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Feature Article

Tailoring macromolecular architecture with imidazole functionality: A perspective for controlled polymerization processes

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Dedicated to Professor Nikos Hadjichristidis in recognition of his contribution to polymer science.

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ABSTRACT

Controlled radical polymerization (CRP) allows for the design and synthesis of functional polymers with tailored composition and unique macromolecular architectures. Synthetic methods that are readily available for controlled radical polymerization include nitroxide-mediated polymerization, reversible addition–fragmentation chain transfer polymerization, and atom transfer radical polymerization. *N*-Vinyl monomers that are typically amenable to free radical methods are often difficult to synthesize in a controlled manner to high molecular weight due to the lack of resonance stabilization of the propagating radical. However, recent advances in the field of CRP have resulted in successful controlled polymerization of various *N*-vinyl heterocyclic monomers including *N*-vinylcarbazole, *N*-vinylpyrrolidone, *N*-vinylphthalimide, and *N*-vinylindole. The incorporation of the imidazole ring into homopolymers and copolymers using conventional free radical polymerization of *N*-vinylimidazole monomer is particularly widespread and advantageous due to facile functionalization, high thermal stability, and the relevance of the imidazole ring to many biomacromolecules. Copolymers prepared with methyl methacrylate displayed random incorporation according to differential scanning calorimetry and amorphous morphologies according to X-ray scattering. Imidazole- and imidazolium-containing monomers have shown recent success for CRP; however, the controlled polymerization of *N*-vinylimidazole has remained relatively unexplored. Future efforts focus on the development of tailored imidazole-containing copolymers with well-defined architectures for emerging biomedical, electronic and membrane applications.

1. Introduction

Controlled radical polymerization allows for the synthesis of functional copolymers with well-defined architectures, controlled molecular weights, and tunable sequences. Controlled polymerization reactions typically produce polymers with predictable molecular weights and narrow polydispersity indices (PDI), as well as various architectures unattainable with conventional free radical techniques, including star-shaped and block copolymers. The most widespread controlled polymerizations include nitroxide-mediated radical polymerization (NMP) [1], reversible addition–fragmentation chain transfer polymerization (RAFT) [2,3], and atom transfer radical polymerization (ATRP) [4–6]. The chemistry of *N*-vinyl monomers presents a fundamental problem for

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their use in controlled polymerizations: the formation of a highly reactive *N*-vinyl propagating radical, due to the lack of resonance stabilization, increases the likelihood for chain transfer and chain termination events. Thus, achieving high molecular weights, which is desired for optimum thermomechanical performance, is often challenging. Despite the apparent difficulty for controlled polymerizations, *N*-vinyl heterocyclic monomers have functioned well in controlled radical polymerizations due to recent advances in the field as described below (Fig. 1).

Polymers with photoactive applications including photovoltaic devices, photorefractive materials, and photocopiers typically contain the monomer *N*-vinylcarbazole (NVC) due to its attractive high hole-transporting capability and high charge carrier properties [7,8]. Interest in the controlled radical polymerization of NVC began with the work of Fukuda et al. [9] who successfully formed NVC-containing block copolymers with styrene using NMP; however, homopolymerization of NVC failed. Later, Schmidt-Naake et al. [10] effectively homopolymerized NVC using NMP, however, molecular weights proved uncontrollable and narrow polydispersities were not reported. The synthesis of a novel NVC block copolymer using NMP for potential photosensitizer applications, poly(sodium styrenesulfonate-*b*-NVC), required acetic anhydride as a rate-accelerating additive, but contained only 5 mol.% NVC [11]. Although the formation of the block copolymer occurred successfully, the PDI of the block copolymer remained unreported as well as the ability to control molecular weight effectively.

