Synthesis of Block Copolymers of 2- and 4-Vinylpyridine by RAFT Polymerization[†]

Anthony J. Convertine,[‡] Brent S. Sumerlin,[‡] David B. Thomas,[‡] Andrew B. Lowe,[§] and Charles L. McCormick*[,‡,§]

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406-0076, and Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406-5043

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Controlled radical polymerization (CRP)[1] techniques such as nitroxide-mediated polymerization (NMP),[2,3] atom transfer radical polymerization (ATRP),[4,5] and reversible addition−fragmentation chain transfer polymerization (RAFT)[6−8] have been the subject of intense research over the past several years. The ability to produce (co)polymers of controlled architecture with predetermined molecular weights, while still maintaining many of the benefits of conventional radical polymerization, holds great commercial appeal. Of the commonly employed CRP techniques, RAFT has the distinction of being the most widely compatible in terms of monomer choice. For example, species such as acrylamide[9,10] and tertiary amine containing monomers[11] are readily polymerized. For this reason our group has used RAFT to prepare functional, water-soluble polymers with precisely controlled architectures.[9−18] However, to date, the controlled polymerization of one important class of water-soluble monomers, specifically vinylpyridines (VP), has not to our knowledge been demonstrated by RAFT. The "living" polymerization of VPs by anionic polymerization,[19−24] and more recently NMP[25−28] and ATRP,[29−31] has been previously reported. The successful homopolymerization of VPs by RAFT, however, may facilitate the synthesis of novel block copolymers with monomers not compatible with other methods. Herein, we report the first successful RAFT polymerizations of 2-vinylpyridine (2VP) and 4-vinylpyridine (4VP). We also demonstrate the ability to synthesize 2VP-4VP (**3**) and 4VP−2VP (**4**) block copolymers in a controlled fashion by chain extending a poly(2VP) (**1**) or poly(4VP) (**2**) macro-chain-transfer agent (CTA) with the appropriate comonomer (Scheme 1).

Homopolymers of 2VP and 4VP were synthesized under bulk conditions by RAFT empoling azoisobutyronitrile (AIBN) as the initiator and cumyl dithiobenzoate (CDB) as the RAFT CTA. All polymerizations were conducted at 60 °C under a nitrogen atmosphere in septa-sealed vials. The initiator:CTA molar ratio was held constant at 1:4.75 with an initial monomer concentration of 9.27 M (bulk monomer). The CTA:monomer ratios ($[\mathrm{CTA}]_0/[\mathrm{M}]_0$:1/374) were such that the theoretical M_n at 100% conversion for both 2VP and 4VP was 39 300 g/mol. Polymerization kinetics and absolute molecular weights were determined by quenching the polymerizations at different reaction times and analyzing the reaction mixture directly by size exclusion chromatography (SEC) [DMF eluent, 0.5 mL/min, 60 °C, Polymer Labs PL gel 5 μm mixed C column (molecular weight range 200−3000K), Viscotek-TDA (301 RI, viscosity, and 7 mW 90° light scattering detector (670 nm))]. Conversions were determined by comparing the area of the RI signal of the monomer at t_0 to that at t_x. The d*n*/d*c* values at 632.8 nm for poly(2VP) (**1**) and poly(4VP) (**2**) in the above eluent at 60 °C were determined to be 0.167 and 0.225 mL/g, respectively.

Table 1. Conversion, Molar Mass, and Polydispersity Data for 2VP and 4VP Homopolymers and the Corresponding 2VP−4VP and 4VP−2VP Block Copolymers

sample[a]	time (h)	% conv[b]	M_n (theory)	M_n (exp)[c]	M_w/M_n[b]
4VP1	5	22	8 700	8 200	1.10
4VP2	8	34	13 500	12 000	1.14
4VP3	24	85	33 200	30 000	1.25
2VP1	5	25	9 700	12 000	1.11
2VP2	8	37	14 300	16 000	1.13
2VP3	24	80	31 500	35 000	1.18
P4VP macro-CTA	6	16	6 300	8 500	1.12
P2VP macro-CTA	6	26	10 200	7 900	1.11
P(4VP-*b*-2VP)	6	37	23 000	26 000	1.22
P(2VP-*b*-4VP)	6	31	20 000	23 000	1.21

[a] Polymers synthesized at 60 °C under bulk conditions ($[\mathrm{CTA}]_0/[\mathrm{M}]_0$: 1/374), ($[\mathrm{M}]_0/[\mathrm{I}]_0$: 1783/1) except for preparation of P(4VP−2VP) which was performed in *N*,*N*-dimethylformamide (DMF) (75:25, 2VP:DMF v/v) under a nitrogen atmosphere with azoisobutyronitrile as the initiator. [b] As determined by size exclusion chromatography (0.5 mL/min, 60 °C, Polymer Labs PL gel 5 μm mixed C column). [c] Conversions were determined by comparing the area of the RI signal of the monomer at t_0 to that at t_x.

