# Acrylonitrile-Containing Polymers via a Combination of Metal-Catalyzed Living Radical and Nitroxide-Mediated Free-Radical Polymerization Routes

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*Received 20 January 2006; accepted 10 March 2006*
*DOI: 10.1002/pola.21443*
*Published online in Wiley InterScience (www.interscience.wiley.com).*

**ABSTRACT:** 2-Phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy] ethyl 2-bromopropanoate was successfully used as an initiator in consecutive living radical polymerization routes, such as metal-catalyzed living radical polymerization and nitroxide-mediated free-radical polymerization, to produce various types of acrylonitrile-containing polymers, such as styrene–acrylonitrile, polystyrene-*b*-styrene–acrylonitrile, polystyrene-*b*-poly(*n*-butyl acrylate)-*b*-polyacrylonitrile, and polystyrene-*b*-polyacrylonitrile. The kinetic data were obtained for the metal-catalyzed living radical polymerization of styrene–acrylonitrile. All the obtained polymers were characterized with $^1$H NMR, gel permeation chromatography, and differential scanning calorimetry. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 3374–3381, 2006

**Keywords:** copolymerization; difunctional initiators; metal-catalyzed living radical polymerization; nitroxide-mediated radical polymerization; polyacrylonitrile; styrene–acrylonitrile

## INTRODUCTION

Polyacrylonitrile (PAN) is an industrially important polymer because of its well-known properties, such as good resistance to solvents, high rigidity, low gas permeability, and exceptional barrier properties to oxygen and carbon dioxide. PAN is produced extensively for fibers, which are used as the starting materials in the formation of carbon fibers.[1,2] However, copolymers of acrylonitrile (AN) with a variety of comonomers are used as plastics or rubbers.

Styrene–acrylonitrile (SAN) copolymers have improved weatherability, crack resistance, and barrier properties. Moreover, the copolymers of AN and alkyl acrylates display superior mechanical properties. The syntheses of PAN and its related copolymers are typically carried out via conventional free-radical polymerization.[3] However, this does not lead to polymers with well-defined molecular weights, narrow polydispersities, and chain-end functionality. The advent of living radical polymerization (LRP) has led to the synthesis of polymers with controlled molecular weights and well-defined architectures. Nitroxide-mediated free-radical polymerization (NMP)[4,5] and metal-catalyzed LRP[6–8] are the most widely used LRP methods. Thus, LRP techniques have been successfully applied to the preparation of PAN homo- and copolymers.[9–14]

The synthesis of block copolymers containing PAN segments has some difficulties, such as the blocking efficiency control and limited solubility in the common solvents used in LRP. Therefore, there have been a few studies on the preparation of block copolymers containing pure PAN segments in the backbone. The preparation of polyacrylonitrile-*block*-poly(*n*-butyl acrylate) was re-

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 44, 3374–3381 (2006)