6692 *Macromolecules* **1995**, *28*, 6692–6693

Kinetics of Decomposition of 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine and Its Implications on Nitroxyl-Mediated Styrene Polymerization

Irene Li and B. A. Howell

Center for Applications in Polymer Science, Central Michigan University, Mount Pleasant, Michigan 48859

K. Matyjaszewski and T. Shigemoto

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

P. B. Smith and D. B. Priddy*

The Dow Chemical Company, Midland, Michigan 48667

Received May 3, 1995
Revised Manuscript Received July 20, 1995

Currently, the most studied example of living free-radical polymerization is nitroxyl-mediated styrene polymerization. This chemistry relies upon the extremely facile and selective ability of nitroxyl radicals to trap carbon-centered radicals and the apparent reversible nature of the C−O bond. Solomon and Rizzardo[1] first reported this chemistry in the mid-1980s but used it to prepare mainly low molecular weight materials. Georges *et al.*[2] reported, in 1993, the use of this chemistry to prepare narrow-polydispersity (<1.5) polystyrene. Over the past 2 years several research groups have been studying nitroxyl-mediated styrene polymerization. The work of Georges *et al.* has focused mainly upon increasing the rate of nitroxyl-mediated styrene polymerization initiated using benzoyl peroxide (BPO). They report that the nitroxyl-mediated styrene polymerization rate is significantly increased if conducted in an acidic environment.[3] The mechanism of this effect is not yet understood. Matyjaszewski *et al.*[4] have focused on the theoretical aspects of nitroxyl-mediated styrene polymerization in the absence of an added initiator. Recently, Hawker[5] synthesized **I** (model of the nitroxyl-mediated styrene polymerization chain end; Scheme 1) and demonstrated its use as an initiator. No effort was made to utilize **I** as a chain-end model to help determine the mechanism of the polymerization. Also, no acid was added to nitroxyl-mediated styrene polymerization initiated using **I**.

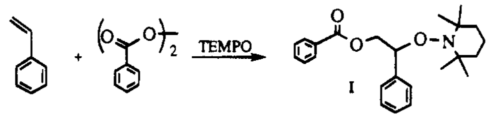
The published data of these researchers consistently show the lack of truly narrow polydispersity, and the polydispersity obtained is generally proportional to the molecular weight being produced.

Georges *et al.* hypothesized that the lack of ability to make truly monodisperse PS using nitroxyl-mediated styrene polymerization was caused by continuous initiation of new PS chains during the polymerization.[3] To suppress the spontaneous polymerization mechanism, camphorsulfonic acid (CSA) was added. They observed that, rather than decreasing the rate of polymerization and the polydispersity, both increased.[3]

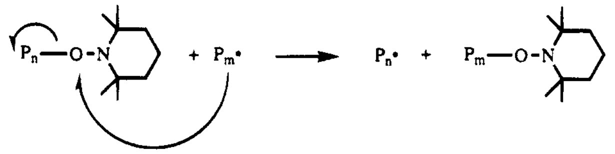
Matyjaszewski *et al.* have proposed that the mechanism of nitroxyl-mediated styrene polymerization includes degenerative chain transfer (Scheme 2).[6] Their evidence in support of this mechanism is the observation that polydispersity narrows as the polymerization temperature is increased. At the higher temperature the rate of degenerative chain transfer increases, causing the polymer chain lengths to average.

One of the tools that has been used which has shed significant light on the development of an understanding of polymerization processes is the use of small molecules to model the living chain end.[7] In this study we synthesized 2,2,6,6-tetramethyl-1-(1-phenylethoxy)-piperidine[8] (TMPEP) and studied both its thermal decomposition and its use as a polymerization initiator.

Scheme 1. Synthesis of Initiator for Nitroxyl-Mediated Styrene Polymerization



Scheme 2. Degenerative Chain-Transfer Mechanism for Nitroxyl-Mediated Styrene Polymerization



HPLC and ^{1}H-NMR were utilized to follow the thermal decomposition kinetics of TMPEP in 1,2,4-trichlorobenzene (TCB), and DMSO-d_6 and toluene, respectively. Decomposition of TMPEP results in mainly the formation of styrene. However, as the decomposition proceeds, 2,3-dipenylbutane (DPB) and ethylbenzene (EB) begin to appear (Figure 1). The decomposition of TMPEP follows first-order kinetics with activation energies of 28.4 and 24.2 kcal/mol in TCB and DMSO-d_6, respectively (Figure 2).

Nitroxyl-mediated styrene polymerization using TMPEP as initiator was studied in both neutral and

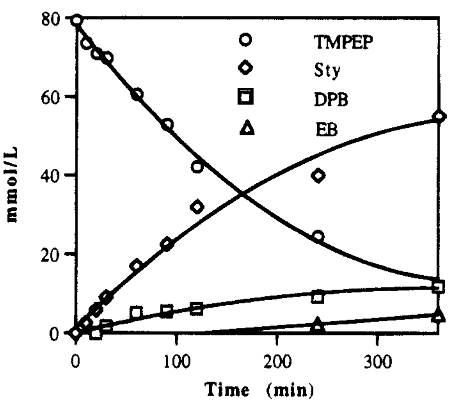


Figure 1. Decomposition of TMPEP in TCB at 140 °C.

