12230 *J. Am. Chem. Soc.* **1996,** *118,* 12230−12231

Polymers Composed of Triangular Repeating Units. Pd^{2+}-Catalyzed Addition Polymerizations of 3,3-Dialkylcyclopropenes

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Received April 11, 1996

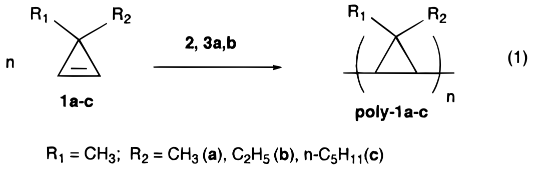
Chiral Pd(II) complexes have recently attracted significant interest due to their utility for asymmetric catalysis.[1] In addition, chiral and achiral Pd(II) catalysts have become important for addition polymerizations of linear and cyclic olefins. Strictly alternating α-olefin/carbon monoxide copolymers with regio- and stereoregular and -irregular structures,[2] polyolefins with functional groups,[3] highly branched amorphous poly(α-olefins),[4] and cycloaliphatic polyolefins based on strained polycyclic olefins[5] can be prepared through careful choice of the ligands and the counterions of Pd(II) complexes. The latter polyolefins containing polycyclic repeating units are interesting materials, since their rigid polymer backbones lead to high heat distortion temperatures.[6]

We here report the addition polymerization of the 3,3-dialkyl-substituted cyclopropenes **1a**−**c**,[7] which are highly strained monocyclic olefins (eq 1).[8] Unsubstituted cyclopropene is thermally unstable and undergoes spontaneous, uncontrolled polymerization when kept above −78 °C.[9] Substituted cyclopropene derivatives produce cyclic dimers and ring-opened polymers when reacted with Pd(II) catalysts without chelating ligands.[10] Oxidative addition with Pd(0) complexes and Pd(0) intermediates leads to cyclooligomerization with the formation of cyclic dimers, trimers, and tetramers.[11] We now describe high molecular weight cycloaliphatic polyolefins **poly-1a**−**c** composed of saturated triangular repeating units. These addition polymers were prepared using (η^3-allyl){(−)-sparteine}palladium(II) (**2**)[12a] and (η^3-allyl)(bisoxazoline)palladium(II) hexafluoroantimonate catalysts (**3a,b**)[12b] (eq 1 and Table 1). **Poly-1a**−**c** of Table 1 were obtained in 32−91% yields from molar ratios of cyclopropene monomer to Pd(II) catalyst ([M]/[C]) between 20:1 and 115:1.[13] The steric bulk of the chelating ligand of the Pd catalyst and the size of the monomer substituents affect the polymerization behavior of the cyclopropene derivatives. 3-*n*-Pentyl-3-methylcyclopropene undergoes polymerization with the phenyl-substituted bisoxazoline Pd(II) complex **3a**, but remains unreacted (over a period of 120 h at 20 °C) when Pd(II) compound **3b** with the bulkier bis(*tert*-butyl)bisoxazoline ligand is used as the catalyst (compare entries 8 and 9 of Table 1). On the other hand, 3,3-dimethylcyclopropene is sufficiently small for the insertion polymerization with complex **3b** (entry 3). The relative number and weight average molecular weights of poly(3-*n*-pentyl-3-methylcyclopropene) (**poly-1c**, entry 7) are M_n(GPC) = 42 000 and M_w(GPC) = 99 000.[14]

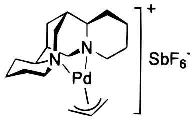
Table 1. Poly(3,3-dialkylcyclopropenes) Prepared with Pd Catalysts **2** and **3a,b**

entry	polymer	catalyst	[M]/[C][a]	*t* (h)[b]	yield (%)[c]
1	**poly-1a**	**2**	115	32	63
2	**poly-1a**	**3a**	90	32	36
3	**poly-1a**	**3b**	100	40	32
4	**poly-1b**	**2**	34	48	91
5	**poly-1b**	**2**	100	32	81
6	**poly-1b**	**3a**	115	32	43
7	**poly-1c**	**2**	20	32	85
8	**poly-1c**	**3a**	90	120	63
9	**poly-1c**	**3b**	50	120	0

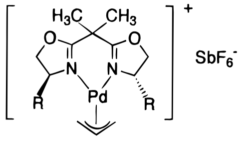
[a] Initial molar ratio of monomer to Pd^{2+} catalyst. [b] Reaction time at 20 °C, the temperature was previously raised from −80 to 20 °C. Reactions were carried out under nitrogen; solvent was CH_2Cl_2 in entries 1, 4, 5, and 7−9; C_6H_5Cl in entries 2, 3, and 6. [c] Polymer synthesis on a scale of 130−340 mg.



