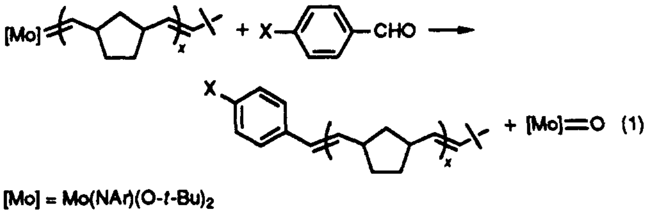
Chain-End Functionalization of Living Polymers Formed by the Ring-Opening Metathesis Polymerization of Norbornene

Well-characterized alkylidene complexes of the type M(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (M = Mo[1], W[2]; NAr = N-2,6-*i*-Pr$_2$C$_6$H$_3$) have been shown to polymerize a range of norbornenes[3] and 2,3-disubstituted norbornadienes[4] by living ring-opening metathesis polymerization. Since these catalysts are deactivated toward reaction with ordinary olefins,[3a] the polymers are cleaved from the metal center in a "Wittig-like" reaction typically using pivaldehyde or benzaldehyde to form the metal oxo–imido species M(NAr)(O)(O-*t*-Bu)$_2$ and a *tert*-butyl or phenyl end-capped polymer, respectively. If substituted benzaldehydes are used in this capping reaction (a wide variety of which are commercially available), the introduction of potentially useful functionalities to the end of the polymer chain may be envisaged according to eq 1.



Here, we report some preliminary studies into the range of functional groups that may be tolerated in this capping reaction.

In experiments[5] designed to test the tolerance of Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ toward a variety of functionalities, Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ was reacted with various para-substituted benzaldehydes (typically 1–2 equiv) in C$_6$D$_6$ to yield Mo(NAr)(O)(O-*t*-Bu)$_2$[6] and *trans*-X-PhCH=CH-*t*-Bu, as shown in eq 2. A representative

$$\mathrm{Mo(NAr)(CH\text{-}\mathit{t}\text{-}Bu)(O\text{-}\mathit{t}\text{-}Bu)_2 + PhCHO \rightarrow Mo(NAr)(O)(O\text{-}\mathit{t}\text{-}Bu)_2 + \mathit{trans}\text{-}PhCH{=}CH\text{-}\mathit{t}\text{-}Bu} \quad (2)$$

^{1}H NMR spectrum for the reaction between Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ and 1 equiv of *p*-NCC$_6$H$_4$CHO is shown in Figure 1.

From the range of para-substituted benzaldehydes evaluated in this manner, only *p*-HOC$_6$H$_4$CHO in C$_6$D$_6$ gave unidentifiable products, suggesting that alternative decomposition pathways, perhaps not surprisingly, are available to the initiator in the presence of the OH functionality. The use of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (in CDCl$_3$) in which the hydroxyl group is sterically protected afforded some of the capped oxo–imido species and ArCH=CH-*t*-Bu, but the reaction was not clean. The "OH protected" trimethylsilyl derivatives may offer a way of circumventing OH tolerance.

If the reactions are monitored by ^{1}H NMR at room temperature, 2-oxametallacycles[6b] are observable for X = CHO, NO$_2$, CN, and CO$_2$Me[7] but not for X = NMe$_2$; this is consistent with the finding that oxametallacycle intermediates are most favored for benzaldehydes with electron-withdrawing substituents in the para position,[6b] however, they do not appear to adversely affect the efficiency of the capping reaction for "living" oligomers. Analysis of a series of polymers prepared by treatment of Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ with 100 equiv of norbornene followed by capping with various benzaldehydes[8] (Table I) showed that, in most cases, the functional group may be introduced with negligible broadening of the molecular weight distribution.

