**ABSTRACT**

The evolution of chain transfer agents (CTAs) was studied for the polymerization of styrene by reverse iodine transfer polymerization (RITP). CTAs are formed during an inhibition period where the radical initiator reacts with molecular iodine. These compounds were studied using *in situ* $^1$H nuclear magnetic resonance (NMR) experiments. The molecular weight of polystyrene was evaluated with size exclusion chromatography (SEC) and $^1$H NMR. Structural analysis of the resulting polymers was done using $^1$H NMR spectroscopy and matrix-assisted laser desorption/ionization time-of-flight (MALDI−ToF) mass spectrometry. The inhibition period of styrene polymerized by RITP was much shorter than expected. This is due to the consumption of iodine in the reaction between styrene and iodine which reversibly forms 1,2-diiodoethylbenzene leading to the subsequent formation of 1-phenylethyl iodide (1-PEI). For the first time the formation of 1,2-diiodoethylbenzene as an intermediate structure in RITP of styrene has been proven experimentally. The active role of 1-PEI in the polymerization process is documented through the detection of phenylethyl end groups by MALDI−ToF and $^1$H NMR.