

Novel Bifunctional Amide-Based Initiator for the Atom Transfer Radical Polymerization of Styrene with Ascorbic Acid Acetonide as Reducing Agent

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The most widely used initiators for ATRP are α -haloesters, but these class of compounds give rise to polymers with decidedly low thermal stability due to the ease with which they undergo decarboxylation. In the case of bifunctional initiators, severe heat treatment of the resulting polymers leads to cleavage of the chains and subsequent deterioration of mechanical properties, as well as loss of telechelcity (Figure 1), as already observed by Altintas et al. for polystyrene from ethylene bis(2-bromoisobutyrate) (Figure 2).[1]

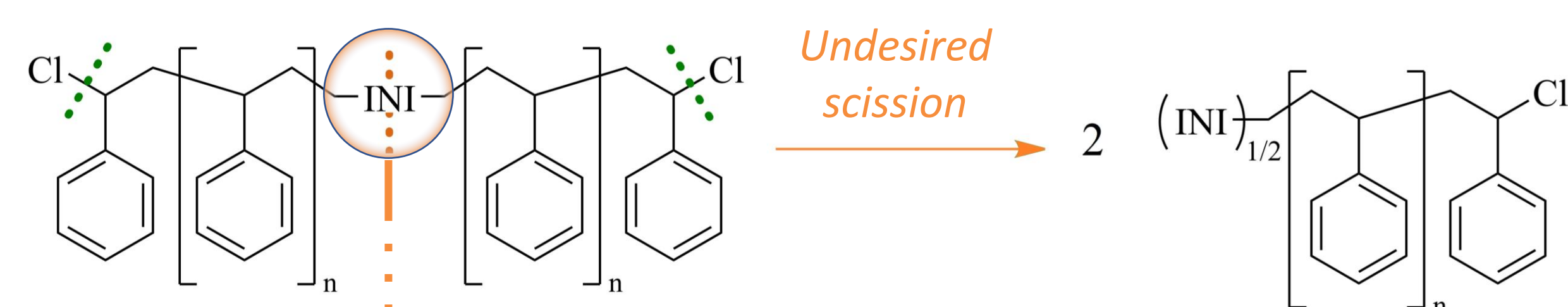


Figure 1

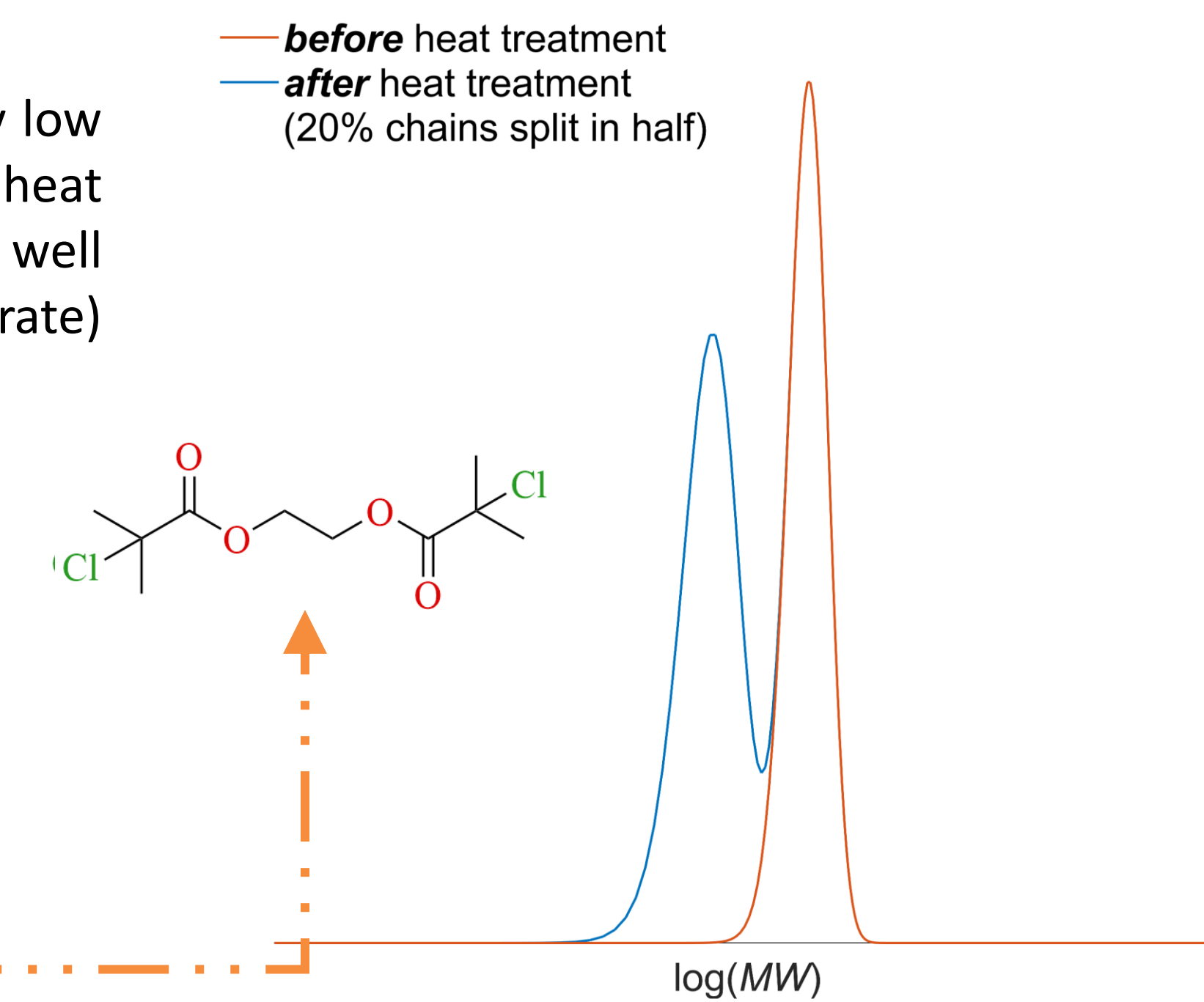
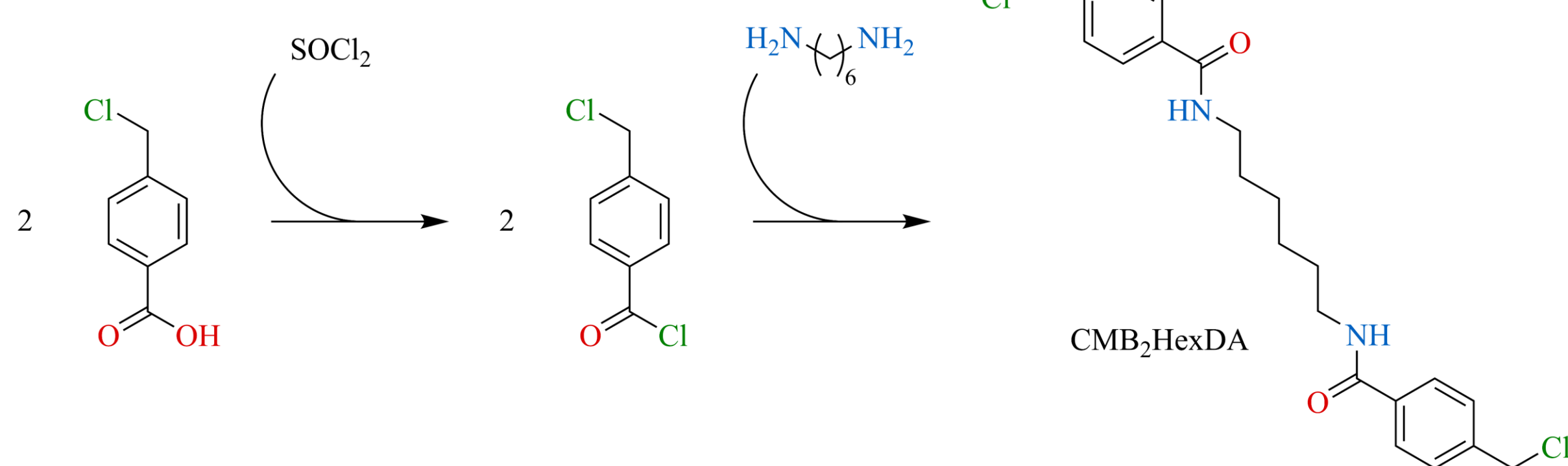
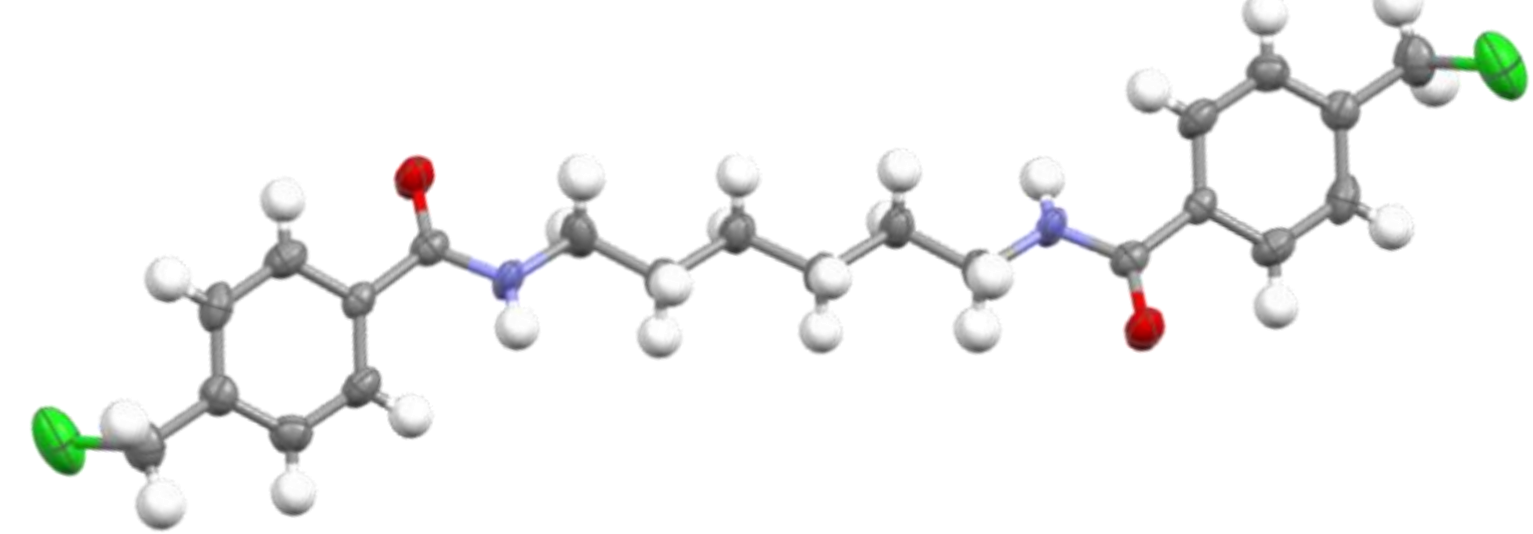


