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Quantitative Study on the Homogeneity of Networks Synthesized by Nitroxide-Mediated Radical

Copolymerization of Styrene and Divinylbenzene

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Abstract

The nitroxide-mediated radical copolymerization (NMRP) of styrene and divinylbenzene was studied

using a Monte Carlo simulation. The model predictions were validated by comparing to experimental

results gathered from literature. Polymer network microstructure was studied through complete molar

mass distribution (including the gel part) of the polymer and by quantitative representation of the

homogeneity of the network, i.e. the broadness of the distribution of the molar mass between

crosslinking points (Mc). The nitroxide mediated radical polymerization led to a narrower Mc

distribution compared to free radical polymerization, and the average Mc did not change significantly

through the reaction. The narrower Mc distribution is an indicator of more homogenous network and

clarifies many conflicting statements in the literature on homogeneity of the network obtained by

controlled radical polymerization.

Keywords: controlled radical polymerization, crosslinking, network homogeneity

Introduction

Crosslinked polymers have been a subject of continuous interest since the beginning of polymer

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