



# Polymerization of methyl methacrylate and acrylonitrile in the presence of copper BIAN complex

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## Abstract

A novel type of copper-based regulating agents was first applied in radical polymerization of methyl methacrylate and acrylonitrile. It was shown that systems based on copper complex with redox-active bis(acetonaphthene) ligand ( $\text{dpp-BIAN} \leftrightarrow \text{CuCl}$ )<sub>2</sub>, carbon tetrachloride and different activating agents such as ascorbic acid or amines (*tert*-butylamine, diethylamine, triethylamine and pyridine) were capable to initiate polymerization of the above monomers in wide temperature range from 25 to 110 °C. The amine structure and basicity were found to make great impact on polymerization and molecular weight parameters of the obtained products. The systems developed are capable of conducting polymerization up to high monomer conversions in a wide temperature range leading to polymers with rather low molecular weight and moderate polydispersity. The most efficient system in terms of controlling the molecular weight characteristics of poly(methyl methacrylate) among others is the system based on ( $\text{dpp-BIAN} \leftrightarrow \text{CuCl}$ )<sub>2</sub> and diethylamine, which makes it possible to obtain polymer with a polydispersity index of 1.36–1.60. In case of acrylonitrile polymerization, the highest polymer yield is achieved using a copper complex and triethylamine. The results of MALDI TOF mass spectroscopy measurements showed the presence of chlorine atoms at the chain ends of macromolecules. The formation of “living” chains during polymerization of methyl methacrylate was confirmed by the synthesis of block-copolymers with styrene.

**Keywords** Radical polymerization · Copper · Methyl methacrylate · Acrylonitrile · Molecular weight

## Introduction

Catalysis of polymerization processes by transition metal complexes is one of the most promising and rapidly growing directions of modern polymer science and material sciences [1, 2]. The use of transition metal complexes allows polyolefin synthesis with high degree of stereoregularity at low pressure [1], to conduct ring opening polymerization [2] and atom transfer radical polymerization (ATRP) [3–5] as well as to realize many other valuable polymerization techniques [6–8]. These methods of polymerization have been demonstrated as an effective route for preparing new polymer

structures such as polymer brushes [9], star polymers [10, 11], block copolymers [12] and graphene nanoplatelets [13]. The efficiency of metal-based catalytic systems may be finely tuned by varying catalyst structure, e.g. by changing ligand environment.

From this standpoint, the use of so-called redox-active ligands, which can dramatically change reactivity of metal centers seems very promising to tune catalyst activity as in organic synthesis so in polymerization processes [14–16]. For example, complexes of d-metals such as palladium [15–17], copper [17], cobalt [18], chromium [19], nickel [20] with diimine ligands including acenaphthene imine derivatives display high catalytic performance in olefin polymerization, exceeding other types of catalysts. Complexes of transition and non-transition metals with redox-active ligands were found to be active regulators of radical polymerization of vinyl monomers [21]. The presence of redox-active ligands in catalyst structure can dramatically change polymerization mechanism. It was shown that bis-(triphenylphosphine)-3,6-di(*tert*-butyl)benzosemiquinone-1,2-copper(I) revealed a high regulating ability in radical polymerization of various monomers under

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