Figure 2

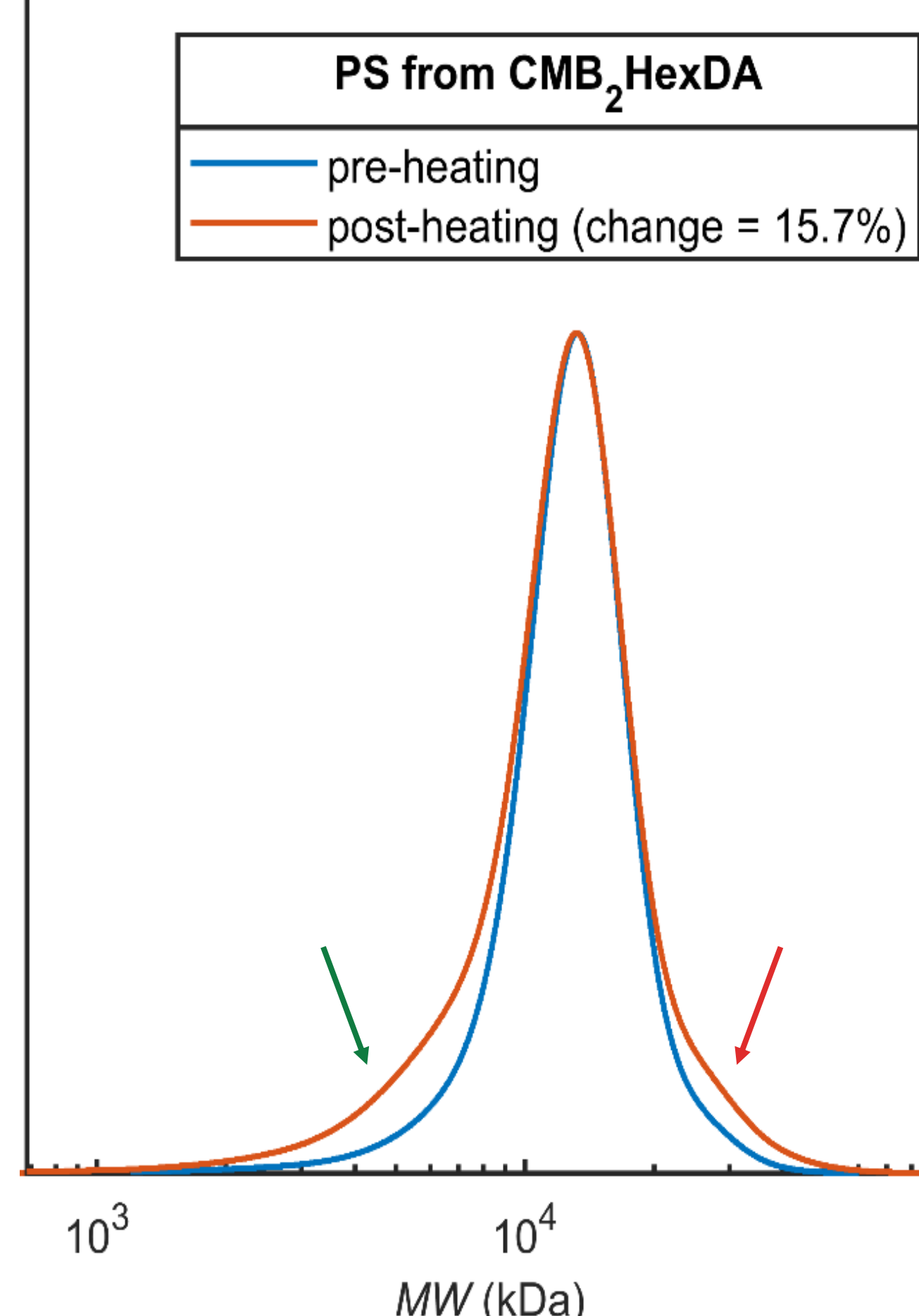
1) Two step synthesis of CMB₂HexDA (INI-Cl₂)



