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Probing the Regiochemistry of Acrylate Catalytic Insertion Polymerization via Cyclocopolymerization of Allyl Acrylate and Ethylene

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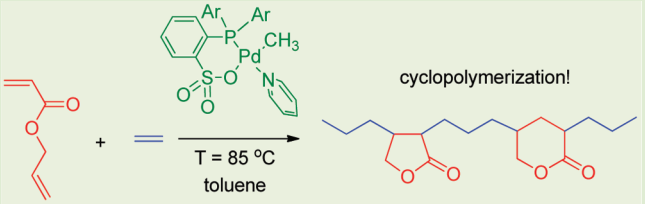
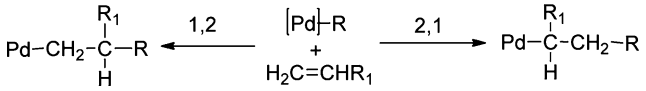
Supporting Information

ABSTRACT: When palladium phosphine sulfonate catalysts were used, ethylene and allyl acrylate were copolymerized. The copolymer structure was analyzed by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) and was found to contain both δ-valerolactone and γ-butyrolactones inserted within the chain. These cyclic structures were determined to be the outcome of 1,2 allyl insertions and 2,1 acrylate insertions except when the acrylate was cyclopolymerized: in this case, regiochemistry of the insertion was 1,2. This first example of cyclopolymerization with Pd phosphine sulfonate catalysts outlines the extraordinary versatility of this family of compounds and paves the way to new polyolefins containing complex repeat units built in.



Palladium phosphine sulfonate catalysts have shown exceptional versatility for the copolymerization of ethylene with polar monomers[1] such as acrylates,[2,3] acrylonitrile,[4] vinyl ethers,[5] vinyl sulfones,[6] vinyl acetate,[7] vinyl fluoride,[8] substituted norbornenes,[9] N-vinyl pyrrolidone,[10] N-isopropyl acrylamide,[10] allyl alcohol,[11] allyl chloride,[11] acrylic acid,[12,13] maleic anhydride,[13] and carbic anhydride.[13] In comparison to cationic palladium (and to a lesser extent nickel) diimines, which have a tendency to promote chain-walking reactions resulting in branched polymers,[14,15] palladium phosphine sulfonate catalysts generate linear polymers where functionalities are in the main-chain position.[16] However, the regiochemistry of the polar olefin insertion is currently debated. The 1,2 pathway would place the substituent in the β-position relative to Pd, which, in certain cases, may lead to chain elimination via β-substituent elimination (Scheme 1). The 2,1

Scheme 1. 1,2 versus 2,1 Insertion of Functionalized Olefins



pathway, on the other hand, generates steric hindrance at the metal center, possibly resulting in slow subsequent insertion of ethylene. To elucidate whether insertion occurs by a 1,2 or 2,1 pathway, two experimental methods have been used: spectroscopic characterization of insertion products and chain-end analysis. Both methods have intrinsic limitations. End-group analysis identifies the regioisomer (2,1 or 1,2), which is the most likely to trigger β-H elimination, and not necessarily the most prominent isomer. Isolation of insertion products, usually in conditions different from polymerization conditions, may lead to the characterization of the most stable regioisomer, but it is not possible to rule out that the other isomer is present and active during the catalytic cycle. Theoretical calculations have shown that preference for 2,1 insertion versus 1,2 insertion is in part due to the decrease of steric repulsion (R, in Scheme 1) between the migrating group and the substituent R_1,[17,18] but the difference between the activation energy of both pathways only differs by a few kcal/mol. Accordingly, Wucher et al. have recently shown that 2,1 versus 1,2 predominant insertion of acrylate could be tuned by increasing the bulk of the ligand scaffold on the Pd complex.[19] Guironnet et al. reported the isolation of $[(P\text{^}O)Pd\{\kappa^2\text{-}COCH(CO_2Me)CH_2CH(C(O)OMe)CH_2CH_3\}_2]$ upon two consecutive 2,1 insertions of methyl acrylate in $[\{(P\text{^}O)\text{-}PdMe\}_n]$ ($P\text{^}O = \kappa_2\text{-}P,O\text{-}Ar_2PC_6H_4SO_3$, with Ar = 2-$MeOC_6H_4$).[20] Furthermore, Drent et al. identified cis and trans $(CO_2Me)CH{=}CH$- end groups in the catalytic polymerization of methyl acrylate by the in situ catalytic system composed of -$Ar_2PC_6H_4SO_3H$ and $Pd_2(dba)_3$ or $Pd(OAc)_2$.[16] This set of observation points toward a 2,1-insertion of acrylates in Pd-alkyl bonds. By contrast, Vela et al. have reported that end groups detected for copolymers of vinyl ethers with ethylene are the result of 1,2 insertion of the vinyl ether.[5]

