PNG 2008

Polymer Networks: Chemistry, Physics, Biology and Applications

19th Polymer Networks Group Meeting
22nd to 26th June, 2008
Larnaca, Cyprus

PNG 2008
Program and Abstracts

www.pngcyprus.org

Kinetic Modeling of the Molecular Architecture of Cross-Linked Copolymers Synthesized by Controlled Radical Polymerization Techniques

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A recently developed general kinetic approach[1,4], based upon population balances in terms of generating functions, is applied to the modeling of the molecular architecture of cross-linked copolymers produced through controlled radical polymerization techniques, namely nitroxide-mediated radical polymerization (NMRP) and atom-transfer radical polymerization (ATRP). Dynamic predictions of molecular weight distributions, sequence length distributions and *z*-average mean square radius of gyration of the products are therefore possible before and after gelation (whenever it occurs) and considering complex irreversible kinetic schemes. A detailed description of the influence of the kinetic parameters on the network structure of these polymers is therefore possible in the framework of this method.
The model chemical systems Styrene + Divinylbenzene (S/DVB) and Methyl Methacrylate + Ethylene Glycol Dimethacrylate (MMA/EGDMA) are experimentally investigated in order to assess the prediction capabilities of the aforementioned approach. The NMRP technique is used to carry out the copolymerization S/DVB mediated by TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy). The copolymerization MMA/EGDMA is performed using ATRP initiated by methyl α-bromophenylacetate (MBPA) and mediated by copper bromide (CuBr) ligated with 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA). Measurements of absolute molecular weights and *z*-average radius of gyration of the copolymers are performed for different times of polymerization using a SEC system with a refractive index detector coupled with MALLS.
A small number of parameters describing gel effect, relative propagation on pendant double bonds and cyclization reactions are fitted using these experimental measurements. Modeling studies for the system S/DVB are more complex due to the presence of m- and p-DVB (with different reactivities) in the commercial DVB[5]. For both systems, most of the kinetic parameters used in the simulations are collected from previous studies[6-9]. We show that a good agreement between measurements and predictions is observed considering different operation conditions (amount of cross-linker, presence of chain transfer agent) and therefore a reliable description of some aspects of the molecular architecture of these products can be achieved. These results can be used to design hyperbranched polymers or networks with an improved control on their structure compared to those obtained by conventional radical polymerization.

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