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Living Vinyl Addition Polymerization of Substituted Norbornenes by a t-Bu_3P-Ligated Methylpalladium Complex

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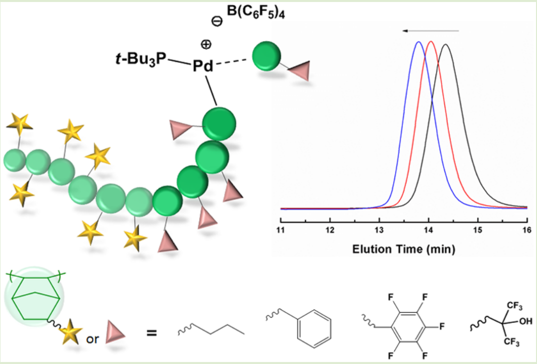
Supporting Information

ABSTRACT: The vinyl addition polymerization of substituted norbornene (NB) monomers, via (t-Bu_3P)PdMeCl activated by $[Li(OEt_2)_{2.5}]B(C_6F_5)_4$, is investigated. NB monomers bearing alkyl, aryl, fluoroaryl, and even hexafluoroisopropanol substituents yield polymers exhibiting monomodal and narrow molecular weight distributions, with molecular weight controlled by reaction time and monomer to initiator ratio, demonstrating the living nature of these polymerizations. These polymers are soluble in common organic solvents and possess excellent thermal stability. Block copolymers are also prepared via sequential monomer addition; these are the first examples of well-defined block copolymers of substituted NB monomers enchained by vinyl addition polymerization.



Norbornene (NB, bicyclo[2.2.1]hept-2-ene) can be polymerized to yield three qualitatively different polymer microstructures, depending on whether the monomers are enchained via ring-opening metathesis polymerization (ROMP), vinyl addition polymerization, or cationic or radical polymerization.[1,2] In comparison to polyNB prepared by ROMP and cationic or radical polymerization, salient features of vinyl addition polyNB are a high glass transition temperature ($T_g \approx 385$ °C[3]), high thermal stability, and low dielectric constant, which all originate from the saturated bicyclic backbone structure.[1,2] The high T_g of vinyl addition polyNB precludes melt-processing; it is also poorly soluble in common organic solvents. Therefore, vinyl addition polymerization of substituted NB monomers is of interest[3−15] to improve polymer solubility and potentially other application-specific properties as well, such as stronger adhesion to substrates[3,5] and reduced dielectric constant.[13]

While there have been many studies of vinyl addition homo- and copolymerization of NB and NB derivatives, there have been only a few reports concerning living vinyl addition polymerization.[6,16−19] Mehler et al. found that $[Pd(NCEt)_4][BF_4]_2$ polymerized NB in a controlled manner, exhibiting polymer chain extension upon injection of additional monomer.[16] More recently, polyNB with relatively narrow molecular weight distribution (dispersity $Đ$ = 1.1−1.4), but poor molecular weight control due to slow initiation, was synthesized by Walter et al. using $[(2\text{-}R\text{-allyl})Pd(mesitylene)]^+$ complex.[17] Hasan et al. studied living vinyl addition polymerization of NB using $(t\text{-}BuNMe_2SiFlu)TiMe_2$/methylaluminoxane.[18,19] Although the above Pd- and Ti-based catalysts were found to be active for living polymerization of NB, they could not achieve controlled polymerizations of NB monomers with functional groups; coordination of polar functional groups, such as ester and ethoxysilyl moieties, to the metal centers strongly decelerates polymerization, even with nonliving catalysts.[4,7] The Ti-based catalyst showed very low activity even for the polymerization of NB monomers bearing vinyl or ethylidene substituents.[7]

To the best of our knowledge, there is only one published paper[6] that demonstrates the living vinyl addition polymerization of a substituted NB. In that pioneering work, Yamashita et al. reported the successful application of (t-Bu_3P)PdMeCl/$NaB[3,5\text{-}(CF_3)_2C_6H_3]_4$ complex for homo- and copolymerization of NB and methoxycarbonyl-substituted NB.[6] A plot of number-average molecular weight (M_n) versus conversion was found to be linear during polymerization of methoxycarbonyl-substituted NB; M_n reached 12 kg mol^{-1}, with $Đ \approx 1.2$. When both NB and methoxycarbonyl-substituted NB were present in the initial monomer charge, the resulting polymer had a gradient-type structure, with NB incorporated preferentially. The same catalyst complex could also polymerize NB bearing a sulfonyl fluoride moiety, yielding polymers with M_n up to 44 kg mol^{-1} and $Đ < 1.2$, suggesting a living character.[8] However, these polymerizations are still slow; the catalyst complex could not completely convert the methoxycarbonyl-[6] and sulfonyl fluoride-substituted[8] NB monomers to polymer within 16−24 h at room temperature. Such incomplete conversion would hamper the synthesis of block copolymers with "chemically pure" (homopolymer) blocks via sequential charging of the monomers. Nonetheless, based on the living characteristics and

