

Addition Polymerization of Norbornene Catalyzed by Palladium(2+) Compounds. A Polymerization Reaction with Rare Chain Transfer and Chain Termination

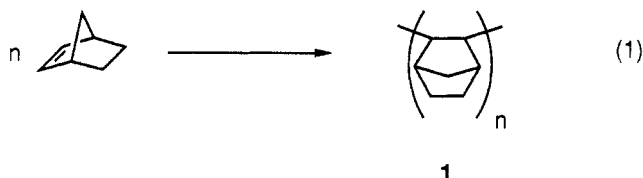
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Received January 20, 1992

Revised Manuscript Received May 11, 1992

A large number of transition-metal compounds are known to catalyze the ring-opening olefin metathesis polymerization (ROMP) of norbornene.¹ The corresponding polymer, poly(1,3-cyclopentylenevinylene), contains one carbon-carbon double bond for each repeat unit. However, some catalysts based on Ti and Pd compounds^{2,3} produce a saturated polymer, poly(2,3-bicyclo[2.2.1]hept-2-ene) (1; eq 1). So far, only a few examples of this addition



polymerization have been examined. Another mode of polymerization is the cationic polymerization of norbornene, resulting in moderate yields of oligomeric poly(2,7-bicyclo[2.2.1]hept-2-ene). Gaylord et al.^{3b} showed that structural rearrangements of the bicyclic unit take place during this reaction.

We used $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ for the preparation of poly(2,3-bicyclo[2.2.1]hept-2-ene) (1). Solubility in unsaturated halogenated hydrocarbons, such as trichloroethylene, tetrachloroethylene, chlorobenzene, 1,2-dichlorobenzene, and bromobenzene, enabled us to conduct molecular weight analyses by gel permeation chromatography (GPC) and vapor phase osmometry (VPO). Poly(2,3-bicyclo[2.2.1]hept-2-ene) samples with molecular weights $M_n(\text{VPO})^4$ between 3500 and 6200 were obtained, when norbornene/ Pd^{2+} ratios ($[\text{M}]/[\text{I}]$) ranging from 40/1 to 91/1 were used in nitromethane as a solvent.⁵ These values of $M_n(\text{VPO})$ were in reasonably good agreement with theoretical molecular weights calculated for a polymerization reaction free of chain transfer and chain termination. However, higher molecular weight samples ($M_n(\text{GPC})^4$ between 24 000 and 70 000) had relatively high polydispersities, M_w/M_n in the range of 1.3–1.5. The limited solubility in nitromethane caused poly(2,3-bicyclo[2.2.1]hept-2-ene) to precipitate before all of the monomer had been consumed.

We achieved nearly homogeneous polymerizations with a solvent mixture of nitrobenzene and chlorobenzene (volume ratio = 1/2) and with $[\text{Pd}(\text{CH}_3\text{CH}_2\text{CN})_4][\text{BF}_4]_2^6$ as the catalyst. Polymer chain growth was found to continue after renewed monomer additions, indicating rare chain transfer and chain termination. The initial molar ratio of norbornene to Pd^{2+} compound ($[\text{M}]/[\text{I}]$) was 50/1. After more than 90% consumption of the monomer, another 50 equiv of norbornene were added, and continued chain propagation was observed. The molecular weight increased from $M_n(\text{GPC}) = 5400$ to $M_n(\text{GPC}) = 11 600$

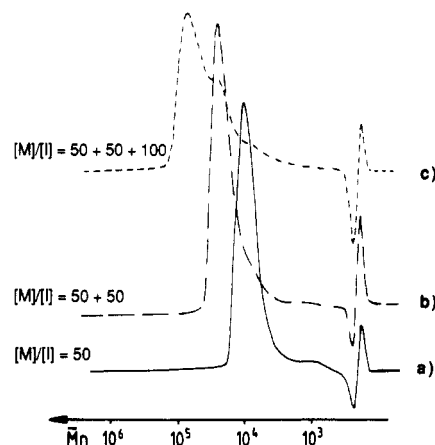


Figure 1. Gel permeation chromatographic analyses of poly(2,3-bicyclo[2.2.1]hept-2-ene) samples obtained following subsequent additions of norbornene. Molar ratio of norbornene to Pd^{2+} compound ($[\text{M}]/[\text{I}]$): (a) 50/1; (b) (50 + 50)/1; (c) (50 + 50 + 100)/1. Calibration with polystyrene; eluent = chlorobenzene.

