Synthesis and Characterization of Precision Polymers via Acyclic Diene Metathesis

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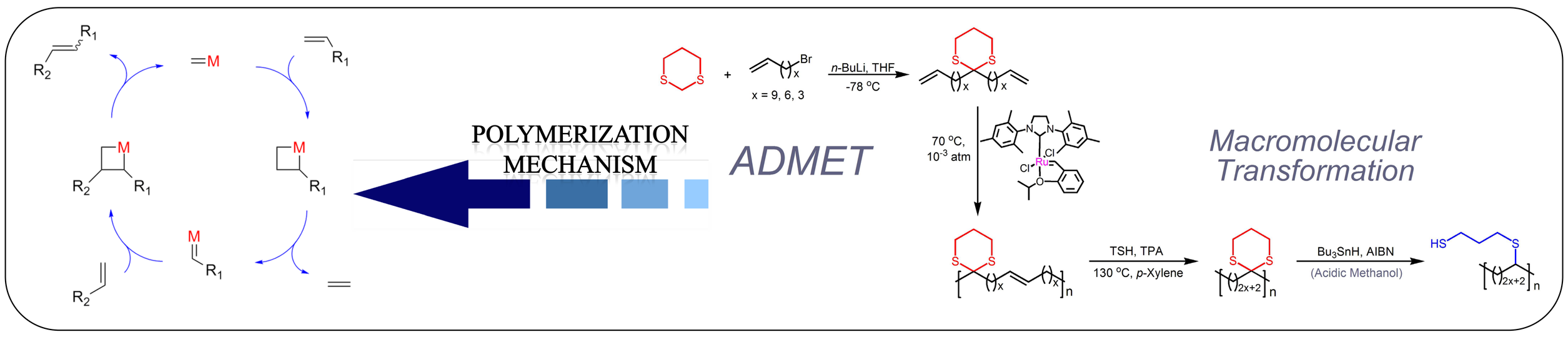
Introduction

1,3-Dithiane and its derivatives are widely used as powerful acyl anion equivalent to a range of useful transformations that are needed in the synthesis of natural products. Herein, a series of polyolefins containing pendant dithiane groups have been designed and synthesized via ADMET polymerization and subsequent hydrogenation. The dithiane units in the ADMET polymer with 20 methylene carbons between the adjacent dithiane groups were transformed into thiol groups via reaction with Bu_3SnH. This work provided a convenient route to synthesize polyethylene with pendant thiol groups that are evenly distributed in the chain.

