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Isotactic Poly(2-vinylpyridine), Coordination Polymers, and Magnetic Nanocomposites from Chromium Atoms

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Alternatives to homogeneous metallocene isospecific polymerization catalysts[1] are few.[2] Such catalysts are important for "engineering" macromolecules[3] that offer enhanced performance based on control of tacticity, molecular weight, polydispersity, chirality, and compositional heterogeneity. In the course of our search for new high-energy atom routes to non-metallocene polymerization initiators and catalysts, we discovered an unusual method of activating vinyl monomers for isospecific polymerization.[4] In this communication we describe our approach to isotactic polymerization and an adaptation to synthesize magnetic polymer nanocomposites in a single reaction vessel. In the first step, we deliver a "free" chromium atom to a monomer molecule of 2-vinylpyridine (2-VP), converting it to an organometallic species active for *isospecific* polymerization. The 2-VP monomer is thus co-opted into behaving as the latent agent of its own activation for polymerization by assigning it a crucial role as a stereodirecting active center. This approach to isospecific polymerization is unprecedented in the literature.[5] Second, polymerization occurs with the conversion of poly(2-VP) into a coordination polymer in which chromium is dispersed as a bound complex. By starting only with atoms and organic monomer, this provides a new synthetic entry to metal-containing polymers. Third, we adapt the above chemistry to prepare a poly(2-VP)/nanoparticle magnetic composite. Geometric (size) constraints are intentionally imposed to alter magnetic properties by forcing an allotropic hcp → fcc phase transition in entrained 20 Å cobalt particles.

When chromium was sublimed into 100 mL of neat −80 °C 2-VP in a rotatable cryostat,[6] the solution turned deep red. If allowed to warm slightly above this temperature in the flask, the activated monomer solution spontaneously polymerized, generating intense heat and producing a brittle, black polymer glass.[7] Prepared in this way, the glass was completely soluble in aromatic and polar solvents, yielding air-sensitive emerald green solutions. The polymer was soluble in aqueous acid, from which white homopolymer was obtained after treatment with an ion exchange resin.[8]

Parallel microscale atom reactions were conducted by quantitative deposition of Cr into monomer on a cooled NaCl optical window attached to the cryotip of a closed-cycle helium gas cryostat. In both this and the reactor-based experiments, the initial low-temperature complex displayed an absorption maximum at 375 nm, red-shifted from the metal-to-ligand charge transfer band of the known complex bis(η^6-2,6-dimethylpyridine)chromium.[9] This suggests that the initial complex formed may be $(\eta^6\text{-2-VP})_2\mathrm{Cr}$, although mixed σ,π-bonded pyridine complexes with Cr cannot be discounted.[10] During the course of the polymerization Cr(0) is converted into an air-sensitive paramagnetic Cr(II) species identified by cyclic voltammetry.[11] After polymerization, new absorption bands appeared at 440, 630, and 680 nm that are characteristic of high-spin Cr(II) in an octahedral coordination complex bound through the nitrogen of pendant pyridyl units.[12] The complete solubility of the polymer suggests that Cr(II) is retained largely by *intramolecular* cross-links in the polymer.

When polymerization was allowed to occur slowly in dry 2-methyltetrahydrofuran solution at −78 °C, highly isotactic polymer was produced, as determined by the isotactic pentad at 166.30 ppm in the ^{13}C NMR spectrum (Figure 1a).[13] In contrast, the spectrum of the polymer formed from the rapid polymerization of the neat monomer displays only a slight increase in the mmmm pentad intensity (Figure 1b) compared with the atactic splitting pattern from the product of the radically initiated polymerization (Figure 1c).