In a series of seminal studies,[21] Waymouth et al. have shown that hexadiene can be used to probe the polymerization mechanism of metallocene and alternating CO−E polymer-

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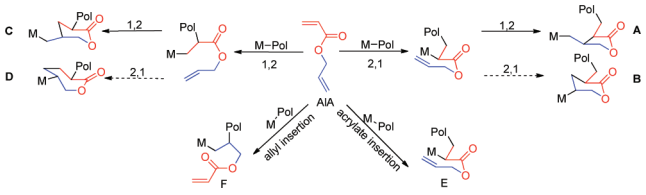
izations as the structure of the resulting polymer is a legacy of the mode of addition of the olefin. Inspired by these studies, we here describe the cyclocopolymerization of allyl acrylate (AlA) and ethylene by Pd phosphine sulfonate catalysts, with the aim of establishing the regioselectivity of the acrylate and of the allyl insertion (Scheme 2). Furthermore, we present here the first

Scheme 2. Overview of the Structures Which Could Be Obtained upon AlA Insertion

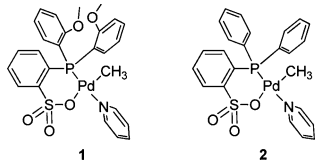


	1st insertion	2nd insertion
A	2,1 acrylate	1,2 allyl
	2,1 allyl	1,2 acrylate
C	1,2 acrylate	1,2 allyl
	1,2 allyl	1,2 acrylate

example of catalytic cyclopolymerization of acrylic monomers. Importantly, radical cyclopolymerization of AlA has already been reported.[22]

The two catalysts used for this study (**1** and **2**, Scheme 3) have been shown to promote the catalytic copolymerization of

Scheme 3. Pd Phosphine Sulfonate Catalysts



ethylene and acrylates, with typical acrylate insertion ranging from 2 to 20 mol %.[2] In such polymers, consecutive acrylate units cannot be detected and we have assumed in the rest of this study all AlA units were isolated within the polymer. This assumption is justified by the fact that AlA incorporations are low (Table 1). Scheme 2 presents the four cyclic structures (A–D) that can theoretically be obtained upon cyclopolymerization of AlA. Importantly, in Scheme 2, insertion of the acrylate moiety occurs first, followed by insertion of the allylic moiety. No new structure is generated when one starts by inserting the allyl group, but the chain grows in the opposite directions: chain beginning, identified as Pol in Scheme 2, and chain end carrying the metal, identified as M, would have to be exchanged in the drawings of structures A–D. Cycles B and D can be ruled out due to obvious steric constraints during the cyclization process (a 2,1 second insertion requires a highly strained intermediate). Thus, cycle A (γ-butyrolactone) corresponds to a 2,1-acrylate first insertion followed by 1,2-allyl insertion, whereas cycle C (δ-valerolactone) corresponds to a 1,2-acrylate first insertion followed by 1,2-allyl insertion. When one starts by inserting the allylic moiety, cycle A results from 2,1-allyl insertion followed by 1,2-acrylate insertion, whereas cycle C results from 1,2-allyl insertion followed by 1,2-acrylate insertion. Structures E and F correspond to acrylate and allyl insertions without cyclization.

The FTIR spectra of the polymers (Supporting Information) showed two characteristic peaks of the carbonyl group for the δ-butyrolactone and for the γ-valerolactone, respectively, at 1780 cm^{-1} and 1734 cm^{-1}.[23] The structure of the polymers and most notably ring microstructures were assessed by ^1H NMR, ^{13}C NMR and COSY correlation analysis (Figures 1 and 2).