Synthetic Scheme



Results and Discussion

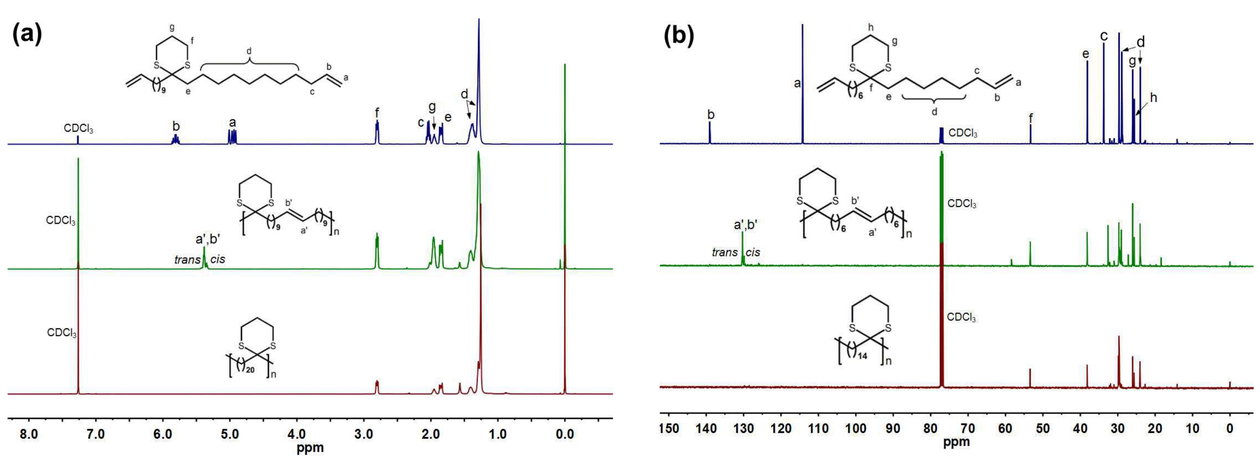


FIGURE 1 (a) ^{1}H NMR of EDT21 and (b) ^{13}C NMR of EDT15

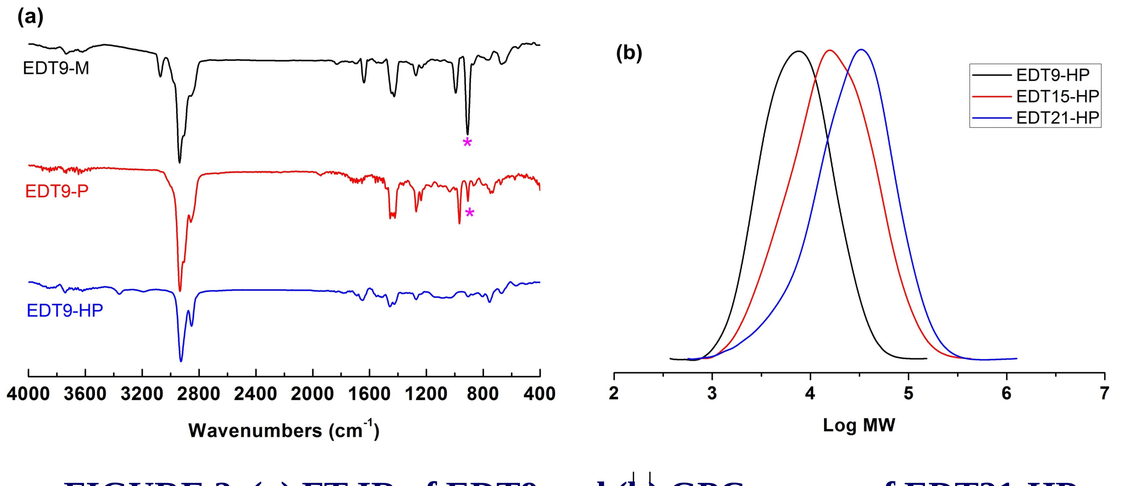


FIGURE 2 (a) FT-IR of EDT9 and (b) GPC curves of EDT21-HP, EDT15-HP, and EDT9-HP

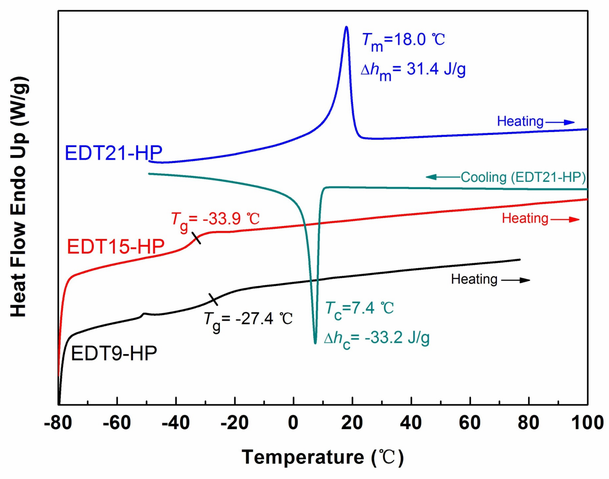


FIGURE 3 DSC curves of EDT21-HP, EDT15-HP, and EDT9-HP

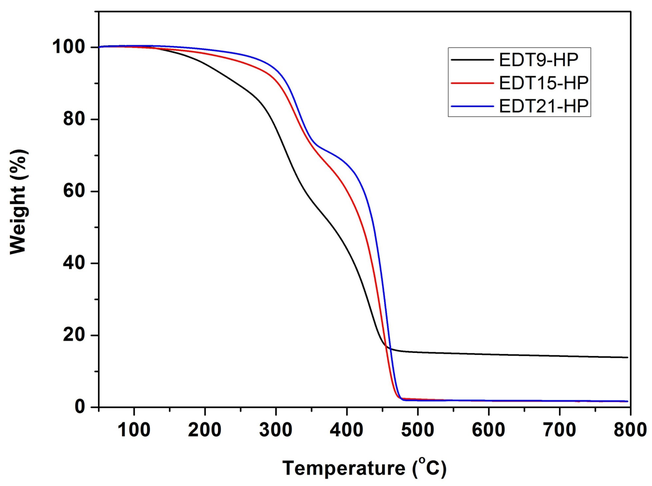


FIGURE 4 TGA traces of EDT21-HP, EDT15-HP, and EDT9-HP

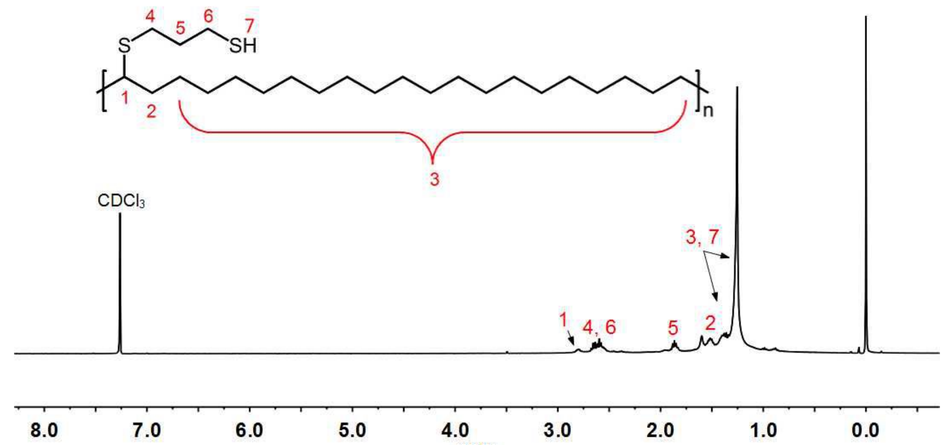


FIGURE 5 ^{1}H NMR of PE containing thiol groups, EDT21-HPT

Conclusions

(1) Three precisely-defined polymers containing dithiane groups spaced by methylene sequences of 8, 14 or 20 carbon atoms were successfully synthesized by the combination of ADMET polymerization and hydrogenation.

(2) Solid state of these ADMET polymers changed from semicrystalline to fully amorphous state with the incorporation of more pendent dithiane moieties. Thermal stability of these polymers decreased with incorporation of more dithiane moieties and displayed a two-stage decomposition profile.

(3)The present work offered a method of introducing an attractive new building block in ADMET polymers.

References

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[2] S. F. Song, Y. T. Guo, R. Y. Wang, Z. S. Fu, J. T. Xu, Z. Q. Fan. *Macromolecules* 2016, 49, 6001-6011.

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