Air-Stable and Recoverable Catalyst for Copper-Catalyzed Controlled/Living Radical Polymerization of Styrene; *In Situ* Generation of Cu(I) Species via Electron Transfer Reaction

GURKAN HIZAL, UMIT TUNCA, SERMIN ARAS, HUMEYRA MERT

Istanbul Technical University, Department of Chemistry, Maslak, 34469, Istanbul, Turkey

Received 27 May 2005; accepted 1 August 2005
DOI: 10.1002/pola.21048
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Copper-catalyzed controlled/living radical polymerization (LRP) of styrene (St) was conducted using the silica gel-supported $CuCl_2$/*N*, *N*, *N*′, *N*′, *N*″-pentamethyldiethylenetriamine (SG-$CuCl_2$/PMDETA) complex as catalyst at 110 °C in the presence of a definite amount of air. This novel approach is based on *in situ* generation and regeneration of Cu(I) via electron transfer reaction between phenols and Cu(II). Sodium phenoxide or *p*-methoxyphenol was used as a reducing agent of Cu(II) complexes in LRP. The number–average molecular weight, $M_{n,GPC}$, increases linearly with monomer conversion and agrees well with the theoretical values up to 85% conversion The molecular weight distribution, M_w/M_n, decreases as the conversion increases and reaches values below 1.2. The catalyst was recovered in aerobic condition and reused in copper-catalyzed LRP of St. For the second run, the number–average molecular weights increased with monomer conversion and the polydispersities decreased as the polymerization proceeded and reached to the value <1.3 at 81% conversion. The recycled catalyst retained 90% of its original activity in the subsequent polymerization. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 77–87, 2006
Keywords: copper-catalyzed living radical polymerization; electron transfer reaction; heterogeneous catalyst; phenol derivatives

INTRODUCTION

There has been a conspicuous growth in the development of controlled/living radical polymerization (LRP) techniques in the last decade. Metal-catalyzed LRP, mediated by Cu, Ru, Ni, and Fe metal complexes, is one of the most efficient methods to produce polymers in the field of LRP.[1–3] Since this method has a catalytic process, the appropriate catalyst can be said as the most important component in the polymerization. Among aforementioned systems, copper-catalyzed LRP in conjunction with alkyl halide initiator and amine ligand, often called as atom transfer radical polymerization (ATRP), received more interest. As taken into consideration, one of the major challenges faced by the metal-catalyzed LRP is the removal and recycling of the catalyst.[4] There are many examples of metal-catalyzed LRP catalysts immobilized on silica,[5–12] cross-linked polystyrene (PS) beads,[5,6] or Janda Jel resin.[13] Moreover, physically adsorbed multidante ligand such as hexamethyltriethylenetetramine (HMTETA) on silica gel has been utilized as supported catalyst for copper-catalyzed LRP.[14–16] Thereby, removal of cata-

Correspondence to: G. Hizal (E-mail: hizal@itu.edu.tr)
Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 44, 77–87 (2006)