

Visible light-induced controlled/“living” radical polymerization of styrene

A. N. PATWA, N. S. TOMER[‡], R. P. SINGH*

National Chemical Laboratory, Organic Chemistry (Synthesis)[‡], and Polymer Chemistry Division*, Pune-411008, India

E-mail: singh@poly.ncl.res.in; www.ncl-india.org

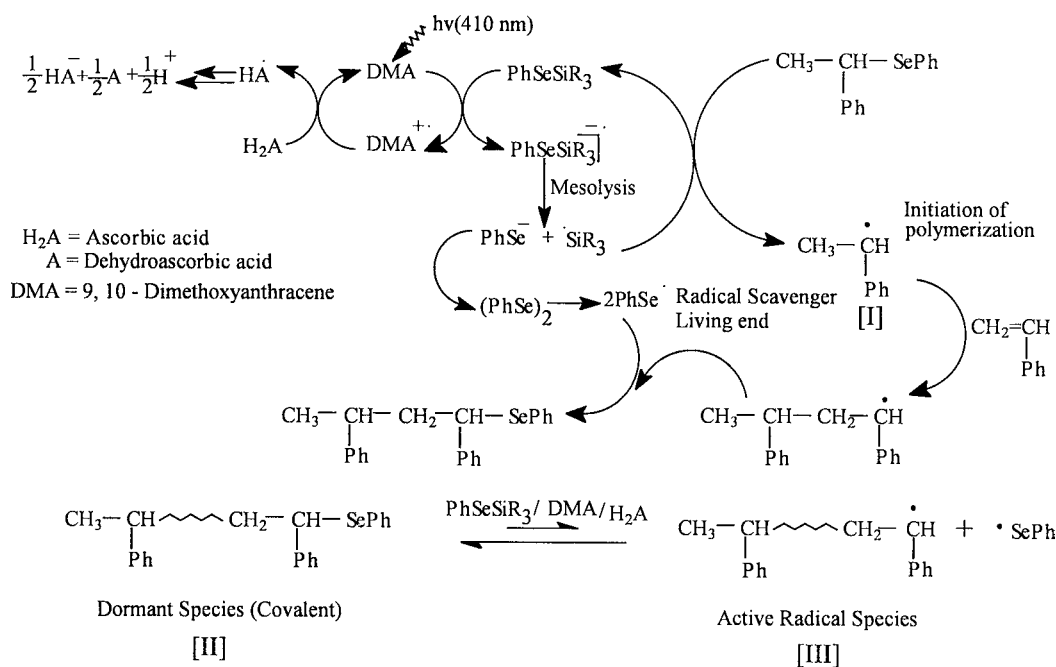
Well-defined polystyrene with low polydispersity index having methyl and phenylseleno (–SePh) groups at α - and ω -chain ends, respectively, was afforded via a controlled/“living” radical polymerization using a new initiating system: (1-phenylethyl)seleno benzene [1-PESePh]/tert.butyl diphenyl (phenylseleno) silane [PhSeSiR₃] and absorbing visible light at room temperature. A novel design initiating living radical polymerization in a catalytic fashion is described. The polymer yields and number average molecular weight (M_n) of the resulting polymer increased with reaction time. Further, a linear relationship was found for a plot of M_n versus polymer yield. These results indicate that this polymerization proceeds through a living radical mechanism.

Recently several remarkable methodologies [1–7] have been developed to design macromolecules via living radical polymerization. Among them, the iniferter method discovered by Otsu *et al.* [8–10] is an effective way to synthesize well-defined polymers [11, 12], which do not polymerize via an ionic mechanism. An iniferter is an initiator, which also functions as chain transfer and/or primary radical terminator.

Organoselenium compounds are useful for synthetic chemistry [13] and photochemistry [14, 15]. Kwon *et al.* [16, 17] reported that photo-polymerization in the presence of diphenyl diselenide afforded polystyrene carrying phenylseleno groups at both chain ends. The generation of [PhSeSiR₃][–] was envisioned through one electron reductive processes involving 9,10-dimethoxyanthracene (DMA) as a light absorbing (>300 nm) electron donor and ascorbic acid (H₂A) as co-reductant [18] (Scheme I).

The objective of the present invention is to provide a narrow polydispersity polymer with photoinitiation at room temperature and providing controlled/“living” radical polymerization utilizing visible light thereby avoiding the use of free radical initiator. Here, we report a novel controlled/“living” radical polymerization by photo electron transfer (PET) process using 1-PESePh/PhSeSiR₃ as the initiating system having methyl (–CH₃) and phenylseleno (–SePh) group at α - and ω -chain ends, respectively, of the resulting polystyrene.

Polymerization of styrene was carried out by irradiation with a 400 W medium pressure mercury lamp



Scheme I

*Author to whom all correspondence should be addressed.