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Controlled radical polymerization of vinyl acetate mediated by a vanadium complex**

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Supporting information:
[†]Electronic supplementary information (ESI) available: Full experimental information, additional figures on experiments at lower temperature and with styrene monomers. Additional characterization data and tabulation of polymer properties. See http://dx.doi.org/10.1039/B922202B

Graphical abstract:
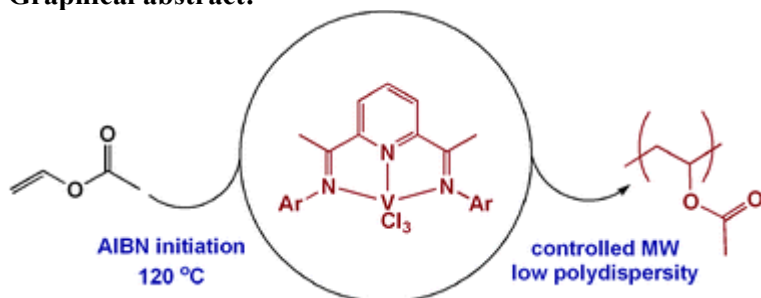
Abstract

Initiation of the polymerization of vinyl acetate with azobis(isobutyronitrile) in the presence of a vanadium bis(iminopyridine) complex generatesvanadium-capped dormant polymer chains with excellent correlation between molecular weight and conversion and good molecular weight distributions.

Introduction

Significant progress in the development of controlled radical polymerization (CRP) has resulted in extraordinary control over polymer molecular weight and molecular weight distributions.[1] Several of these processes exploit transition metal based complexes to control the radical concentrations, minimize bimolecular termination reactions and exchange growing and dormant polymer chains. These include atom transfer radical polymerization (ATRP),[2] where a halogen-capped polymer chain and a transition metal complex are in reversible equilibrium with a polymeric radical and the corresponding higher oxidation state metal halide. Organometallic mediated radical polymerization (OMRP) is based upon the lability of metal–carbon bonds under thermal or photolytic treatment, where the reversible formation of an organometallic dormant chain is in equilibrium with a lower oxidationstate metal complex and a polymeric radical. The OMRP process has been most thoroughly studied for cobalt-mediated radical polymerization,[3] and has also been implicated in molybdenum[4] and iron systems,[5] including significant study into the interplay between ATRP and OMRP in these systems.[6]

For these CRP processes, vinyl acetate has proven to be a particularly challenging monomer to control[7] due to an imbalance between metal–halogen and carbon–halogen bond strengths in ATRP and strong metal–carbon bonds in OMRP. Jérôme *et al.* reported an intriguing cobalt system that can efficiently control the polymerization of vinyl acetate, albeit with an extremely long initiation time (>10 h) and a radical initiator, 2,2′-azo-bis(4-methoxy-2,4-dimethyl valeronitrile), which must be stored at −20 °C and requires reaction temperatures to remain at 30 °C.[3,8] Further work has shown this same principle can be applied to chromium complexes,[9] although polydispersities remained high and challenges exist in reaching high conversions.

In this communication, we report the first controlled radical polymerization mediated by a vanadium complex which also represents a novel OMRP of vinyl acetate using a standard 2,2′-azo-bis(isobutyronitrile) (AIBN) initiator. Our lab is keenly interested in controlled radical polymerizations mediated by early-mid transition metals. In recognition of the importance non-innocent ligands play in catalysis, the bis(iminopyridine) complex [BIMPY]VCl$_3$ ([BIMPY] = 2,6-(ArN=CMe)$_2$C$_5$H$_3$N, Ar = 2,6-(^{i}Pr)$_2$C$_6$H$_3$)[10] was screened for the CRP of styrene and vinyl acetate (VAc) initiated by AIBN at 120 °C. Under these conditions, two potential equilibria could be established; an ATRP equilibrium, where the starting V(III) complex provides the halogen to cap growing polymer chains or an OMRP equilibrium, where the V(III) complex could trap growing