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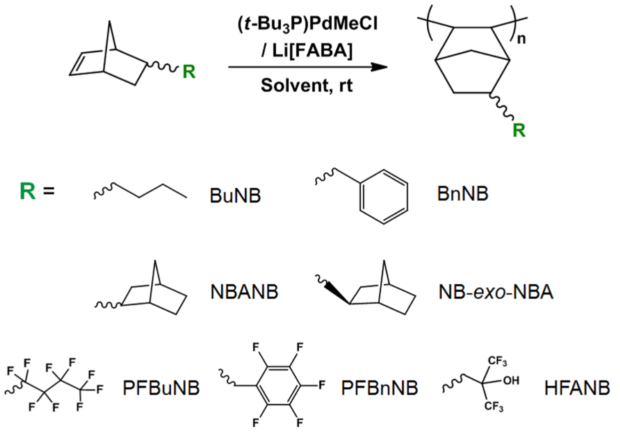
functional group tolerance of this t-Bu$_3$P-ligated methylpalladium complex, we sought to explore its use in the polymerization of other substituted NBs, as well as its potential to synthesize block copolymers of targeted block molecular weights.

Herein, we report for the first time the synthesis of well-defined NB homo- and block copolymers with various substituents via living vinyl addition polymerization. The substituted NBs studied herein are presented in Scheme 1.

Scheme 1. Vinyl Addition Polymerization of Substituted Norbornenes by (t-Bu$_3$P)PdMeCl/Li[FABA]



The alkyl/aryl (BuNB, BnNB, NBANB, NB-*exo*-NBA) and fluorinated (PFBuNB, PFBnNB, HFANB) substituents should increase the solubility of the polymers in organic solvents. The fluorinated substituents can also provide advantages for dielectric materials[13] and lithographic applications.[5] Vinyl addition polymerization of these monomers was carried out using (t-Bu$_3$P)PdMeCl, in the presence of 1 equiv of [Li(OEt$_2$)$_{2.5}$]B(C$_6$F$_5$)$_4$, denoted Li[FABA], as an activator, in toluene or a toluene/α,α,α-trifluorotoluene (TFT) mixture (50/50 wt %) at room temperature. Note that 1 equiv of Li[FABA] is more than sufficient to completely convert the (t-Bu$_3$P)PdMeCl proinitiator to the cationic Pd complex which is active for polymerization.[6]

First, we examined the living characteristics of the polymerization using BuNB, which has a high propagation rate. Figure 1a shows the plot of M_n versus conversion, which was confirmed to be linear (GPC traces in Figure S1). Also, a linear relationship between M_n at full conversion and the molar monomer to initiator feed ratio ([M]$_0$/[Pd]), when the latter ranged from 100 to 400, was observed (Figure 1b). In all cases, $Đ < 1.2$. The $M_{n,LS}$ values determined by GPC coupled with a multiangle laser light scattering detector are in good agreement with the theoretical values ($M_{n,theo}$).

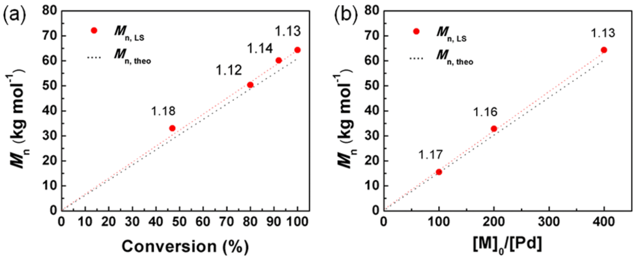


Figure 1. Plots of (a) M_n vs conversion ([M]$_0$/[Pd] = 400) and (b) M_n vs [M]$_0$/[Pd] (conversion = 100%) for the vinyl addition polymerization of BuNB. The label next to each data point is that polymer's molecular weight dispersity ($Đ$) value from GPC-RI.

