

Reverse Atom Transfer Radical Polymerization of Methyl Methacrylate Initiated by *p*-Chlorobenzenediazonium Tetrafluoroborate

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Received 10 September 2002; accepted 14 April 2003

ABSTRACT: The controlled polymerization of methyl methacrylate (MMA) in bulk was initiated with *p*-chlorobenzenediazonium tetrafluoroborate (**1**) and Cu(II) or Cu(I)/Cu(II)/*N,N,N',N'',N'''*-pentamethyldiethylene triamine (PMDETA) complex system at various temperatures (20, 60, and 90 °C). The proposed polymerization mechanism is based on the Meerwein-type arylation reaction followed by a reverse atom transfer radical polymerization. In this mechanism, aryl radicals formed by the reaction with **1** and Cu(I) and/or PMDETA initiated the polymerization of MMA. The polymerization is controlled up to a molecular weight of 46,000 at 90 °C. Chain extension was carried out to confirm the controlled manner of the polymerization system. In all polymerization systems, the polydispersity index and initiator efficiency ranged from 1.10–1.57 to 0.10–0.21, respectively. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 2019–2025, 2003

Keywords: atom transfer radical polymerization (ATRP); methyl methacrylate; *p*-chlorobenzenediazonium tetrafluoroborate

INTRODUCTION

Various controlled or living radical polymerizations have been used^{1–5} for the synthesis of polymers having well-defined structures, narrow polydispersities, and quantitative end functionality from a wide range of radically polymerizable monomers. Atom transfer radical polymerization (ATRP) is one of the most versatile methods for the controlled radical polymerization of typical monomers including styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile.^{6–8} ATRP consists of the monomer, an initiator with transferable halogen, and a catalyst (composed of a transition-metal species with any suitable ligand). The ATRP process involves the reversible activation and deactivation of organic halides by a

redox reaction of transition-metal complexes. This rapid, reversible interchange reaction repeats until the monomer is consumed. Throughout the process, a very small instantaneous concentration of propagating radicals is produced that, therefore, suppresses the termination reaction leading to the formation of a polymer with a narrow polydispersity.

This type of ATRP has two major disadvantages: the toxicity of organic halides and the oxidation of the catalyst by oxygen in the air. To overcome these problems, reverse ATRPs have been described by Wang and Matyjaszewski,⁹ Moineau et al.,¹⁰ Chen and Qiu,¹¹ and Wang et al.¹² This process is usually based on a conventional radical initiator and transition-metal catalyst complex in a higher oxidation state.

The aryl diazonium salts react with halide ions in the presence of the corresponding Cu(I) salts yielding an aryl halide (Sandmeyer reaction).¹³ In this reaction, Cu(I) acts as a reducing agent converting the aryl diazonium cation to the free rad-

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 41, 2019–2025 (2003)
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