There is considerable incentive to prepare nanostructured composite materials[14] based on the extraordinary deviations from their bulk physical and chemical properties caused by geometric and size quantization effects.[15] A recent example[16] of this is the preparation of an optically transparent magnetic $\gamma\text{-Fe}_2\mathrm{O}_3$ polymer resin nanocomposite that exhibits the largest saturation magnetization for a transparent ferromagnetic material. The near instantaneous polymerization of 2-VP by atomic chromium offered the possibility of quenching magnetic nanoparticles into the glass. Our objective was to impose a size restriction on the growing nanoparticle to cause it to manifest a magnetic

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(4) The first unambiguous demonstration of atom-induced *anionic* polymerization is described in the following: Heffner, S.; Andrews, M. P.; Galvin, M. E. *Polym. Rep.* **1988**, *29*, 335. Subsequently, Vann and El-Shall (Vann, W.; El-Shall, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 4385) showed that energetic transition metal cations could be introduced into isobutylene and polymerize it cationically.

(5) The earliest attempts to use a similar approach can be dated to Blackborow and co-workers: (a) Blackborow, J. R.; Eady, C. R.; Koerner von Gustorf, E. A.; Scrivanti, A.; Wolfbeis, A. *J. Organomet. Chem.* **1976**, *C3*, 111. (b) Blackborow, J. R.; Grubbs, R.; Myashta, A.; Scrivanti, A. *J. Organomet. Chem.* **1976**, *C49*, 120. But these experiments led to low polymer yields (10−40% by weight) and low molecular weights (oils) or intractable materials.

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(7) The polymer, produced in 93% yield by weight, displayed ^{1}H and ^{13}C NMR spectra characteristic of poly(2-VP) and contained between 0.25 and 0.5% by weight of Cr by elemental analysis. Control experiments showed that 2-VP does not polymerize in the presence of freshly deposited chromium mirror nor with empty alumina crucibles operating at the sublimation temperature of Cr. Transmission electron microscopy did not detect the presence of chromium particles in the polymer.

(8) Number average molecular weight, $M_n = 20\,000$; $M_w/M_n = 1.8$ (by GPC) after removal of Cr by ion exchange with acidic resin.

(9) Wucherer, E. J.; Muetterties, E. L. *Organometallics* **1987**, *6*, 1691.

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(11) Anaerobic cyclic voltammetry experiments were done in THF ($\mathrm{Ag/Ag^+}$ reference electrode) and displayed an irreversible anodic peak at −0.95 V with respect to the ferrocene/ferrocenium couple.

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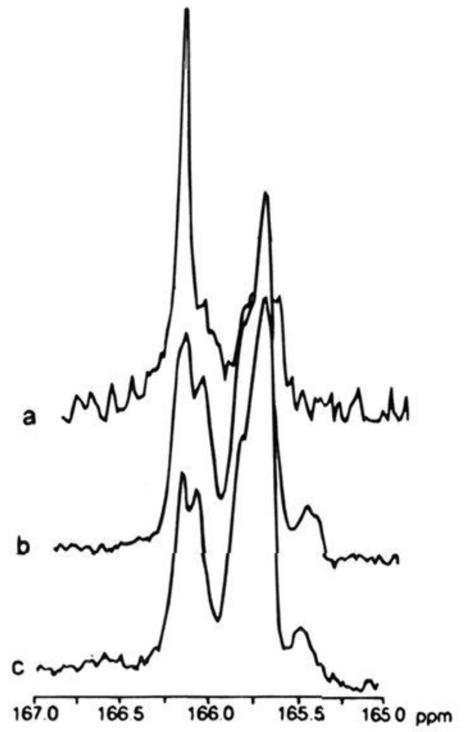

Figure 1. ^{13}C NMR (C_6D_6) of the poly(2-vinylpyridine) quaternary carbon from (a) low-temperature solution polymerization with Cr; (b) polymer glass prepared by Cr atom initiated rapid polymerization of the neat monomer, and (c) free radical (azobisisobutyronitrile) initiated polymerization of neat 2-VP.

property distinct from the bulk. Cobalt was selected for this purpose, since it is known to undergo an allotropic hcp → fcc phase transition.[17] Ferromagnetic resonance (FMR) at 9.5 GHz is selective for the fcc phase only. Accordingly, cobalt atoms were deposited into a cold solution of the neat monomer that had been activated with chromium.[18] Cobalt atoms diffuse and recombine under these conditions, producing particles approximately 20 Å in diameter according to transmission electron microscopy (Figure 2a).[19] The FMR response[20] demonstrated that a portion of the cobalt had converted to the fcc phase. These cobalt particles are superparamagnetic down to 6 K as indicated by the anhysteretic magnetization loops (Figure 2b).

