



Controlled free radical copolymerization of styrene and divinylbenzene by bimolecular NMRP using TEMPO

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Abstract – Nitroxide-mediated radical copolymerization (NMRP) of styrene and divinylbenzene using 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) as the controller and tert-butylperoxy-2-ethylhexyl carbonate (TBEC) as initiator was performed with the purpose of enhancing the reaction rate while keeping the controlled and living characteristics of the polymer synthesized (low polydispersity and molecular weights increasing linearly with conversion).

Living free radical polymerization is a promising route for the production of polymers with highly controlled microstructure (narrow molecular weights distributions). Living free radical polymerization is different from the conventional free radical polymerization route due to a reversible reaction. In which the chains experience cycles of radical activation-deactivation over the period of polymerization, and as result all the chains have a chance to grow approximately to equal lengths, which leads to a low polydispersity of the final product. Free radical polymerization pathways, are more versatile in relation to viable monomers and are more robust to impurities than traditional ionic polymerization methods, and so offer an attractive alternative production route to polymers with controlled structures.

One disadvantage of controlled radical process is related to the low polymerization rate due to the reversible reaction that maintains the polymer chain as a dormant species for long periods of time. In the literature almost all papers on NMRP process use BPO or AIBN as initiator. The objective of this work is to try to enhance the polymerization rate by using a different kind of initiator (TBEC) that presents a lower decomposition rate compared to BPO and AIBN.

Most of the published works about NMRP consider the homopolymerization of styrene. Tuinman et al. (2006) performed the co-polymerization of styrene-divinylbenzene (Sty-DVB), but using BPO as initiator. In this work the copolymerization of styrene and divinylbenzene by living polymerization (NMRP) using TEMPO as controller, and TBEC as the initiator was investigated. All the experiments were performed in ampoules. To better understand this system, many experiments were performed at different temperatures, DVB concentrations, initiator concentrations and molar ratios between controller and initiator.

Table 1: Effects of studied factors on variables of interest.

	Conversion	Molecular weights	Poydispersity
↑ Molar ratio [TEMPO]/ [TBEC]	↓	↓	↓
↑ Temperature	↑	—	—
↑ TBEC and TEMPO concentration	↑	↓	↓
↑ Divinylbenzene concentration	—	—	—

↑ increase; ↓ decrease; ↑ slight increase; ↓ slight decrease; — no detectable effect

References

[1] E. Tuinman, N. McManus, M. Roa-Luna, E. Vivaldo-Lima, L. Lona, A. Penlidis, Journal of Macromolecular Science. Pure and Applied Chemistry, 43 (2006), 995-1011.