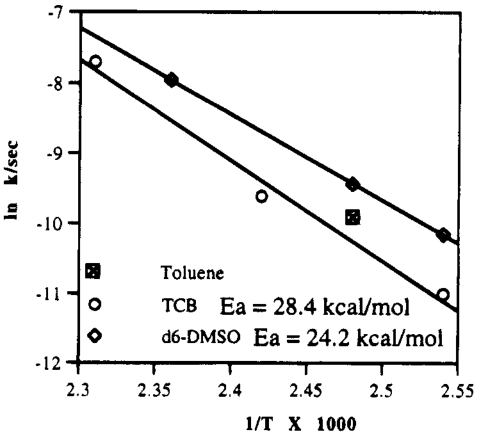


Figure 2. Arrhenius plot of TMPEP decomposition in various solvents.

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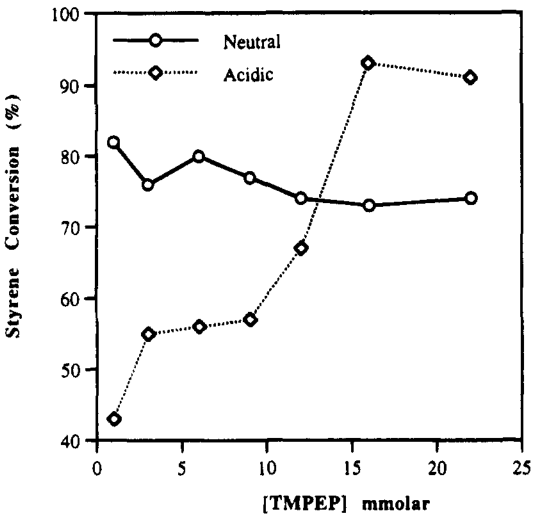


Figure 3. Effect of acid upon styrene conversion after 4 h at 140 °C vs TMPEP concentration.

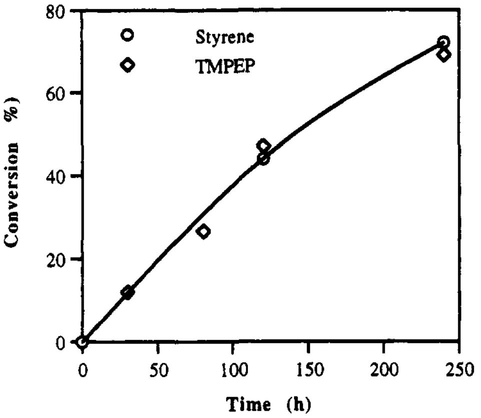
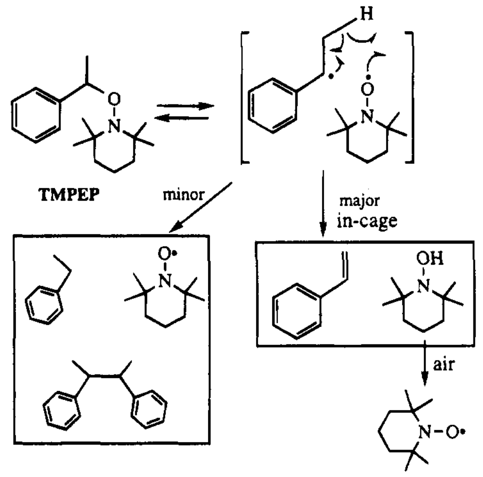


Figure 4. Comparison of the rates of styrene polymerization (inititated using TMPEP (12 mmol/L) under acidic conditions) and TMPEP decomposition at 140 °C.

acidic (i.e., 2000 ppm CSA) conditions. Under acidic conditions, increasing the TMPEP concentration increases the polymerization rate. However, under neutral conditions, the polymerization rate slightly decreases (Figure 3). At low TMPEP concentrations, the polymerization rate under neutral conditions is faster than that in the presence of CSA due to more efficient initiation by the spontaneous mechanism.[9] As the concentration of TMPEP increases in the neutral environment, nitroxyl-mediated styrene polymerization begins to dominate. Since the rate of nitroxyl-mediated styrene polymerization is slower than conventional styrene polymerization, the polymerization rate decreases as TMPEP concentration increases. Since CSA suppresses spontaneous initiation, the rate of styrene polymerization under acidic conditions increases with TMPEP initiator concentration. At high initiator concentration, a crossover results where the rate of the acid-catalyzed polymerization becomes faster than that in the neutral environment. This confirms that CSA indeed accelerates nitroxyl-mediated styrene polymerization; i.e., once the initiator concentration is high enough to dominate the contribution of the spontaneous initiation, nitroxyl-mediated styrene polymerization is faster in an acidic environment.

Scheme 3. Proposed Mechanism of TMPEP Decomposition



Comparison of the relative rates of styrene polymerization and TMPEP decomposition at 140 °C shows that the two are competitive (Figure 4). This indicates significant decomposition of the chain ends during polymerization.

Scheme 3 summarizes our hypothesized decomposition chemistry of TMPEP. We believe that the nitroxyl–polystyryl chain end undergoes similar decomposition chemistry during nitroxyl-mediated styrene polymerization and is likely a major source of polydispersity broadening.

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MA950593B