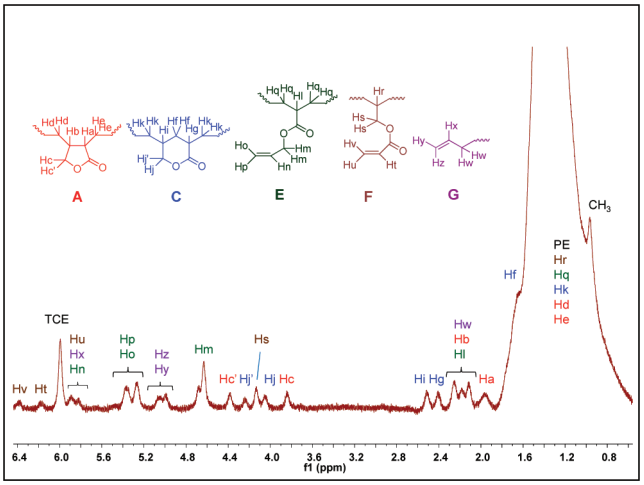


Figure 1. ^1H NMR spectrum of a representative sample of poly(ethylene-*co*-AlA), in $C_2D_2Cl_4$ (TCE) at 85 °C (entry 1, Table 1).

The ^1H NMR spectrum in Figure 1 clearly indicates the presence of both γ-butyrolactone (A) and δ-valerolactone (C), as well as vinyl chain ends (G) and noncyclized AlA (E and F). Structures A, C, E, and F were consistently found in all polymers (Table 1). Other structures could be observed in one other sample: they correspond to end-groups consisting of 5-member unsaturated lactones (entry 4, Table 1, see Supporting

Table 1. Experimental Conditions and Polymer Characteristics for the Catalytic Copolymerization of Ethylene with AlA

					AlA containing structures				
cat	*P* psi	AlA mol/L	AlA[a] mol %	M_n g/mol	A[a] %	C[a] %	E[a] %	F[a] %	other[a] %
1	250	0.3	1.0	5900[b]	33	25	36	16	0
1	300	0.1	0.3	11900[b]	30	16	34	16	0
1	100	0.1	0.5	8100[b]	38	23	25	14	0
1	100	0.8	6.4	3000[a]	29	14	<1	10	46
2	200	0.8	2.4	1500[a]	25	16	53	6	0

[a]Determined by ^1H NMR in $C_2D_2Cl_4$ at 85 °C. [b]Determined by HT-GPC in trichlorobenzene at 160 °C.

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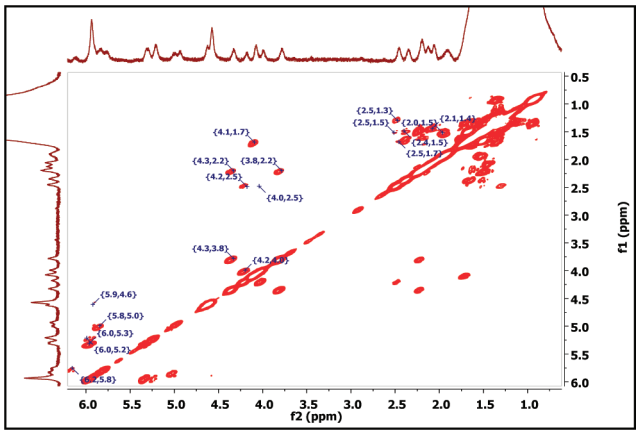


Figure 2. COSY of a representative sample of poly(ethylene-*co*-AlA), in $C_2D_2Cl_4$ at 85 °C (entry 1, Table 1).

Information). The presence of such chain-ends is expected, as this polymer has low molecular weight (Table 1).

