

Photo-induced controlled/living copolymerization of styrene and acrylic acid and determination of reactivity ratios

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Abstract A controlled/living photopolymerization of styrene (St) and acrylic acid (AA) mediated by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /tetramethylethylenediamine (TMEDA) was performed in *N,N*-dimethylformamide using 4-bromomethylbenzophenone (4-BMBP) as photoinitiator at room temperature under UV irradiation. 4-BMBP was first used as ATRP initiator and photoinitiator. A well-defined poly(styrene-*co*-acrylic acid) with predetermined molecular weight and narrow molecular weight distribution was obtained. The kinetic rule of controlled free radical photopolymerization of St and AA was studied. The kinetic results showed that the obtained random poly(St-*co*-AA) copolymers produced narrow polydispersity (PDI) within the range of 1.25–1.32 when the conversion was beyond 16.5 %, which was characterized by GPC. The plots of number average molecular weight versus conversion and $\ln([M]_0/[M])$ versus time were linear, indicating a controlled/living photopolymerization process. The system proceeded

under mild and environmentally friendly conditions. The effects of initiator, catalyst, ligand, and vitamin C(VI) concentrations on polymerization process were investigated. The copolymers were characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (^1H NMR). The methods of Mayo-Lewis (ML), Kelen-Tudos (KT), and Yzrielev-Brokhina Roskin (YBR) were used to calculate the monomer reactivity ratios of controlled/living photopolymerization of St and AA at low conversions under selected conditions. The monomer reactivity ratios of St and AA were calculated to be $r_{\text{St}} = 0.82$ and $r_{\text{AA}} = 0.30$, respectively in this system. The living characteristics were demonstrated by chain extension experiment.

Keywords Styrene · Acrylic acid · Photoinitiated · Living polymerization · Reactivity ratio · Photopolymerization

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Introduction

Living polymerization has been successfully exploited for preparing polymers with designed architectures, narrow molecular weight distribution, and functionalities. Atom transfer radical polymerization (ATRP) is one of the most extensively studied living polymerization methods due to its versatility and compatibility with a variety of monomers, rendering the precision synthesis of functional polymers with well-defined compositions possible [1] since its discovery, independently by Sawamoto et al. [2] and Wang and Matyjaszewski [3, 4] in 1995. The advantage of ATRP originates from the high degree of freedom in the choice of alkyl halides as initiators, the transition-metal catalysts, solvents, monomers, etc. The mechanism of ATRP is illustrated in Scheme 1.

ATRP uses a deactivator that reacts reversibly with a propagating polymeric radical to yield a dormant chain and