ATRP of NVC led to the first reported homopolymerization of a narrow PDI ($M_w/M_n = 1.33$) with $C_{60}Cl_n/CuCl/2,2'$-bipyridine (bpy) as the catalyst [12]. Ultimately, using a C_{60} core with multiple initiation sites caused the formation of star-like architectures; the size exclusion chromatograms showed a bimodal nature, further suggesting the formation of nonlinear architectures. Brar et al. [13] optimized the ATRP reaction of NVC with $Cu(I)Cl/Cu(II)Cl_2$/bpy catalyst in toluene, which produced the homopolymer in 76% yield. The number-average molecular weight (M_n) versus percent conversion resulted in a linear plot, and the polymers obtained exhibited low PDIs (1.01–1.38), suggesting a controlled polymerization. Mori et al. [14] demonstrated excellent control of NVC homopolymerization using RAFT polymerization methods with xanthate-based chain transfer agents. The reported M_n ranged from 3000 to 48,000 g/mol with PDIs between 1.15 and 1.20. This optimized RAFT polymerization produced poly(NVC) four-arm star polymers and amphiphilic star block copolymers for the first time, as shown in Scheme 1 [15]. The amphiphilic block copolymers consisted of a poly(acrylic acid) star modified with xanthate end groups for subsequent RAFT polymerization with NVC. Due to the success of the controlled polymerization of NVC, recent publications have focused on the synthesis of block copolymers to optimize the photosensitizing properties of NVC as well as the synthesis of supramolecular structures for drug delivery applications [16,17].

An additional *N*-vinyl monomer for use with controlled radical polymerization techniques, *N*-vinylpyrrolidone (NVP), is attractive for the pharmaceutical, food, and textile industry industries due to its reported biocompatibility [18,19]. Devasia et al. [20] and Wan et al. [21] first reported the controlled polymerization of poly(NVP) using RAFT techniques. The polymerization of Devasia et al. used a dithiocarbamate chain transfer agent and showed pseudo-first order kinetics with a linear increase in M_n with conversion. Wan et al. chose a xanthate-based chain transfer agent dissolved in fluoroalcohol solvents for tacticity control. The results demonstrated narrow PDIs and M_n showed a linear increase with monomer conversion as shown in Fig. 2. The polymers also contained high syndiotacticity (60%) due to the use of fluoroalcohol solvents, verifying simultaneous control of molecular weight and tacticity during polymerization. Later studies confirmed xanthates as the chain transfer agent necessary to obtain controlled molecular weight and narrow PDIs when homopolymerizing NVP [22–24]. These studies utilized xanthate-mediated RAFT polymerization to synthesize novel architectures of poly(NVP) forming linear, star, and block copolymers. Novel amphiphilic block copolymers formed with NVP include poly(NVP-*b*-vinyl acetate)[23,25] and poly(ethylene glycol-*b*-NVP) [26]. Targeted applications included materials for coating catheters or drug encapsulation as well as stabilizers in emulsion polymerizations.

Recently, Pound et al. [27] discovered side reactions occurred when employing xanthate-mediated RAFT polymerization, including dimerization of NVP in bulk and in solution. In addition, the NVP unit adjacent to the xanthate mediator underwent elimination at high temperatures (>70 °C). These side reactions affected polymerization kinetics and molecular weight control, which led to the growth of other controlled polymerization methods for NVP. Ray and coworkers demonstrated organostibine-mediated living radical polymerization as a highly effective method to synthesize well-defined poly(NVP) and its block copolymers [28]. As shown in Fig. 3, organostibine mediators resulted in high molecular weight polymers with low PDIs (1.07–1.29), as well as molecular weight that

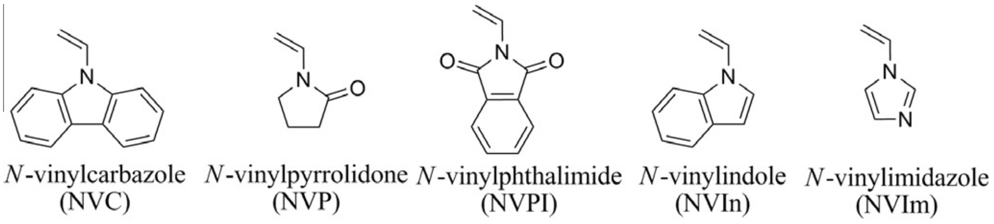

Fig. 1. Structures of *N*-vinyl heterocyclic monomers available for controlled radical polymerization.