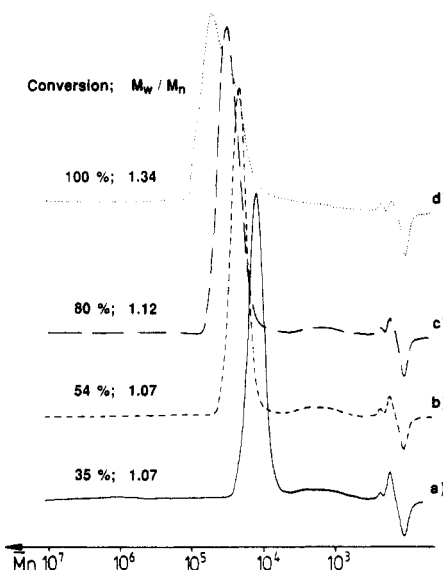


Figure 2. Gel permeation chromatographic analyses of poly(2,3-bicyclo[2.2.1]hept-2-ene) samples prepared at 0 °C ($[\text{M}]/[\text{I}] = 250/1$); 0.044 mmol of $[\text{Pd}(\text{CH}_3\text{CH}_2\text{CN})_4][\text{BF}_4]_2$, 10.8 mmol of norbornene, 5 mL of dichloromethane, 12 mL of chlorobenzene, 6 mL of nitrobenzene. (a) 35% conversion (after 6 min), $M_n(\text{GPC}) = 11 200$, $M_w/M_n = 1.07$. (b) 54% conversion (after 20 min), $M_n(\text{GPC}) = 21 400$, $M_w/M_n = 1.07$. (c) 80% conversion (after 60 min), $M_n(\text{GPC}) = 29 400$, $M_w/M_n = 1.12$. (d) 100% conversion (after 15 h), $M_n(\text{GPC}) = 35 900$, $M_w/M_n = 1.34$.

(Figure 1a,b). The addition of another 100 equiv of norbornene led to a further increase of molecular weight to $M_n(\text{GPC}) = 22 300$ (Figure 1c).⁷

Poly(2,3-bicyclo[2.2.1]hept-2-ene) samples with polydispersities M_w/M_n as low as 1.07 were obtained when the polymerization was run to 35 and 54% conversion at 0 °C ($[\text{M}]/[\text{I}] = 250/1$; Figure 2).⁸ Polydispersities were well below 1.2 for monomer conversions up to 80%. The high molecular weight sample (100% conversion; Figure 2d) was bimodal due to partial precipitation of the polymer. Similar studies were conducted for norbornene/ Pd^{2+} ratios $[\text{M}]/[\text{I}]$ of 500/1. Approximately linear plots of molecular weight versus conversion were obtained (Figure 3). These results indicate that the addition polymerization of norbornene proceeds in a well-behaved manner with rare chain transfer and chain termination, when reaction conditions are carefully controlled.

