ORIGINAL RESEARCH

The effects of catalyst and deactivator species in atom transfer radical polymerization of *n*-butyl methacrylate

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Abstract

Atom transfer radical polymerization (ATRP) of *n*-butyl methacrylate (*n*-BMA) was performed using Cu^{I}Br/*N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) as catalyst and tosyl chloride (TsCl) as initiator, and different poly(*n*-butyl methacrylate) samples were prepared by changing the ratios of monomer/initiator and monomer/catalyst. Comparison was made with the data of another ATRP system with 4,4′-di(5-nonanyl)-2,2′-bipyridine (dNbpy) ligand (*n*-BMA/Cu^{I}Br/dNbpy/TsCl). ^{1}H NMR spectroscopy was used successfully to study monomer conversion during polymerization. For lower degree of polymerization (DP) $\leq$ 200, the corresponding products displayed narrow molecular weight distribution ($D \leq 1.1$). Number average molecular weights (M_n) obtained by gel permeation chromatography (GPC) were higher than those calculated ($M_{n,theory}$), while in products with higher degree of polymerization (DP = 300), the $M_{n,theory}$ surpassed $M_{n,GPC}$ and molecular weight distribution enhanced ($D \leq 1.25$). UV–visible spectroscopy was employed to study the probable coordination of monomer to copper bromide and/or ligand. Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were used for characterization of prepared poly(*n*-butyl methacrylate)s. Cyclic voltammetry (CV) for Cu^{II}/Cu^I redox couple was performed in solvent mixtures of isobutyl butyrate (saturated form of *n*-butyl methacrylate) and acetonitrile having different volume fractions (acetonitrile/butyl isobutyrate: 100/0, 80/20, 60/40, 40/60 and 20/80). By introducing moderately nonpolar butyl isobutyrate to polar aprotic acetonitrile, peak-to-peak separation increased. This implied slow electron transfer (lower K_{ET} in presence of monomer) that adjusted K_{ATRP}.

Keywords ATRP · Copper complex · Cyclic voltammetry · *n*-Butyl methacrylate · PMDETA

Introduction

Nowadays, synthesis of materials having predetermined structure is of crucial importance in many research fields such as medicine, drug delivery, electronic industry, nanotechnology, etc. Polymeric materials are excellent candidates for these applications owing to their availability, ease of production and numerous structures they offer. Atom transfer radical polymerization (ATRP) is confirmed to be the most versatile synthetic method for production of well-defined architectures. ATRP was first introduced in 1995 [1, 2], and

since then, was considerably developed and used as the main synthetic route for preparation of numerous polymers [3, 4]. Almost all effective parameters of this method such as the type of monomer, ligand, initiator, solvent, polymerization temperature [5, 6] and transition metal complex [7, 8] have been studied in details.

Obviously, the most important parameter in ATRP is the catalyst (usually a complex of copper with nitrogen based ligands) which plays a key role in establishment of an equilibrium between active, P_n^*, and dormant, $P_n - X$, states (Scheme 1). In this mechanism, the active species polymerize a few monomers in their numerous but short activation periods and they remain in dormant state for most of the time due to the higher k_{da} relative to k_a in their state of equilibrium $(k_a \ll k_{da})$. Scheme 1 represents a simplified equilibrium and does not exhibit all reactions that might take place and intermediates that might form in the reaction [9–11]. It is clearly known that the reaction medium can affect all the predictions and expected equilibriums in polymerization process, particularly

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