(1)



2



3a,b **a:** R = Ph, **b:** R = *tert*.-Bu

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(2) For selected references about $(CH_2CH_2C(O))_n$, $(CH(Ar)CH_2(CO))_n$, and $(CH(CH_3)CH_2(CO))_n$ oligomers and polymers, see: (a) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (b) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 135. (c) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Ait Haddou, H. *J. Am. Chem. Soc.* **1994**, *116*, 3641. (d) Corradini, P.; DeRossa, C.; Panuzzi, A.; Petrucci, G.; Pino, P. *Chimia* **1990**, *44*, 52.

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(7) Synthesis of **1a,b** according to the following: (a) Binger, P. *Synthesis* **1974**, 190. (b) Nesmeyanova, O. A.; Rudashevskaya, T. Y.; Dyachenko, A. I.; Savilova, S. F.; Nesedov, O. M. *Synthesis* **1982**, 296. See Supporting Information for preparative details on the synthesis of **1c**. These three-step syntheses involve the addition of dihalocarbenes to geminally disubstituted olefins, reduction, and elimination of hydrogen halide. They are suitable for monomer preparations on scales of up to several grams. Different monomer syntheses with potential for scale-up are required in order to improve the overall practicality. For other cyclopropene syntheses, see: (c) Closs, G. L.; Closs, L. E.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796.

(8) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

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(13) See Supporting Information for preparative details and characterization. Polymer yields were consistently higher with the sparteine-based catalyst. Polymerization with $[(\eta^3\text{-allyl})(2,2'\text{-bipyridyl})Pd^{II}][SbF_6]$ resulted in only a 20% yield of **poly-1a** indicating that catalyst stability and polymer yields decrease when less bulky and less rigid chelating ligands are used.

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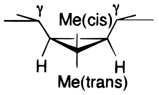
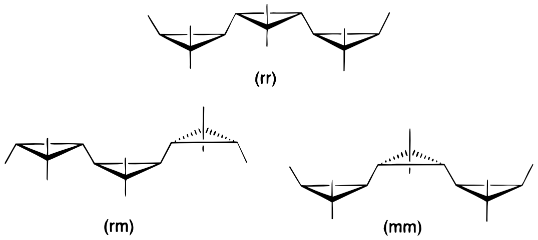
Scheme 1. 1,2-Cis-Linked Repeating Unit of poly-1a

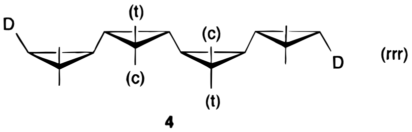


Scheme 2



The ^{1}H NMR spectra show that the three-membered ring structure of the monomers is retained during the polymerization (e.g., two broad signals at $\delta = 1.2$ and 0.5 ppm correspond to the methyl and cyclopropyl protons of poly(3,3-dimethylcyclopropene) (**poly-1a**)). ^{13}C NMR spectra reveal a polymer structure with 1,2-cis-linked triangular repeating units.[15] Characteristic is the substantial chemical shift difference of $\Delta\delta >$ 11 ppm for the two methyl groups of the repeating units of **poly-1a**, which results from additive γ-syn and γ-anti effects imposed by the two neighboring cyclopropyl units on Me(cis) and Me(trans), respectively (Scheme 1). The ^{13}C NMR spectrum consists of four sets of signals.[16] The presence of one slightly more pronounced signal within each of these four sets of signals at δ 30.2 ppm (Me(trans)), $\delta = 24.0$ ppm (cyclopropyl-CH), $\delta = 18.0$ ppm (quaternary cyclopropyl-C), and $\delta = 16.6$ ppm (Me(cis)) indicates that poly(3,3-dimethylcyclopropene) prepared with **2** and **3a** is partially stereoregular.