polymer chains to form a dormant organometallic complex. Additionally, these two reactions could both be at work, where radicals extract halogens from V(III) complexes to form V(II) species *in situ*. These V(II) species can then reversibly trap growing polymer chains. This potential interplay is shown in Scheme 1.
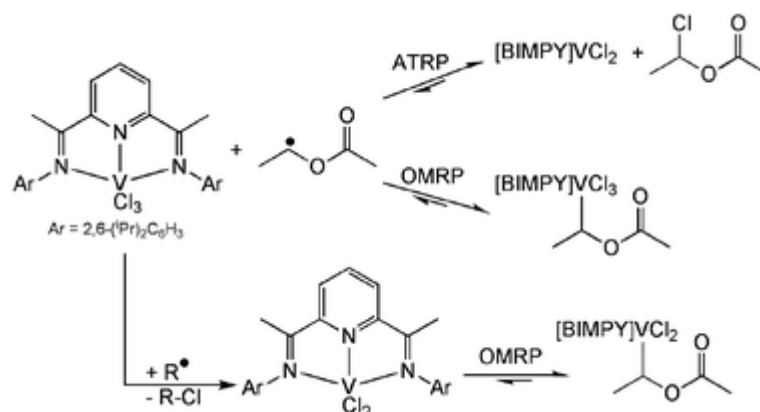
Scheme 1. [BIMPY]VCl$_3$ as an ATRP and/or OMRP complex.

For vinyl acetate, a controlled process is observed, as assessed by the linear increase of the molar mass with monomer conversion, while styrene polymerizations were uncontrolled. For VAc, polymer molecular weights accurately matched the chain length expected from monomer conversion and in addition to the molecular weight of the vanadium complex (Fig. 1). Slight deviations are noted at high conversions, and correlate with a change in solution color signifying the decomposition of the complex. Polydispersities (M_w/M_n) are relatively low ($\sim$1.3) compared to styrene polymerizations ($\sim$1.6–1.8), but non-ideal. The distributions remain constant throughout the polymerization, suggesting inefficient initiation of AIBN. Polymeric material isolated by repeated precipitation in pentane or purification by silica-gel column chromatography retained a strong red color reminiscent of the complex, and ^{1}H NMR characterization of the polymer showed no halogen-terminated polymer chains. Discerning the end-groups through 2-D NMR was inconclusive, potentially due to the proximity of the paramagnetic vanadium complex. The kinetics of this process are first order in monomer, as exhibited by the linear dependence of $\ln([M]_0/[M])$ *versus* time, supporting a constant radical concentration (Fig. 2). A short burst of uncontrolled polymerization as the reaction reaches equilibrium supports an inefficient initiation process. However, no long initiation period is observed and productive polymerization begins immediately, but the rate and level of control in the reaction varies based upon reaction temperature. Higher than expected molecular weights that are independent of conversion and broadened polydispersities are noted when polymerizations are conducted at 70 °C and 90 °C suggesting inferior initiation and chain exchange at these temperatures (see Fig. S2, ESI†). We are currently investigating alternative radical initiatorsto achieve better control at these lower temperatures.
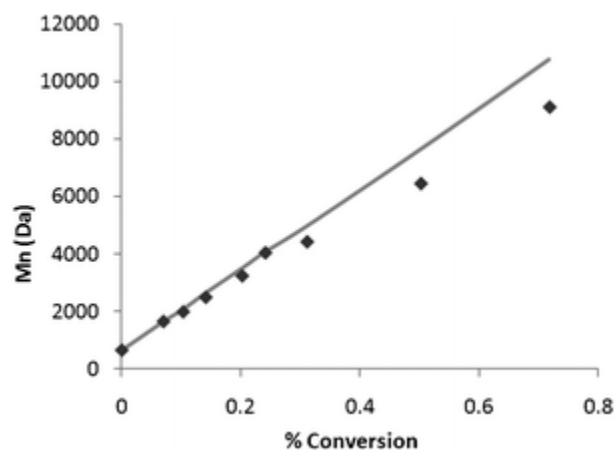
Figure 1. Dependence of PVAc M_n on monomer conversion for the bulk polymerization of vinyl acetate at 120 °C. [BIMPY]VCl$_3$: AIBN : VAc is 1 : 0.6 : 100.
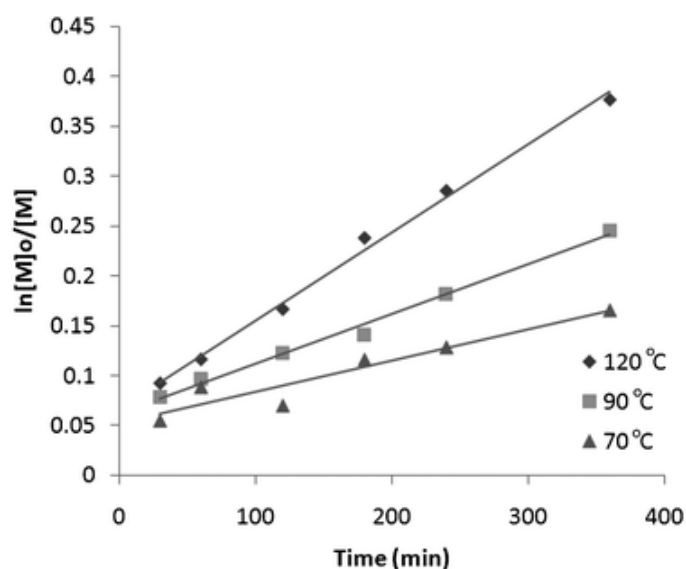