The results for the homopolymerizations are summarized in Table 1. For both homopolymers, there is excellent agreement between the theoretical and observed molecular weights. The polydispersity indices (PDI) (M_w/M_n) for all samples ranged between 1.10 and 1.25, which is well below the theoretical lower limit of 1.50 for a conventional free radical polymerization. Figure 1A shows an overlay of the RI traces from the SEC analysis for the homopolymerization of poly(2VP) (**1**) and clearly illustrates the observed increase in molar mass with time, which is qualitatively indicative of a controlled polymerization. The linearity of the of M_n vs conversion plot (Figure 1B) and the pseudo-first-order rate plot (Figure 1C) reveals the absence of nondegenerative chain transfer and termination, respectively. A brief induction period of less than 1 h was observed in the pseudo-first-order rate plot of 2VP. An induction period is often observed in RAFT polymerization and is particularly common when CDB is employed as the CTA.[12,18,32−34] Such an induction period has been shown theoretically to be consistent with a slow rate of addition of the cumyl radical to monomer relative to the rate of addition to dithioester.[34]

During polymerization, the reaction became viscous and even glassy at extremely high conversions. Surprisingly, good control was maintained with only a small increase in the PDI value from 1.1 for 2VP1 at 25% conversion to 1.18 for 2VP3 at 80% conversion.

To further demonstrate the controlled nature of these polymerizations, block copolymers of 2VP and 4VP were prepared, and the incorporation of both monomers was confirmed by NMR spectroscopy. Poly(2VP) (**1**) and poly-

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[‡] Department of Polymer Science.
[§] Department of Chemistry and Biochemistry.
* To whom correspondence should be addressed.

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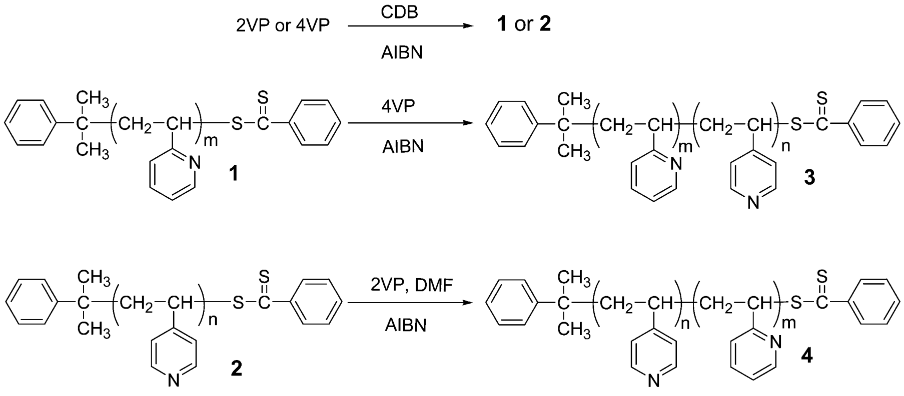
Scheme 1. Synthetic Pathways for the Polymerization of Poly(2VP) and Poly(4VP) and Block Copolymers of 2VP and 4VP at 60 °C via RAFT



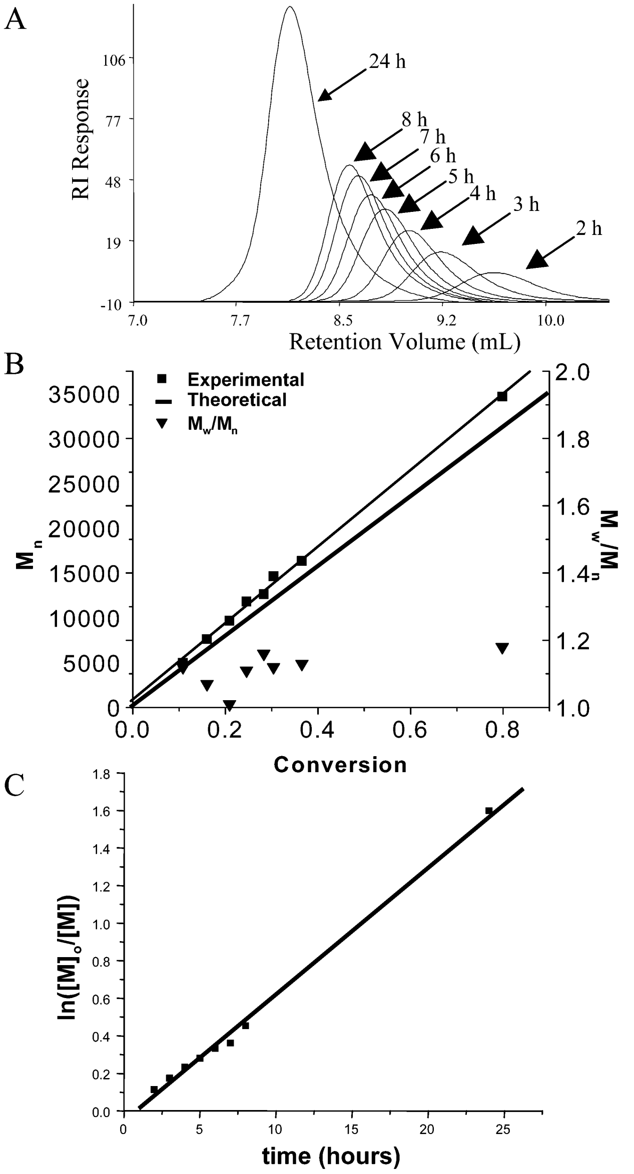


Figure 1. (A) SEC chromatograms for poly(2VP) showing the evolution of molecular mass with time. (B) Plots of M_n and M_w/M_n vs conversion. (C) The corresponding pseudo-first-order rate plot for poly(2VP).