The vinyl addition polymerization of other monomers was also examined (Table 1, polystyrene-equivalent molecular weight distributions in Figure S2). In the case of PFBuNB (Scheme 1), only low molecular weight oligomers were obtained, which did not precipitate in methanol or hexane (entry 10 in Table 1, molecular weight distribution in Figure S2). In all other cases, the resultant polymers were found to be soluble in different common organic solvents such as THF, CHCl$_3$, or DMSO, depending on the substituent (Table S1). No olefinic proton peaks were observed in ^{1}H NMR spectra of the polymers (Figure S3), confirming that the polymerization mechanism was vinyl addition polymerization, not ROMP.[20] As with BuNB, $M_{n,LS}$ is close to $M_{n,theo}$, and most polymers showed $Đ < 1.3$ (Table 1 and Figure S2), with the sole exception of the norbornyl-substituted NB monomers (NBANB and NB-*exo*-NBA).

NB monomers with butyl, benzyl, and pentafluorobenzyl moieties exhibit complete conversion within 48 h, although BnNB and PFBnNB are slower to reach complete conversion compared with BuNB; 3 and 48 h are needed for the complete conversion of BnNB and PFBnNB, respectively. HFANB shows very slow polymerization kinetics; complete conversion is not reached after 48 h even at a lower [M]$_0$/[Pd] ratio of 100. This sluggish polymerization could be due to coordination of the hexafluoropropan-2-ol moiety of the HFANB (*endo*/*exo* ratio of 82/18) to the metal center of the catalyst, which is favored for the majority *endo*-isomer.[21,22] Indeed, *exo*-HFANB polymerizes much faster than HFANB, reaching complete conversion within 21 h (entry 7 in Table 1).

By contrast, slow polymerizations yielding relatively large values of $Đ$ (>1.5) were observed for NB monomers bearing a norbornyl substituent. Even when the substituent does not bear a coordinating group, it is known that insertion of the *endo*-isomer into the *endo*-inserted complex is slower than insertion of *exo*-isomer into the *exo*-inserted complex due to steric restriction.[9] This fact, coupled with the steric bulk of NBA, explains the slow rate of polymerization of NBANB. NB-*exo*-NBA, which is synthesized from *exo*-vinylnorbornane, shows a similarly slow polymerization as NBANB, confirming that it is the *endo*/*exo* configuration of the NB ring (not the NBA ring in the substituent) which has the dominant influence on rate. The relatively large values of $Đ$ observed with both monomers suggest significant spontaneous termination in these polymerizations.

Since the HFANB, NBANB, and NB-*exo*-NBA polymerizations in Table 1 did not achieve full conversion, the *endo*/*exo* ratio in the polymer can differ from that in the monomer feed. As noted above, the *exo*-isomer is commonly[4,9,21,22] enchained preferentially; ^{1}H NMR spectra from aliquots of the reaction mixture (Figure S4) revealed this to be the case for these three monomers as well, such that the *exo*-isomer was entirely consumed even before the limited conversion indicated in Table 1 was reached. From the overall monomer conversion and the monomer *endo*/*exo* ratio, we can thus determine the *endo*/*exo* ratio in each polymer (footnote *k* in Table 1). Since the conversions are all >50%, the *exo*-enhancements in the polymers are modest, but they do indicate the presence of a down-chain *exo*-gradient in each case (and likely in the polymers derived from the other mixed *endo*/*exo* monomers as well).

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Table 1. Vinyl Addition Polymerization of Substituted Norbornenes Using (t-Bu_3P)PdMeCl/Li[FABA][a]

entry	monomer[b] (*endo*/*exo*)	solvent[c]	$[M]_0/[Pd]$[d]	time (h)	conv.[e] (%)	$Đ$[f]	$M_{n,theo}$[g] (kg mol^{-1})	$M_{n,LS}$[h] (kg mol^{-1})
1	BuNB (77/23)	Tol	100	0.5	100	1.17	15.0	15.5
2	BuNB (77/23)	Tol	200	0.75	100	1.16	30.1	32.8
3	BuNB (77/23)	Tol	400	1	100	1.13	60.1	64.3
4	BnNB (76/24)	Tol	200	3	100	1.19	36.9	40.4
5	PFBnNB (80/20)	Tol/TFT[i]	200	48	100	1.28	54.8	57.8
6	HFANB (82/18)[k]	Tol/TFT[i]	100	48	78	1.16	21.4	22.1
7	*exo*-HFANB (0/100)	Tol/TFT[i]	100	21	100	1.19	27.4	28.2
8	NBANB (83/17)[k]	Tol	100	48	58	1.73	10.9	13.6
9	NB-*exo*-NBA (82/18)[j,k]	Tol	100	48	54	1.56	10.2	12.4
10	PFBuNB (72/28)	Tol/TFT[i]	200	24	14	1.27	8.7	4.7[l]