2) Characterization of the CMB₂HexDA

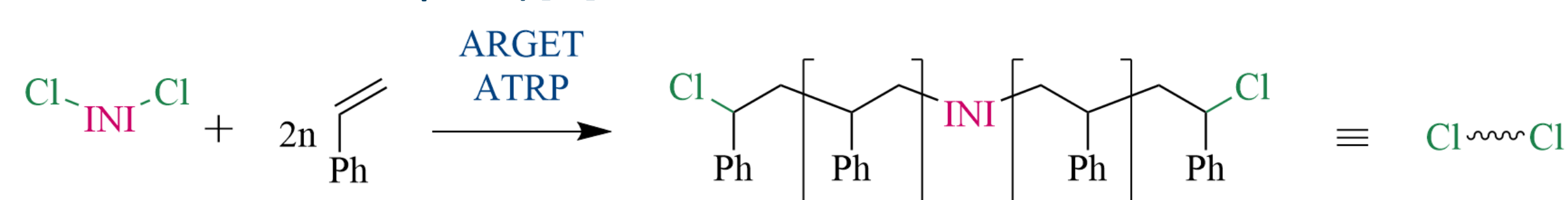


4) Comparison between GPC of α,ω -dichloropolystyrene before and after the thermal treatment

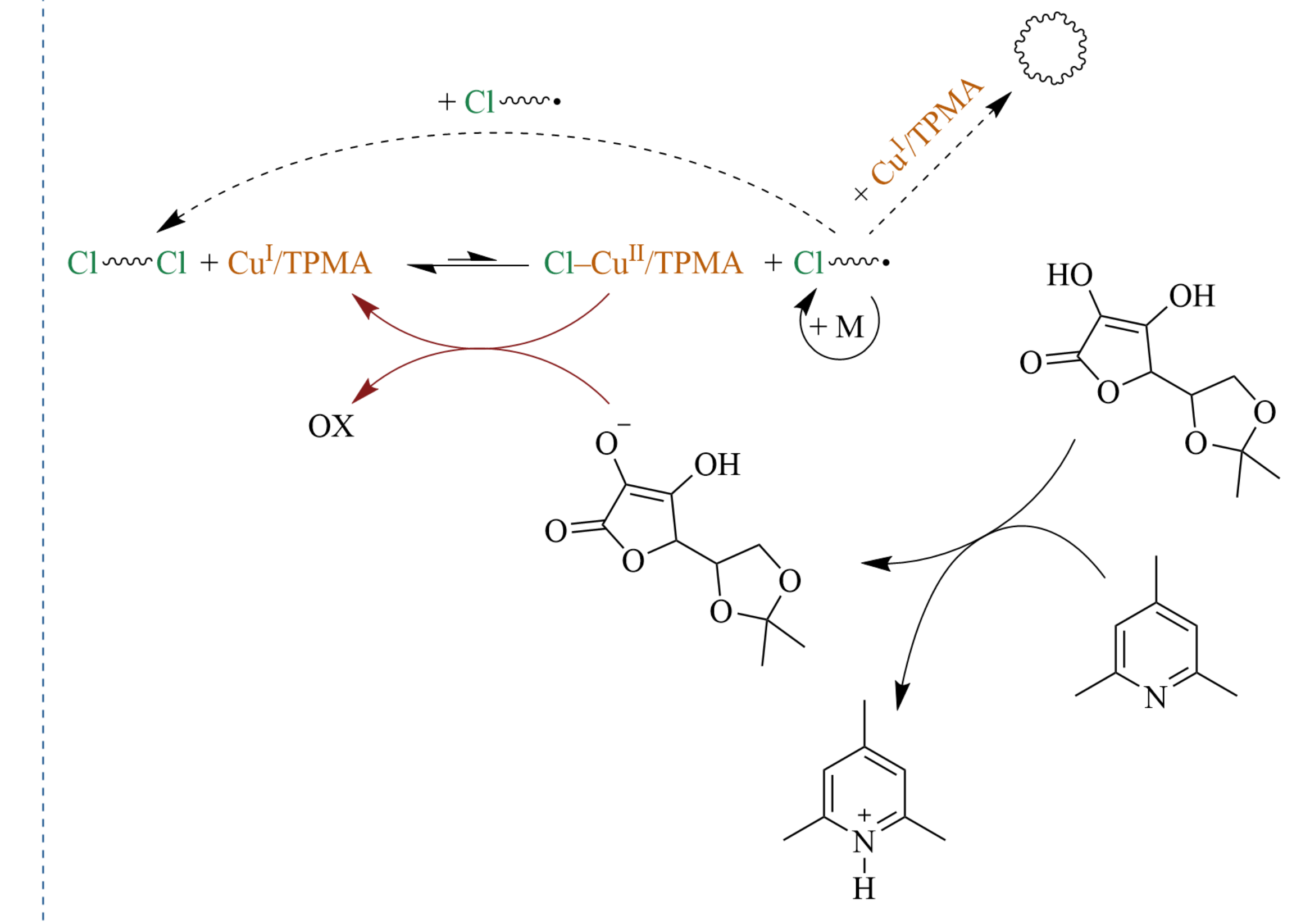


Polystyrenes with enhanced thermal stability are required for an industrial development being the extrusion temperature of polystyrene 150-220°C. Furthermore, since we have recently developed a method to obtain α,ω -dialkenopolystyrene (a useful intermediate for further post-functionalizations [2]) by solventless thermal dehydrogenation, is clear that the thermal stability is another time important. Herein we explore a possible solution by synthesizing a bifunctional benzamide initiator improving the thermal stability with respect to the ester ones.