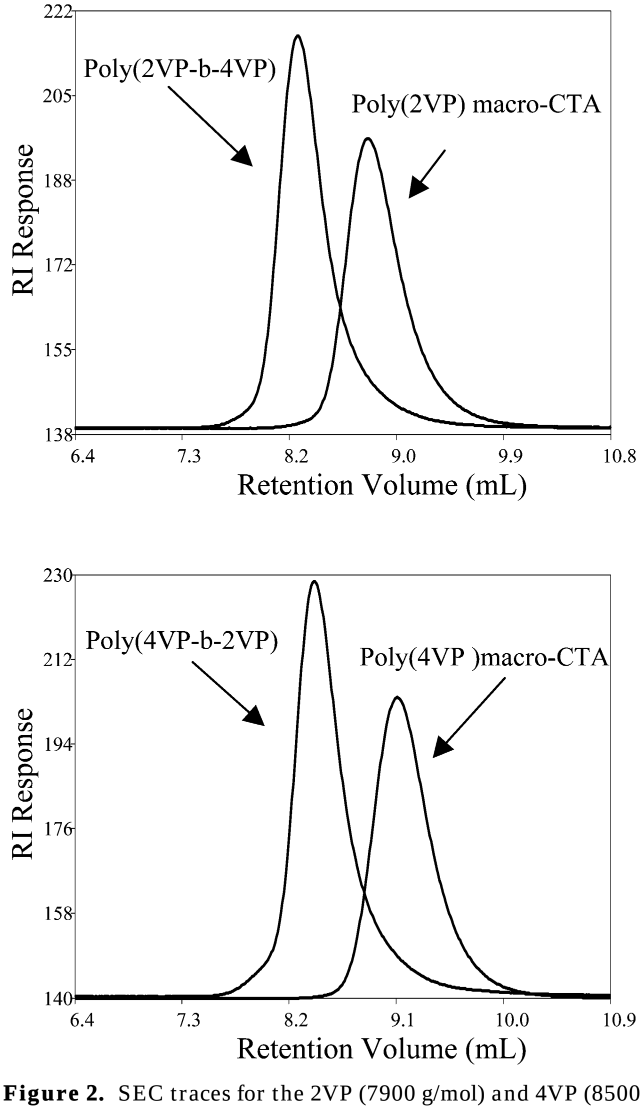


Figure 2. SEC traces for the 2VP (7900 g/mol) and 4VP (8500 g/mol) macro-CTAs and the corresponding P(2VP-*b*-4VP) (23 000 g/mol) and P(4VP-*b*-2VP) (26 000 g/mol) diblock copolymers.

(4VP) (**2**) hompolymers were precipitated from the bulk at room temperature into a 30 fold excess of hexane or toluene, respectively. These polymers were then utilized as macro-CTAs for the block copolymerization of the opposite monomer. Because of the limited solubility of poly(4VP) macro-CTA (**2**) in 2VP monomer, a small amount of DMF was added to solubilize the macro-CTA. Near-quantitative blocking efficiency (percentage of macro-CTA converted to diblock copolymer) was confirmed by the clear shift in the SEC refractive index traces for the macro-CTAs and the corresponding diblocks (Figure 2). The block copolymer derived from the poly(2VP) macro-CTA (**1**) had a theoretical M_n of 20 000 while the experimental value was 23 000 with a corresponding PDI of 1.21 (Table 1). The agreement between theoretical and experimentally determined molecular weights for the block copolymers further confirms the controlled nature of these polymerizations.

In summary, we have demonstrated the first successful RAFT polymerizations of 2VP and 4VP under bulk conditions employing cumyl dithiobenzoate as the CTA. Significantly, the polymerizations can be conducted in the absence of organic solvents up to high conversion while still maintaining control. For both monomers, the M_n vs conversion plot and the pseudo-first-order rate plot are linear. Good end-group control is demonstrated by utilizing the resulting homopolymers as macro-CTAs to prepare poly(2VP-*b*-4VP) (**3**) and poly(4VP-*b*-2VP) (**4**) diblock copolymers with near quantitative blocking efficiency. Absolute molecular weights were determined by online light scattering, utilizing the d*n*/d*c* values for poly(2VP) (**1**) and poly(4VP) (**2**) determined in DMF at 60 °C. Thus, RAFT provides a facile route for the synthesis of AB diblock copolymers from 2VP and 4VP. The novel aqueous solution properties of these responsive, pyridine-based diblock copolymers will be disclosed in a future publication.

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