[a]4 wt % of monomer in solvent, at room temperature. [b]See Scheme 1; (*endo*/*exo*) is the ratio of *endo*- to *exo*-isomers (referring to the norbornenyl ring) in the monomers. [c]Tol = toluene, TFT = α,α,α-trifluorotoluene. [d](t-Bu_3P)PdMeCl/Li[FABA] = 1/1. [e]Determined by ^1H NMR spectroscopy. [f]Determined by GPC using differential refractive index (RI) detector, calibrated with narrow distribution polystyrene standards (THF). [g]Theoretical molecular weight, calculated from $[M]_0/[Pd] \times MW_{monomer} \times$ conversion/100. [h]Determined by GPC using multiangle laser light scattering (LS) detector (THF). [i]50/50 wt % mixture. Phase separation occurred when toluene was used as a solvent. [j]NB-*exo*-NBA was prepared by reaction of dicyclopentadiene with *exo*-vinylnorbornane (>95%). [k]*endo*/*exo* ratios in polyHFANB, polyNBANB, and poly(NB-*exo*-NBA) were 77/23, 71/29, and 67/33, respectively. [l]Polystyrene-equivalent molecular weight obtained from GPC-RI.

Table 2. Synthesis of Block Copolymers[a]

entry	monomer[b]	solvent[c]	$[M]_0/[Pd]$[d]	time (h)	conv. (%)	$Đ$[f]	$M_{n,theo}$[g] (kg mol^{-1})	$M_{n,LS}$[h] (kg mol^{-1})
1	BuNB	Tol/TFT[i]	100	0.5	100[e]	1.17	15.0	15.9
	HFANB	Tol/TFT[i]	200	48	71[j]	1.16	54.8[k]	56.9
2	BnNB	Tol/TFT[i]	80	1	100[e]	1.18	14.7	16.2
	PFBnNB	Tol/TFT[i]	200	36	94[j]	1.28	67.8[k]	72.5
3	BuNB	Tol	70	0.5	100[e]	1.24	10.5	10.3
	BnNB	Tol	110	1.5	100[e]	1.19	30.8	33.1
	NBANB	Tol	200	48	28[j]	1.46	43.6[k]	44.9

[a]Polymerizations run at room temperature; concentration of first monomer, 4 wt %; subsequent monomers charged as 4 wt % solutions. [b]See Scheme 1; all monomers in this table are mixtures of endo/exoisomers. [c]Tol = toluene, TFT = α,α,α-trifluorotoluene. [d](t-Bu_3P)PdMeCl/Li[FABA] = 1/1. [e]Confirmed by ^1H NMR spectroscopy. [f]Determined by GPC using differential refractive index (RI) detector, calibrated with narrow distribution polystyrene standards (THF). [g]Theoretical molecular weight. [h]Determined by GPC using multiangle laser light scattering (LS) detector (THF). [i]50/50 wt % mixture. [j]Calculated from $\{[M_{n,LS,1st(or\ 1st+2nd)block} \times (\text{weight fraction}_{2nd(or\ 3rd)block}/\text{weight fraction}_{1st(or\ 1st+2nd)block})]/MW_{2nd(or\ 3rd)monomer}\}/([M]_0/[Pd]_{2nd(or\ 3rd)monomer}) \times 100$. See Figure S6 for weight fractions of block copolymers. [k]Calculated from $M_{n,LS,1st(or\ 1st+2nd)block} + ([M]_0/[Pd]_{2nd(or\ 3rd)block} \times MW_{2nd(or\ 3rd)monomer} \times \text{conversion}/100)$.

Thermogravimetric analysis (TGA, Figure S5) shows that all homopolymers in Table 1 exhibit insignificant weight loss until above 200 °C, with 5% weight loss occurring near 400 °C. Differential scanning calorimetry (DSC) up to 200 °C did not reveal a glass transition for any of the polymers; the T_g of polyBuNB has been previously reported as 340 °C,[3] but polymer decomposition at such high temperatures makes an accurate determination of T_g difficult. Thus, the present polymers retain the high T_g and good thermal stability imparted by the saturated, bicyclic-ring backbone, while having greatly improved solubility over polyNB.

