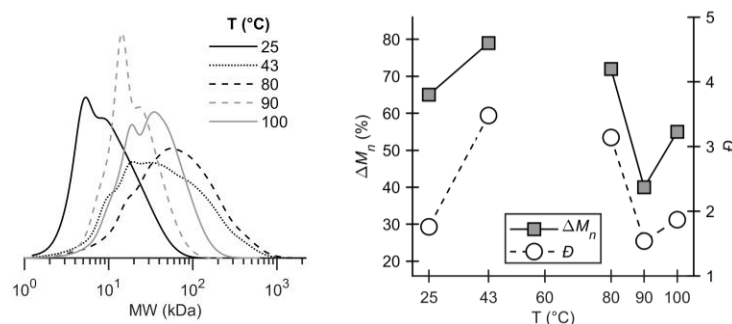


## Branched polystyrene by ARGET ATRP, from a bifunctional initiator and no cross-linking agents

The production of branched and crosslinked polymers via Atom Transfer Radical Polymerization (ATRP) is a well-known and widely employed practice owing to the control allowed over the reaction. In the polymerization of styrene, the addition of specific crosslinking reagents is required since it does not branch on its own [1-3]. Recently, we reported that at certain polymerization conditions crosslinked polystyrene can form even without the addition of branching / crosslinking molecules [4,5]. When performing an Activators Regenerated by Electron Transfer (ARGET) ATRP using: *i*) an excess of reducing agents (in our case ascorbic acid, H<sub>2</sub>AA, and sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>), *ii*) a bifunctional initiator (ethyl 2,2-dichloropropionate, DCPE) and *iii*) a slightly polar solvent mixture (ethyl acetate with ethanol); gelation spontaneously occurs at certain temperatures (Figure 1).



**Figure 1:** GPC analyses of the PS obtained at different T (18 h) in VSt:VAcOEt:VEtOH = 3:3:1 mL. With n%EDCP : n%CuCl<sub>2</sub> : n%TPMA : n%AAH<sub>2</sub> : n%Na<sub>2</sub>CO<sub>3</sub> = 1.06 : 0.2 : 0.2 : 0.5 : 1.5 mol%.

Styrene polymerization begins as a well-behaved ARGET ATRP process [4], with chain growth by polyaddition. However, a decisive drift towards a polycondensation mechanism is observed soon. This is due because polystyrene radicals terminate mostly by coupling. Since the chains are bifunctional, livingness is preserved at both ends. This is true only when the coupling is intermolecular. On the contrary, when the process is intramolecular a ring is formed, and the apical functionalities are lost. If during this last process linear chains are entangled, this phenomenon should lead to physical crosslinking points ( branched catenanes).

In our previous works we studied mostly the competition between polyaddition and polycondensation, since we had to favor the addition reaction to obtain controlled linear macromolecules (low polydispersity and predictable average molecular weights). While ATRP usually is a tool that minimizes termination reactions, these instead occur easily when the polycondensation regime arises. This fact stresses the importance of the competition between intramolecular and intermolecular coupling, whose result determines if branching happens. To further our understanding of the system a kinetic approach is thus needed, meaning that we should address the moment at which deviations from the expected ARGET ATRP arise. Moreover, we should address which are the variables that influence the appearance of this discontinuity in kinetic behavior.

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