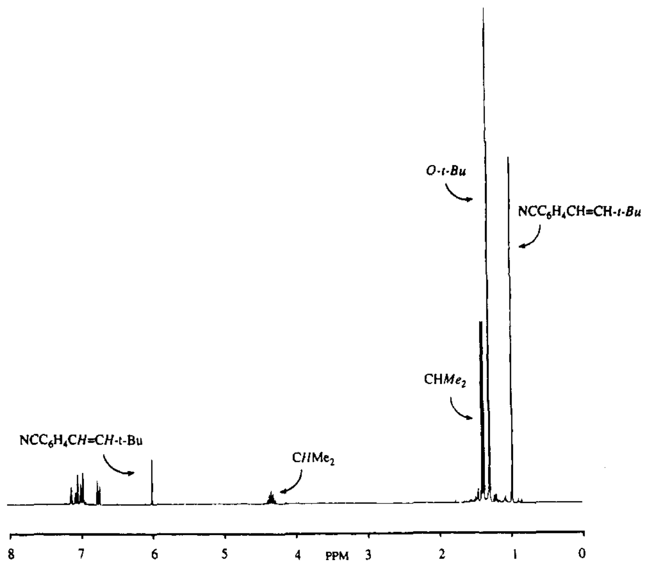


Figure 1. 250-MHz ^{1}H NMR spectrum (C$_6$D$_6$) of the reaction between Mo(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)(CH-*t*-Bu)(O-*t*-Bu)$_2$ and *p*-NCC$_6$H$_4$CHO affording Mo(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)(O)(O-*t*-Bu)$_2$ and *p*-NCC$_6$H$_4$C=CH-*t*-Bu.

Table I
GPC Data for Living 100-mers of Norbornene Capped with Various Functionalized Benzaldehydes

p-XC$_6$H$_4$CHO	M_n(found)[a]	M_w(found)	PDI = M_w/M_n
X = H	17 620	18 610	1.06
X = CF$_3$	17 710	19 080	1.08
X = OMe	15 850	16 660	1.05
X = NMe$_2$	16 560	17 770	1.07
X = CN	15 090	15 940	1.06
X = NO$_2$[b]	17 800	20 660	1.16
X = CHO[b]	18 410	21 280	1.16
X = CO$_2$Me	16 842	17 786	1.06
X = NH$_2$[b]	19 117	21 487	1.12
X = Cl[b]	17 254	19 182	1.11

[a] Relative to polystyrene standards in THF. [b] Shoulders to high molecular weight.

In the case of *p*-CHOC$_6$H$_4$CHO and *p*-NO$_2$C$_6$H$_4$CHO, there is a slight increase in the PDI of the 100-mers, which for the dialdehyde is likely to arise due to some dimerization through the reaction of the living 100-mer with the CHO end-capped polymer. Therefore, a larger excess of this capping agent is required to maintain the narrowest of distributions. The explanation for the broadening observed with *p*-NO$_2$C$_6$H$_4$CHO is less clear; however, in a separate experiment involving the treatment of Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ with nitrobenzene (1 equiv), the initiator was found to react slowly to give the oxo–imido species plus other, as yet, unidentified products. Therefore, this group may also facilitate cross-linking when in contact with living alkylidenes.

In conclusion, we have shown that a range of functionalities can be introduced to the end of a polymer chain via means of a Wittig-like capping reaction between the living polymer and a functionalized benzaldehyde derivative. This technique, in conjunction with the use of substituted styrene chain-transfer reagents,[9] will enable both ends of the polymer chain to be functionalized.

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(5) Typically, 10 mg of Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ was dissolved in 350 μL of C_6D_6 and a solution of 1–2 equiv of aldehyde in 350 μL of C_6D_6 added. This resulting solution was transferred to an NMR tube and sealed under nitrogen.

(6) Mo(NAr)(O)(O-*t*-Bu)$_2$ subsequently equilibrates with Mo(O)$_2$(O-*t*-Bu)$_2$ and Mo(NAr)$_2$(O-*t*-Bu)$_2$: (a) Mitchell, J. P.; Gibson, V. C., unpublished observations. (b) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics*, in press.

(7) Characteristic shifts for the α and β protons of the 2-oxametallacycles (see ref 6b) are observed at δ 2.08 and 6.16 ($J_{H_\alpha H_\beta}$ 7.1 Hz) for X = CHO, δ 1.96 and 6.07 ($J_{H_\alpha H_\beta}$ 7.4 Hz) for X = NO$_2$, δ 1.95 and 6.02 ($J_{H_\alpha H_\beta}$ 7.1 Hz) for X = CN, and δ 2.16 and 6.18 ($J_{H_\alpha H_\beta}$ 7.6 Hz) for X = CO$_2$Me.

(8) Polymerizations were performed by using stock solutions of Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (45 μL, 0.1 M), norbornene (90 μL, 5.0 M, 100 equiv), and capping benzaldehyde (450 μL, 0.1 M, 10 equiv) in toluene (THF solutions of the benzaldehydes *p*-ClC$_6$H$_4$CHO and *p*-NH$_2$C$_6$H$_4$CHO were used due to their low solubility in toluene). The initiator plus norbornene were stirred vigorously for 10 min, and then the benzaldehyde was added and the mixture stirred for a further 30 min. The resulting polymer was precipitated from methanol and dried in vacuo. In each case, the polymer was isolated in >95% yield, and, where possible, infrared spectroscopy on a thin film was used to confirm the presence of the functional group in the polymer.

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