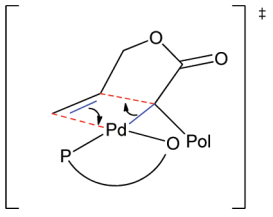
The presence of structures E and F is proof that cyclopolymerization does not always occur. For catalyst **1** (entries 1−3), E/F is in 2:1 molar proportion, indicating that the acrylate is about twice more reactive than the allylic monomer for this catalyst. The presence of C structures in the polymer clearly demonstrates that 1,2 insertions of acrylates are possible with Pd phosphine sulfonate catalysts. It remains to be determined whether such 1,2 insertions occur by direct 1,2 insertion of an unreacted AlA monomer or by insertion of a pendant acrylate unit once the allyl unit is already inserted. To clarify this point, we have considered four possible scenarios for the first insertion of the acrylate and of the allyl groups, assuming that the rate of cyclization is approximately the same following initial acrylate insertion or following initial allyl insertion. This is a reasonable hypothesis, as a very slow rate of cyclization for the allyl (resp the acrylate) group would result in the presence of significant amounts of E (resp F) in the final polymer. If we consider that acrylate and allyl insertions exclusively occur via a 2,1 regiochemistry, then only cycle A should be observed. Similarly, if we consider that both acrylate and allyl insertions occur via 1,2 regiochemistry, then only cycle C should be present. Before examining the two other scenarios, it should also be pointed out that, for catalyst **1**, A/C is in 1.5:1 molar proportion, which is approximately equal to the ratio of reactivities of acrylate and allyl fragments. If we suppose that allyl is inserted with a 2,1 regiochemistry and acrylate with a 1,2 regiochemistry, then A would be obtained when an allyl group is first inserted and C when an acrylate is first inserted. Based on the relative reactivities of acrylate and allyl units, a A/C mol ratio of 1:2 would be expected, which is quite different from the experimental value. By contrast, if the allyl insertion occurs via a 1,2 regiochemistry and the acrylate via a 2,1 insertion, then both A and C structures are present in a 2:1 ratio. Thus, we have demonstrated that catalyst **1** inserts allyl groups in a 1,2 fashion and acrylates in a 2,1 fashion, except in the case of a cyclopolymerization (second insertion), for which acrylate 1,2 insertion becomes possible. Therefore, 1,2 acrylate insertion is possible when steric constraints do not permit 2,1 insertion. This is reminiscent of the results reported by Wucher et al.,[19] whereby increasing the bulk of the catalyst scaffold drives the insertion from a 2,1 to 1,2 regiochemistry. The fact that C units are seen as main chain repeat units in the polymers also indicate that ethylene can insert after a 1,2 acrylate insertion. Therefore, the 5-member chelate (P^O)$\overline{\text{PdCH}_2-\text{CHR1}-\text{COOR}}$ generated upon 1,2 acrylate second insertion can be opened by ethylene, which contrasts with chelates obtained with Pd cationic diimines.[14,15]

With cationic Pd diimines, 1,5-difunctional olefins are usually cyclopolymerized and pendant unreacted double bonds are not observed.[24] In our case, such pendant double bonds are observed (E and F), yet, the polymers are never cross-linked. For entries 1−3 the ratio A/E and C/F is approximately 1:1, thus, after an acrylate or an allyl first insertion, cyclopolymerization has 50% chance to occur. Once the first insertion has occurred, the pendant double bond is positioned to coordinate Pd, but it is displaced by ethylene in 50% of the cases. Thus, by decreasing ethylene pressure, one would expect to favor cyclopolymerization. This is indeed the case (entry 4, for which E and F have nearly totally vanished); however, in this case, molecular weight also decreases, and chain-ends consisting of unsaturated lactones are now observed. This is indicative of the propensity to undergo β-hydride elimination after an inserted lactone rather than after an inserted ethylene under polymerization conditions favoring cyclopolymerization (low ethylene pressure, high AlA concentration).

For catalyst **2**, the ratio of E/F is close to 10:1, indicating that catalyst **2** is much more reactive toward acrylates than toward allyl groups. In a previous report, we indeed found that catalyst **2** has a tendency to generate polymers with higher acrylate incorporations than **1**, but of lower molecular weight.[25] Although the ratio of E/F is close to 10:1, the ratio of A/C is only 1.5:1. This can be once again explained by the greater reactivity of **1** toward acrylates; to obtain both cyclic structures, an allyl and an acrylic functionality must be reacted, resulting in proportions of A and C, which are not significantly different.

Importantly, ^{13}C NMR signals of A and C units in the copolymer appear as single peaks, which would indicate that the cyclopolymerization reaction is stereoselective. Unfortunately, due to the low signal over noise of these resonances, we were unable to unequivocally determine whether the lactone substitution pattern is *cis* or *trans*. The ring-closing step for A (respectively, C) is believed to proceed via a four-member coplanar transition state, for which two of the adjacent carbons are within a five (resp six) member cycle (Scheme 4). A *trans* junction would induce considerable strain, and we believe that the rings are, therefore, *cis*-substituted.

Scheme 4. Putative Transition State for the Insertion of the Allyl Double Bond and Formation of A (the Newly Formed Bonds Are Represented As Dash Lines)



To conclude, this study provides the first example of cyclopolymerization with a Pd phosphine sulfonate catalyst. The regiochemistry of monomer insertion has thus been elucidated; allyl groups are inserted in a 1,2 fashion, whereas acrylic groups are inserted in a 2,1 fashion except when it is sterically constrained: in this case, 1,2 insertion becomes possible. This study also highlights the great versatility of these

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catalysts, which are able to simultaneously insert allylic and acrylic groups. In this sense, it provides an interesting approach to design complex macromolecular architectures from simple building blocks; using this cyclcopolymerization strategy, it is possible to generate lactones within a polyethylene chain.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental methods and ^{1}H, ^{13}C NMR, FTIR spectra, and GPC chromatograms. 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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