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Crosslinking nitroxide-mediated radical copolymerization of styrene with divinylbenzene

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ABSTRACT

Results from the crosslinking kinetics of nitroxide-mediated radical polymerization (NMRP) of styrene (STY) in the presence of a small amount of divinylbenzene (DVB) are presented. The performance of styrene polymerization with N-tert-butyl-N-(2-methyl-1-phenylpropyl)-O-(1-phenylethyl) hydroxylamine (referred to as TIPNO-based alkoxyamine or I-TIPNO) is first examined to see if the system exhibits controlled behavior. Then, typical profiles for crosslinking NMRP of STY/DVB in the presence of this alkoxyamine (as controller) are presented and contrasted with crosslinking under regular free radical polymerization, and NMRP of styrene (in the absence of crosslinker). Subsequently, the performance of crosslinking NMRP is evaluated based on rate of polymerization, molecular weights, polydispersity values and gel content under different operating conditions (different crosslinker and nitroxide concentrations). Finally, prediction profiles from a mathematical model are contrasted with experimental data to check the validity of the developed model with respect to both NMRP and crosslinking NMRP of STY/DVB with this TIPNO-based alkoxyamine.

1. Introduction

A crosslinked polymer can be defined as a macromolecule in which essentially all units are connected to each other. A highly crosslinked polymer results in a polymer network which is characterized by having an "infinite" molecular weight. Crosslinked polymers exhibit completely different properties when compared to linear polymers with identical chemical composition. Crosslinking is especially important from a commercial point of view; many commercial polymers owe their value to their crosslinked structures, which can range from slightly crosslinked materials (as in the case of elastomers) to highly crosslinked materials (as in the case of thermosets). Crosslinked polymers are very important in several areas, including medicine, biotechnology and agriculture, with multiple applications such as super-absorbent materials, chromatography packings, ion-exchange resins, dental restorative materials, and additives in surface coatings. They are also used in cosmetics and pharmaceuticals, drug-delivery systems, artificial organs, sensors, optics and electronics [1].

Regular free radical copolymerization (FRP) of a vinyl monomer with a small amount of a divinyl monomer offers one of the simplest routes for the preparation of crosslinked

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Abbreviations: AIBN, azobisisobutyronitrile; ATRP, atom-transfer radical-polymerization; BPO, benzoyl peroxide; CRP, controlled radical polymerization; DMA, dynamic mechanical analysis; DRI, differential refractometer; DVB, divinylbenzene; FRP, free radical polymerization; GC, gas chromatography; I-TIPNO, N-tert-butyl-N-(2-methyl-1-phenylpropyl)-O-(1-phenylethyl) hydroxylamine; LALLS, low-angle laser light scattering; MALLS, multi-angle laser light scattering; MW, molecular weight; NMR, nuclear magnetic resonance; NMRP, nitroxide-mediated radical polymerization; PDI, polydispersity index; RAFT, reversible addition-fragmentation chain-transfer; RALLS, right-angle laser light scattering; SEC, size exclusion chromatography; STY, styrene; TBS, *t*-butyl styrene; TEMPO, 2,2,6,6-tetramethyl-1-piperidinyloxy; THF, tetrahydrofuran; UV, ultraviolet.

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Table 1
Relevant literature on crosslinking NMRP.

Group	Main studies	Comments
Solomon and coworkers [3,4]	• Synthesized statistical and star microgels of TBS/DVB via NMRP using a unimolecular initiator; solution polymerization with benzene • Multimodal distribution observed in the DRI detector • Displayed a considerably higher molecular weight through SEC-MALLS than that determined with SEC using polystyrene standards for calibration	• First group to report NMRP for preparing crosslinked networks • No trajectory for conversion or MWs • No mention of homogeneity • Attempts to prepare microgels using AIBN (instead of the alkoxyamine), at the same concentrations of reactants used in their study, gave extensive gelation • Impossible to make star microgels via FRP, as there are no functionalities at the ends of the chain to facilitate the formation of such molecular architecture
Fukuda and coworkers [6,7]	• Copolymerization of styrene with a small amount of 4,4′-divinylbiphenyl, in the presence of an oligomeric polystyryl adduct (PS-TEMPO), at 125 °C • Evaluated pendant vinyl reactivity before the gel point – The pendant vinyl concentration before the gel point (C_p) was determined using UV spectroscopy; the plot of C_p vs. styrene polymerization (C_1) for NMRP showed an almost linear behavior; in contrast, the same plot for FRP showed high values of C_p at relatively low C_1, which indicates the consumption of pendant double bonds via intramolecular (cyclization) reactions • Evaluated gelation behavior – Determined swelling ratio, gel content and molecular weights between crosslinks (M_c) according to Flory and Rehner – Showed that the polymer synthesized under NMRP swelled more and the gelation was delayed. In addition, M_c was claimed to be much higher for NMRP samples. However, M_c values were shown for low conversions only!	• Study completed at almost the same time as Solomon and coworkers, above • Conclusions about network homogeneity are made based on the pendant vinyl concentration before the gel point! • M_c is an average value and does not give any information about the distribution, which basically dictates the homo- or hetero-geneity of the network! • Made a sweeping statement in the conclusions that NMRP would be more homogenous than FRP based on DMA studies, but no experimental evidence was offered
Fréchet and coworkers [8,9]	• Solution copolymerization of styrene and divinylbenzene in the presence of different NMRP controllers to produce porous poly(styrene-co-divinylbenzene) monoliths for chromatographic applications	• Showed that unique porous structure resulted not from the controlled free radical nature of the polymerization, but rather from the effect of the elevated reaction temperature on the solvency of the specific porogen employed
Zetterlund and coworkers [10–15]	• STY/DVB ($f_2^0 = 0.01$) with PS-TEMPO initiator at $T = 125$ °C in both bulk and miniemulsion – Pendant double bond conversion determined from combination of NMR and GC – Higher crosslink density and rate of polymerization in bulk compared to miniemulsion – Detailed analysis of inter- and intra-molecular pendant conversion with monomer conversion carried out for bulk/solution and miniemulsion – Comparison of experimental gelation points with theoretical predictions based on Flory–Stockmayer (FS) gelation theory for solution and miniemulsion • STY/DVB copolymerization via NMRP (with TEMPO) at 125 °C compared to STY/DVB copolymerization via FRP at 70 °C, in micro-suspension – Mechanical properties of individual micron-sized particles were compared – Crosslinked polymer particles prepared by NMRP exhibited different mechanical properties than crosslinked particles prepared by FRP at low to intermediate conversion: compressive strength, deformation at break and breaking energy remained approximately constant from low to high conversion in FRP, while in NMRP these quantities increased linearly with conversion	• Relatively high pendant conversion, even at low polymer content in bulk, could be indicative of intramolecular crosslinking • No comparison with FRP in bulk was presented • Showed that, at low to intermediate conversion, crosslinked particles synthesized through NMRP exhibited different mechanical characteristics than particles synthesized through FRP; however, at higher conversions (>70%) both systems exhibited very similar mechanical properties
Sato and coworkers [16]	• Polymerization of DVB in the presence of nitrobenzene as a retarder, using excess dimethyl 2,2′-azobisisobutyrate to promote the formation of hyperbranched structures, at 70 °C and 80 °C	• No comparison with FRP in bulk was presented • No mention of homogeneity