Since several of these substituted NB monomers undergo living polymerization with this catalyst complex, we further explored the possibility of synthesizing well-defined block copolymers by sequential monomer addition. Monomers which polymerize to complete conversion within a reasonable time (BuNB, BnNB, *exo*-HFANB) are most suitable for block copolymer synthesis, as these could, in principle, be combined in any order to make block copolymers with an arbitrarily complex sequence. Monomers which polymerize slowly (PFBnNB, HFANB), or which show some spontaneous termination (NBANB, NB-*exo*-NBA) can still be incorporated into well-defined block copolymers, but only as the final block (B block in an AB diblock, C block in an ABC triblock, etc.). As an example (entry 1 in Table 2), BuNB was polymerized to give the first block, followed by the addition of HFANB after 30 min. After 2 days, polyBuNB-*b*-polyHFANB was obtained with $M_{n,LS}$ = 56.9 kg mol^{-1} and $Đ$ = 1.16. GPC analysis shows a uniform shift of the peak to shorter elution time upon chain extension with HFANB (Figure 2a). As a second example, polyBnNB-*b*-polyPFBnNB was successfully synthesized ($Đ$ = 1.28, entry 2 in Table 2), and GPC analysis again confirms the block copolymer structure (Figure 2b). As a final example, an ABC-type triblock copolymer, polyBuNB-*b*-polyBnNB-*b*-polyNBANB, was synthesized (entry 3 in Table 2). Figure 2c displays the GPC results, showing that a narrow distribution was preserved throughout polymerization of the BuNB and BnNB blocks, but that the distribution broadened (to $Đ$ = 1.46) after polymerization of the NBANB block, consistent with the relatively large $Đ$ observed in NBANB homopolymerizations (Table 1). Compositions of the block copolymers were determined using quantitative ^{13}C NMR spectroscopy (Figure S6) and were found to be close to those calculated from the $M_{n,LS}$ values given in Table 2, which in turn closely match the $M_{n,theo}$ values.

In conclusion, we have demonstrated that (t-Bu_3P)PdMeCl, activated by Li[FABA], can execute the living vinyl addition polymerization of various substituted NB monomers. We also report the first examples of well-defined vinyl addition block copolymers from substituted NB monomers. In addition to

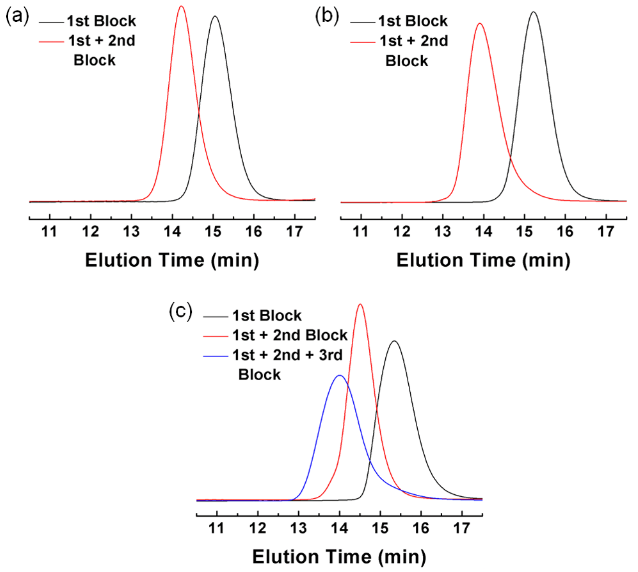

Figure 2. GPC-RI traces for (a) polyBuNB-*b*-polyHFANB, (b) polyBnNB-*b*-polyPFBnNB, and (c) polyBuNB-*b*-polyBnNB-*b*-polyNBANB block copolymers.

providing a route to the synthesis of functional block copolymers for targeted applications, we believe that the present work provides insight into the design of catalysts for living vinyl addition polymerization of substituted NBs. In particular, modification of the phosphine ligand could increase the polymerization rate and suppress spontaneous termination in the polymerization of monomers with bulky substituents, such as NBANB; such studies are underway.

■ ASSOCIATED CONTENT

Supporting Information

General description of monomer syntheses; detailed experimental procedures for polymerization and characterization; GPC-RI traces for polyBuNB aliquots corresponding to Figure 1a; PS-equivalent molecular weight distributions of homopolymers; ^{1}H NMR spectra of homopolymers; ^{1}H NMR spectra of reaction mixture aliquots during NB-*exo*-NBA polymerization, showing preferential consumption of the *exo*-isomer; TGA traces of homopolymers; and quantitative ^{13}C NMR spectra and compositions of block copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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