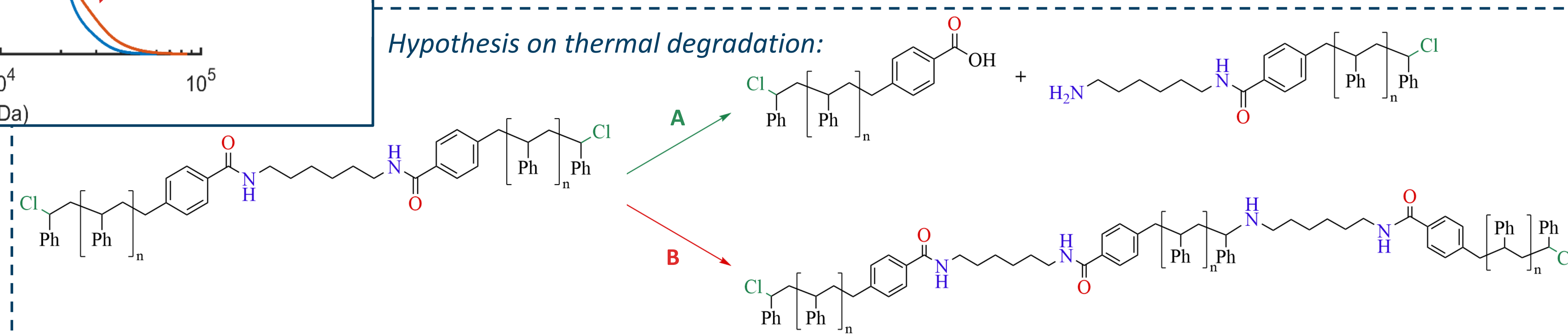
3) ARGET ATRP of styrene with ascorbic acid acetonide as reducing agent and TMP as the organic base (the latter needed to produce, in situ, the ascorbate anion which has a higher reducing power than the protonated counterpart)[3].



via the following mechanism



Hypothesis on thermal degradation:



References:

- [1] Altintas, O. et al.; Polymer Chemistry, 2015, 6, 2854;
- [2] Thesis Piccinini «Polistirene telechelico da ARGET ATRP e sue post funzionalizzazioni, nell'ottica di uno sviluppo industriale»;
- [3] Ghelfi, Ferrando, Longo, Buffagni WO 2019/215626 A1