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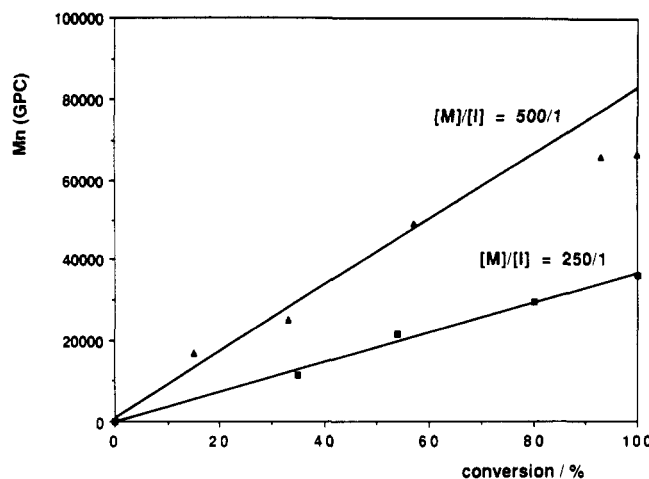
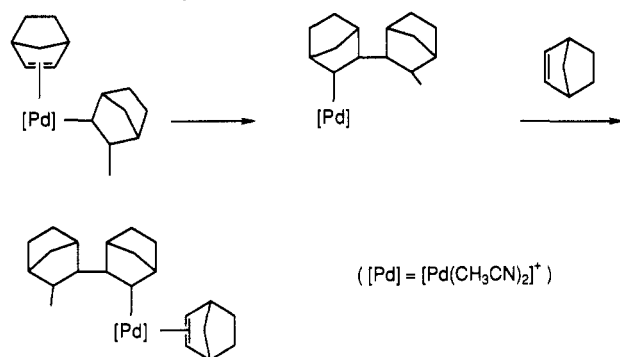
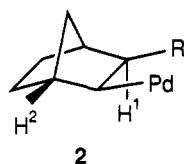


Figure 3. Plots of molecular weight versus conversion for addition polymerizations of norbornene starting from $[M]/[I] = 250/1$ and $500/1$.

Scheme I
Suggested Chain Propagation in the Addition Polymerization of Norbornene



The well-behaved nature of the $[Pd(CH_3CH_2CN)_4][BF_4]_2$ -catalyzed polymerization of norbornene suggests an insertion type mechanism (Scheme I) in preference to a cationic mechanism.⁹ Pd^{2+} -catalyzed intramolecular insertion reactions typically proceed by cis insertion,¹⁰ thus resulting in structure 2, when applied to norbornene.¹¹



R = alkyl or polymer chain

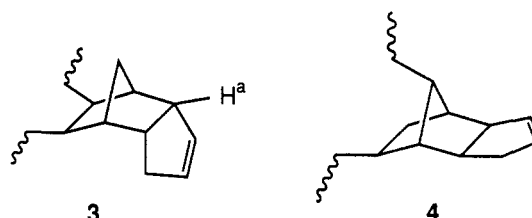
Decomposition of species 2 via β -hydride elimination¹² is unfavorable, as both β -hydrogen atoms H^1 and H^2 are not easily accessible for a Pd-H bond-forming process.

The Pd-C bond of the polymer end group remained intact after all of the monomer had been consumed. It was possible to cleave the Pd-C bond by insertion of carbon monoxide and subsequent addition of methanol. Pd(0) precipitated, and poly(2,3-bicyclo[2.2.1]hept-2-ene) with methyl ester end groups was formed.^{13,14}

The polymerization of norbornene still occurred, when 1000 equiv of water (molar ratio of H_2O to $Pd^{2+} = 1000/1$) was added to a monomer solution containing 200 equiv of norbornene (molar ratio of norbornene to $Pd^{2+} = 200/1$). Water is known to trap free carbocations, thus reducing the likelihood of a cationic polymerization mechanism.¹⁵

We prepared the addition polymer of *endo*-dicyclopentadiene.¹⁶ The 1H NMR spectrum of this polymer shows

a signal at 2.97 ppm, which can be assigned to the allylic bridgehead proton (H^a in 3). The intensity corresponds



to one proton per repeat unit. The absence of structural rearrangements indicates that free carbocations are not involved in chain propagation. For comparison, *endo*-dicyclopentadiene was subjected to cationic polymerization initiated by BF_3 -etherate.¹⁷ This reaction produced a different polymer with the predominant structure 4; no 1H NMR signal at 2.97 ppm could be detected.

