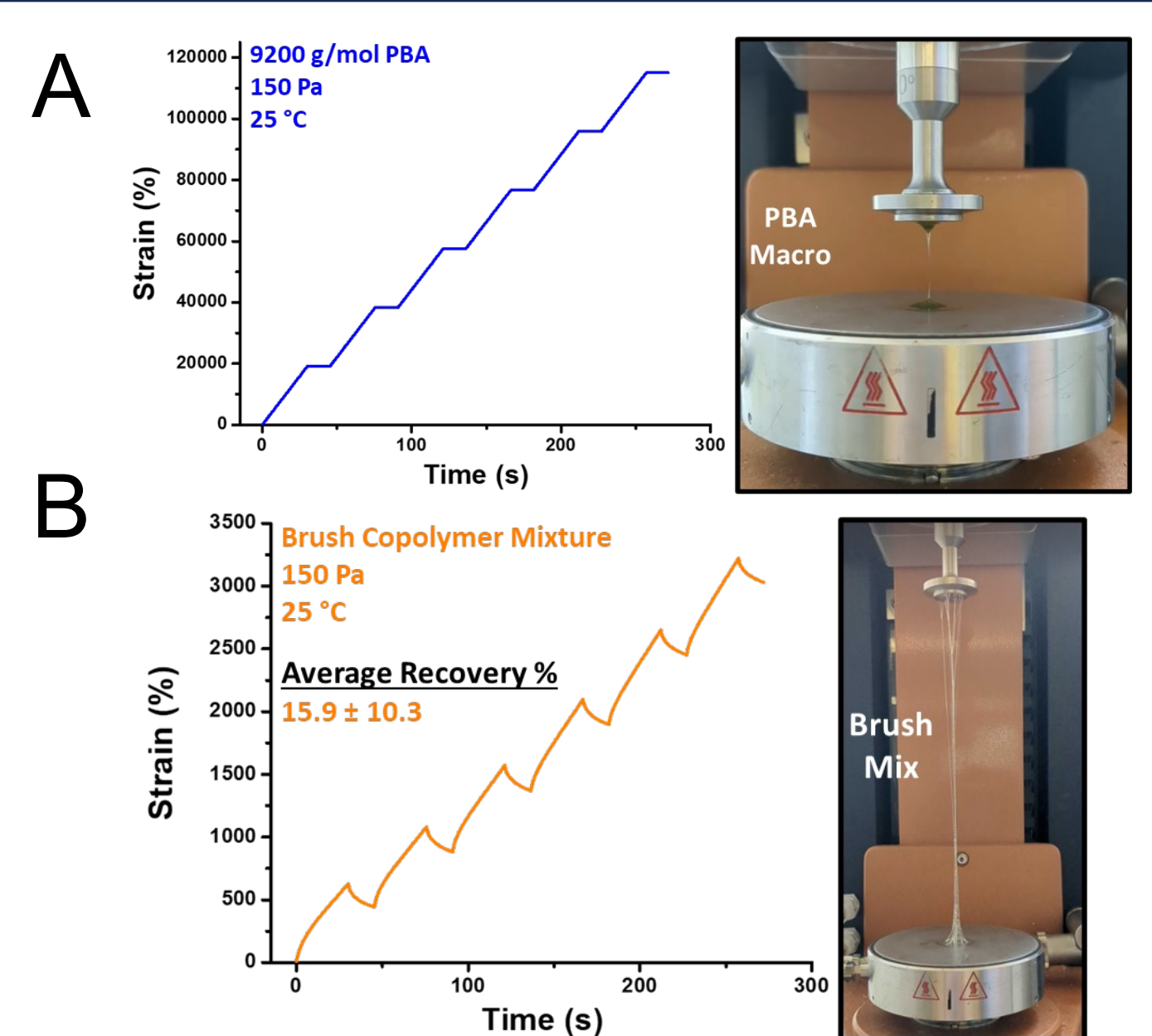
1. Synthesis of UHMW polystyrene using styrene and pentafluorostyrene.

2. Post-functionalization with dodecanethiol, resulting in a soft and rubbery material.

3. Grafting of short polymer chains of polybutyl acrylate, yielding a brush copolymer.


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Results



Rheological analysis of the dodecanethiol-functionalized polymer. (A) (B) demonstrate the polymer's elasticity, recovering nearly 90% of total deformation. (C) (D) show characteristics commonly seen in thermosets, such as (C) a continued rubbery plateau past 150 °C and (D) the storage modulus [closed circle] above the loss modulus [open circle], indicating network formation within the material caused by extreme amounts of entanglements at UHMW.



Creep Recovery experiment demonstrating the strength provided by an UHMW backbone: On its own, the polybutyl acrylate (A) shows no elastic recovery, while the brush copolymer mixture (B) shows an average elastic recovery of 16%. Images to the right provide a visual demonstration of the improved strength and elasticity of the material.

Conclusion

Ultra High Molecular Weight Polymers show extremely valuable properties; however, synthesizing them has often proven difficult. I developed a simple and low-energy method for synthesizing UHMW polystyrenes.

By modifying my polymer, I showed that it had properties similar to unrecyclable plastics known as thermosets, while also maintaining recyclability. This suggests my polymer could be used as a more sustainable alternative to some of these materials.

Future Work

Another method of creating more sustainable plastics is to source them from biologically derived materials. One promising resource for synthesizing similar UHMW polystyrenes is ferulic acid, a chemical found in rice bran and other vegetables.

The polymerization of styrene and pentafluorostyrene demonstrates remarkable stability, which suggests that it is possible to reach even higher molecular weight polymers with potentially superior properties.