Figure 2. Time dependence of $\ln([M]_0/[M])$ for the bulk polymerization of vinyl acetate at various temperatures. [BIMPY]VCl$_3$: AIBN : VAc is 1 : 0.6 : 100 and $[M]_0$ and [M] are the [VAc] at times 0 and t respectively.

The purple [BIMPY]VCl$_3$ complex is sensitive to oxygen and moisture but the resultant red polymers are surprisingly stable. Polymerizations can be stopped by simply lowering the temperature, and restarted by raising the temperature to 120 °C, reinitiating the polymerization at the same rate to generate polymers which continue to match monomer conversion (Fig. 3). This start–stop experiment confirms the ability of the vanadium species to trap active radical chains and a lack of increase in polydispersity suggests a good level of control. Similarly, polymers can be isolated, purified by precipitation with pentane or silica-gel column

chromatography outside of an inert atmosphere, and subsequently used as macroinitiators with the addition of a new aliquot of vinyl acetate. The macroinitiators are stable up to one month in the solid state under an atmosphere of air, showing no signs of decomposition.
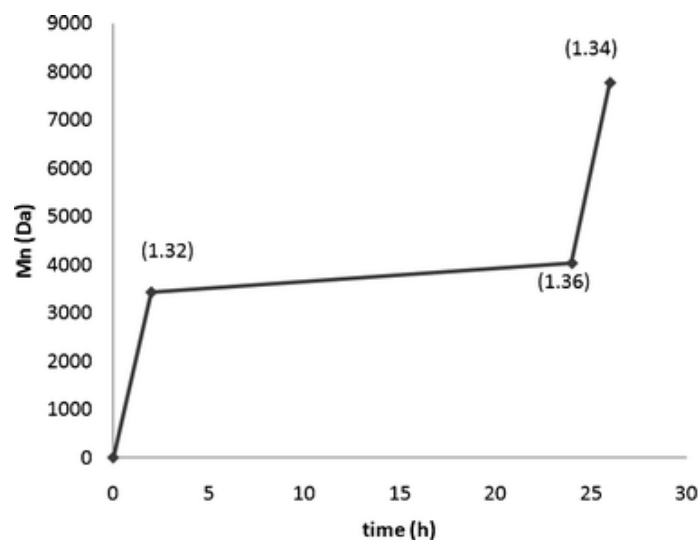

Figure 3. Start–stop experiment for the bulk polymerization of vinyl acetate. [BIMPY]VCl$_3$: AIBNVAc 1 : 0.6 : 100. T = 120 °C/−30 °C. Polymer PDIs are indicated in brackets for the relevant peaks.