It is notable that the double bond of the considerably less strained five-membered ring remains intact during the Pd^{2+} -catalyzed addition polymerization. A similar result was obtained for the Pd^{2+} -catalyzed polymerization of *exo*-dicyclopentadiene.¹⁸

At present, further work is in progress to apply this Pd^{2+} -catalyzed addition polymerization to different norbornene derivatives and to the synthesis of block copolymers.

Acknowledgment. We thank Prof. W. Heitz, Dr. I. Tritto, Dr. C. Bennett, and Prof. R. More O'Ferrall for many helpful discussions. Financial support by the Deutsche Forschungsgemeinschaft (DFG), BMFT, and BASF (Doktorandenstipendium to C. M.) is gratefully acknowledged.

References and Notes

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- $M_n(VPO)$ = number-average molecular weight determined by vapor phase osmometry in chlorobenzene at 90 °C; $M_n(GPC)$ = number-average molecular weight determined by gel permeation chromatography (in chlorobenzene), calibration with polystyrene standards. A correction factor of 0.7 was determined by light scattering studies for a sample with $M_n(GPC) = 75\,000$ ($M_w/M_n = 1.41$): $M_n(corr) = 0.7 M_n(GPC)$.
- Molecular weights $M_n(VPO) = 3500, 4600, 5000$, and 8200 were obtained from $[M]/[I] = 40/1, 50/1, 67/1$, and $91/1$, respectively.
- We prepared $[Pd(CH_3CH_2CN)_4][BF_4]_2$ similar to a procedure by: Schramm, R. F.; Wayland, B. B. *J. Chem. Soc., Chem. Commun.* 1968, 898.
- Synthesis of poly(2,3-bicyclo[2.2.1]hept-2-ene), renewed monomer additions: a catalyst solution prepared from 0.11 mmol of $[Pd(CH_3CH_2CN)_4][BF_4]_2$, 0.55 mmol of norbornene, and 3 mL of dichloromethane was added to a monomer solution of 5.0 mmol of norbornene, 2 mL of nitrobenzene, and 4 mL of chlorobenzene. After 5 min at 25 °C, 4.5 mL of the mixture was added to methanol to precipitate the polymer, $M_n(GPC) = 5400$; 85% yield. A solution of 2.75 mmol of norbornene in 1.5 mL of nitrobenzene and 3 mL of chlorobenzene was added to the remainder of the reaction mixture. After 5 min at 25 °C, the polymer was isolated from half of the mixture, M_n -