Poly-1a can adopt the three different triad structures, rr, mr, and mm, presented in Scheme 2. The tetramer of 3,3-dimethylcyclopropene, quater(3,3-dimethylcyclopropyl) (**4**), with a syndiotactic sequence of three-membered ring units (rrr-tetrad),[17] serves as a model compound to aid assignment of the moderately predominant stereochemical configuration of poly(3,3-dimethylcyclopropene) (entries 1 and 2). The chemical shifts δ 17.4 and 29.3 corresponding to Me(c) and Me(t) of **4** are very similar to those of the low-intensity signals of **poly-1a** but differ by nearly 1 ppm from the dominant Me(cis) and Me(trans) signals. This result suggests to us that poly(3,3-dimethylcyclopropene) samples synthesized with **2** and **3a** contain a moderate excess of meso units.[18] This excess is slightly more pronounced in **poly-1a** (entry 2) prepared with the phenyl-substituted bisoxazoline Pd catalyst **3a** than in the product (entry 1) obtained with the sparteine-based catalyst **2**.[19]



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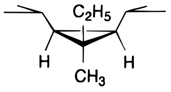
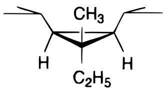
The relatively moderate degree of tacticity indicates that both catalytic site control and chain-end control contribute to the overall stereocontrol in the polymerization of **1a** catalyzed by **3a**. The catalytic site control exerted by the C$_2$-symmetric bisoxazoline ligand is assumed to be partially compensated by the steric contribution of the structurally rigid polymer chain-end linked to Pd(II). This contrasts with (bisoxazoline)Pd(II)-catalyzed alternating copolymerizations[2c] of *p-tert*-butylstyrene and CO in which the chain-end control mechanism can be overridden by the C$_2$-symmetric ligand due to the higher flexibility of the growing polymer chain.

Poly(3-ethyl-3-methylcyclopropene) (**poly-1b**) can adopt additional stereochemical configurations to those presented in Scheme 2 as the ethyl substituent can be either cis (**poly-1b,c**) or trans (**poly-1b,t**) to the bonds of the polymer main chain.



poly-1b,c



poly-1b,t

Trans-linked ethyl groups (**poly-1b,t**) are slightly predominant due to moderately less hindered π-coordination of the methyl-substituted monomer face during chain propagation. The mole fraction of **poly-1b,t** is 0.65 in entry 4 and 0.60 in entry 6, as determined from the intensity of the ^{1}H NMR signals at δ 1.2−1.1 (**poly-1b,c**) and 0.98 (**poly-1b,t**).

In conclusion, polycyclopropenes with molecular weights above 10 000 were obtained by the addition polymerization of 3,3-dialkyl-substituted cyclopropenes with Pd complexes bearing nitrogen-containing bidentate ligands.

Acknowledgment. We thank Dr. K. Glass for helpful discussions, Dr. A. Provasoli and Mrs. G. Fitzpatrick for valuable technical assistance, Dr. Lynda K. Johnson for very kind support, Eolas (now Forbairt), the EC-Human Capital and Mobility program, BFGoodrich and BASF for funding, Loctite Ireland for thermal analyses, and Johnson Matthey for a generous loan of transition metal compounds.

Supporting Information Available: Details of catalyst, monomer, and polymer syntheses, NMR spectroscopic characterization of **poly-1a,b**, and thermogravimetric analysis of **poly-1b** (16 pages). See any current masthead page for ordering and Internet access instructions.

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(14) GPC calibration with polystyrene standards. The relatively high M_n(GPC) and the broad molecular weight distribution indicate that initiation is considerably slower than chain propagation. **Poly-1c** (entry 8) has M_n(GPC) = 54 000 and M_w(GPC) = 104 000. Cationic [(ligand)Pd(Me)(NCMe)] compounds are potential catalysts for polymers with lower polydispersities. **Poly-1a,b** (entries 1−6) are only partially soluble at 20 °C in chlorobenzene.

(15) This 1,2-cis structure contrasts with the 1,2-trans enchainments of the antifungal agent FR-900848: Barrett, A. G. M.; Kasdorf, K.; Tustin, G. J.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1143.

(16) Me(trans), Me(cis), cyclopropyl-CH, and quaternary-C each give rise to one set of ^{13}C NMR signals. See Supporting Information for spectroscopic details.

(17) Tetramer **4** (rrr) was obtained via reductive cleavage of a palladacycle[11b] composed of four three-membered ring units with NaBD$_4$. See Supporting Information for synthetic and spectroscopic details.

(18) **Poly-1a** obtained with the achiral catalyst [(η^3-allyl)(2,2′-bipyridyl)Pd^{II}][SbF$_6$] shows less pronounced ^{13}C NMR signals at δ 30.2 and 16.6 ppm indicating that these signals correspond to meso-units.

(19) Approximately 70% meso-units for **poly-1a** prepared with **3a** and 65% meso-units for the polymer made with **2**, estimated from the intensity of the ^{13}C NMR signals at $\delta = 30.2$, 30.1, 30.0, 29.9, 29.6, and 29.5 (set of signals corresponding to the stereoconfigurations of Me(trans)).