An essential requirement for commercial application of these polymers will be the ability to remove the vanadium to produce the cosmetically-preferable white polymers. While the vanadium-capped polymer chains are robust, the complex can still be readily removed. The thermal homolytic cleavage of the V–C bond at 50 °C in the presence of propane thiol affords the desired proton terminated polymer chains and the corresponding disulfide,[11] as confirmed by ^{1}H and COSY NMR spectroscopy, generating nearly colorlesspolymer when recovered. Polymer chains can also be readily converted to poly(vinyl alcohol) by a base-catalyzed methanolysis,[12] removing the vanadium end-cap in the process. These reactions are shown in Scheme 2.
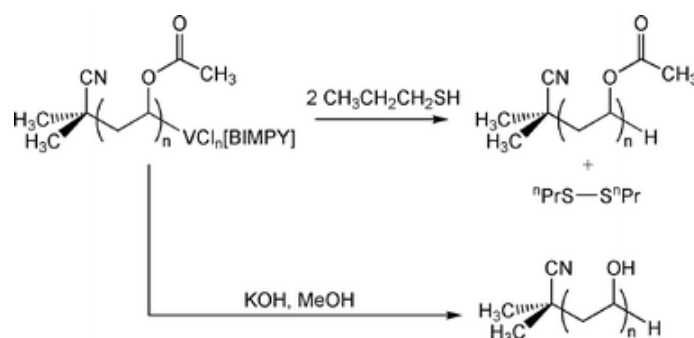
Scheme 2. Removal of vanadium end-groups from polymer chains.

The red polymer color, the lack of halogen end groups and the reactivity of these macroinitiators suggest an organometallic mediated radical polymerization mechanism, wherepolymer chains are reversibly trapped by vanadium complexes. The identity of these organometallic species is in question, as Scheme 1 suggests that V(III) or *in situ* generated V(II) species had the potential to trap organic radicals. However, observed molecular weights suggest that the reaction proceeds through a V(II) intermediate. Molecular weights are in agreement with those predicted when the initiating AIBN species produces only one radical per molecule ($M_{n(th)}$ = $[M]_0$/[AIBN] (86.04 g mol^{-1}) (%conv); Table S1, ESI†). This suggest that either the $(CH_3)_2(CN)C^.$ radical or short-chain, oligomeric VAc radicals abstract a halogen to form Cl-terminated molecules and the active trapping species, [BIMPY]VCl$_2$. This would imply that molecular weights would be double that expected from a standard radical initiation (observed) and that V(III) organometallics are present. While several alkyl derivatives of V(III) exist,[13] no 7-coordinate alkyl vanadium(IV) complexes of the formula VCl$_3$RL$_3$ have been reported, supporting this mechanism. Gas-chromatographic analysis of the monomer feed indicates the presence of small quantities of $(CH_3)_2(CN)CCl$, supporting this hypothesis, although quantification of this compound and correlation to the original AIBN concentration suggest some complexity to this process. Contrasting this supporting evidence, characterization of the P(VAc) by EPR spectroscopy indicates that the end-capped polymer chain is clearly V(IV). This suggests that the non-innocent bis(imino)pyridine ligand may be playing a significant role in theoxidation state changes involved in these reactions. A full mechanistic study is underway, including further characterization of the metal complex, end-capped polymer chain and any potential by-products.

Controlled radical polymerization remains a major challenge. With this report, we have shown the first example of a vanadium-mediated radical polymerization, and one of the very few transition-metal systems to function as OMRP mediators for the CRP of vinyl acetate. Current efforts are focussed upon understanding the mechanism of the reaction and the nature of the complex and metal-capped polymer chains, meeting the challenge of reaching high conversions without complex decomposition, as well as exploiting this system to generate tailored polymers, copolymers and macromolecular architectures incorporating controlled poly(vinyl acetate) and poly(vinyl alcohol) building blocks.

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