A convenient bench-top source of chromium "atoms" has now been obtained with bis(1-methylnaphthalene)chromium. This complex undergoes facile ligand displacement in the presence of 2-VP, which subsequently polymerizes. Detailed studies of this reaction are currently underway.

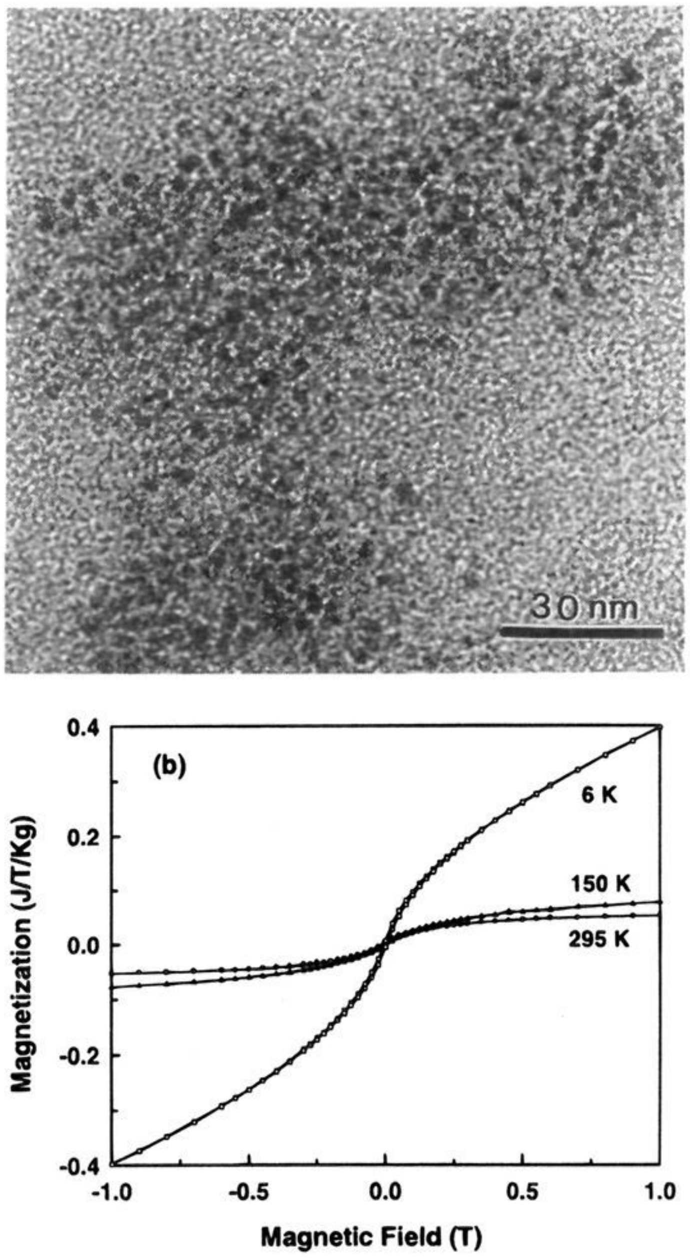

Figure 2. (a, top) Transmission electron micrograph of cobalt/polymer nanocomposite. (b) Variable temperature anhysteretic magnetization loops obtained by SQUID magnetometry.

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(18) Separate experiments showed that cobalt alone initiates slow polymerization of 2-VP to give a gel after standing at room temperature for 24 h. This polymerization pathway is uncompetitive compared to the near instantaneous polymerization caused by chromium atoms. At any rate, any putative Co/2-VP complex must be thermally unstable, since Co ends up as particles.

(19) These particles were confirmed as being composed of cobalt by energy dispersive X-ray analysis.

(20) The FMR spectrum displayed a *g* value of 2.15 and peak-to-peak line width of 440 G at room temperature.