- (GPC) = 11 600, 83% yield. A third addition of a monomer solution comprising 2.71 mmol of norbornene in 1.5 mL of nitrobenzene and 3 mL of chlorobenzene was added. After 5 min at 25 °C, a polymer with M_n (GPC) = 22 300, 86% yield, was isolated.
- (8) The monomer norbornene serves as a solubilizing reagent for poly(2,3-bicyclo[2.2.1]hept-2-ene).
 - (9) At present, the mechanism of this polymerization is still under debate. A cationic mechanism had been assumed for polymerization reactions catalyzed by $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$.¹⁹ However, Gaylord et al.,^{3b} Corner et al.,^{3c} and Schulz^{3a} ruled out a cationic polymerization mechanism for norbornene polymerizations catalyzed by Pd-based catalysts $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ and PdCl_2 , respectively. These authors based their conclusions on the absence of any linkages between C-2 and C-7 of the monomer unit. Kiennemann et al.^{3c} proposed an insertion type mechanism for the polymerization by $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ as a result of their identification of a Pd-norbornene π -complex.
 - (10) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
 - (11) The isolation and characterization of products resulting from monoinsertion of norbornene into Pd-allyl bonds was described in: (a) Hughes, R. P.; Powell, J. J. *Organomet. Chem.* **1973**, *60*, 387. (b) Gallazzi, M. C.; Hanlon, T. L.; Vitulli, G.; Porri, L. *J. Organomet. Chem.* **1971**, *33*, C45. These authors found cis-exo addition of the Pd-allyl bond to norbornene.
 - (12) β -Hydride elimination is one of the major pathways for chain transfer or chain termination in other insertion polymerizations: Boor, J. *Ziegler Natta Catalysis and Polymerizations*; Academic Press: New York, 1979.
 - (13) The methyl ester end group was identified by IR (absorption at 1735 cm^{-1}) and by ^1H NMR spectroscopy (δ = 3.82 ppm). In addition, it was possible to cleave the Pd-C bond of poly-(2,3-bicyclo[2.2.1]hept-2-ene) by reduction with NaBH_4 . This second reaction displaced Pd by H.
 - (14) A value of 1.24% of N (elemental analysis) was determined for a low molecular weight polymer with M_n = 1050, which suggests incorporation of the nitrile by an initiation mechanism similar to the Pd analogue of the Ritter reaction.^{20b} Additional studies on oligomers are in progress to elucidate the initiation step.
 - (15) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley-Interscience: New York, 1981.
 - (16) At 25 °C, 0.08 mmol of $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ was added to 8 mmol of *endo*-dicyclopentadiene in 10 mL of nitromethane. After 24 h at 25 °C, precipitation with methanol gave a 13% polymer yield. Anal. Calcd for $(\text{C}_{10}\text{H}_{12})_n$: C, 90.85; H, 9.15. Found: C, 90.79; H, 9.21. IR (KBr): 3020 (m), 2950 (s), 2850 (m), 1450 (m), 1350 (w), 1280 (m), 940 (m), 810 (w), 740 (s), 695 (m) cm^{-1} . ^1H NMR (300 MHz, CD_3Cl , 25 °C): δ 5.63 (b m, 2 H, olefin), 2.97 (b m, 1 H, allyl), 2.45 (b m, 2 H, allyl), 2.2 (b m, 5 H, >CH), 1.6 (b m, 1 H, >CH₂), 1.2 (b m, 1 H, >CH₂).
 - (17) At 40 °C, 4.1 mmol of BF_3 -etherate was added to 15.1 mmol of *endo*-dicyclopentadiene. After 30 min, addition of 20 mL of dichloromethane and 0.5 mL of triethylamine and precipitation with methanol gave a 35% yield of polymer. IR (KBr): 3025 (w), 2950 (s), 2910 (m), 2850 (w), 1450 (m), 1280 (w), 1020 (w), 940 (w), 790 (w), 735 (w), 705 (m) cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 5.66 (b m, 1 H), 5.45 (b m, 1 H), 2.52 (b m, 3 H), 2.3–1.1 (b m, 7 H).
 - (18) Addition polymer prepared from *exo*-dicyclopentadiene. Anal. Calcd for $(\text{C}_{10}\text{H}_{12})_n$: C, 90.85; H, 9.15. Found: C, 90.47; H, 9.53. IR (KBr): 3020 (m), 2940 (s), 2900 (s), 2850 (m), 1620 (w), 1460 (m), 1450 (w), 1350 (w), 1280 (m), 1020 (w), 940 (m), 740 (m), 695 (s) cm^{-1} . ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 5.66 (ps, 1 H), 5.48 (m, 1 H), 2.59 (b m, 3 H), 2.2–1.8 (b m, 5 H), 1.25 (b m, 2 H).
 - (19) Compound $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{PF}_6]_2$ is also known as a reagent, which catalyzes Friedel-Crafts alkylation reactions,^{20a} addition reactions of nitriles to olefins,^{20b} and the rearrangement of *tert*-butylethylene and 1,1,2-trimethylcyclopropane.^{20a} In addition, this Pd^{2+} catalyst polymerizes styrene, phenylacetylene, and 1,3-cyclohexadiene.^{3d}
 - (20) (a) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627. (b) Hegedus, L. S.; Mulhern, T. A.; Asads, H. *J. Am. Chem. Soc.* **1986**, *108*, 6224.

Registry No. $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$, 21797-13-7; $[\text{Pd}(\text{CH}_3\text{CH}_2\text{CN})_4][\text{BF}_4]_2$, 142067-50-3; poly(2,3-bicyclo[2.2.1]hept-2-ene), 25038-76-0.