

From Regiospecific to Regioirregular Alternating Styrene–Carbon Monoxide Copolymerization

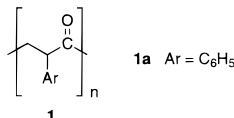
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We report here on how to copolymerize styrene and carbon monoxide to poly(styrene-*alt*-CO) in a nonregiospecific way, thus disclosing the synthesis of a previously unknown polymeric material.

The alternating copolymerization of styrene (or of homologues thereof) with carbon monoxide catalyzed by cationic palladium complexes modified by dinitrogen ligands¹ has attracted much attention in the past few years.^{2–14} The catalytic systems used were reported to give regiospecifically syndiotactic poly[1-oxo-2-arylpropane-1,3-diyl] (**1**) as a consequence of the secondary



migratory insertion³ of the styrene units into the palladium-acyl bond. The same regiospecificity of the insertion was observed when catalytic systems were used, which were modified by hybrid phosphine or by diphosphine ligands both for the synthesis of **1** and of ketones.^{15–19} Model studies also showed regiospecific secondary insertion.^{4,20,21} This type of insertion is also quite

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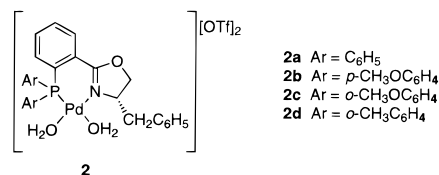
Table 1. Copolymerization of Styrene and Carbon Monoxide^a

catalyst precursor	reaction time (h)	polymer (g)	productivity [mmol/(g Pd·h)]	$\Delta\epsilon^b$ [l·mol ⁻¹ ·cm ⁻¹]	m.p. [°C]	M_n^c [g mol ⁻¹]
2a	40	5.004	80.9	-9.45	228–235	6000
2b	41	1.791	28.0	-9.09	175–180	9700
2c	43	4.775	71.0	-5.47	127–132	20000
2d	138	2.524	11.7	-0.41	80–85	n.d.

^a Reaction conditions: styrene (50 mL, 435 mmol); methanol (10 mL); 1,4-benzoquinone (0.216 g, 2.0 mmol); catalyst precursor **2** (0.11 mmol); 320 bar of CO; reaction temperature: 50 °C. ^b Measured in (CF₃)₂CHOH/CHCl₃ 1:10 ($c = 1.6$ mg mL⁻¹) at ~280 nm. ^c Estimated from end groups in the ¹H NMR spectra.

common in styrene oligomerization^{22,23} or polymerization²⁴ under homogeneous conditions. By contrast, results obtained with heterogeneous Ziegler–Natta catalysts were interpreted assuming a regioselective primary insertion; in fact, the less regular fractions showed some secondary insertion into the methyl–titanium initiating species.²⁵ Secondary insertion of styrene is normally assumed to be driven by some stabilization of the benzylic product through η^3 -interaction.^{4,22} Therefore, the problem arises as to whether it would be possible to produce poly(styrene-*alt*-CO) without regularity of regiochemistry of the olefin insertion, as is the case for aliphatic 1-alkenes.^{26,27} On the other hand, the nature of the irregularities in the above styrene copolymers, as recognized by NMR and particularly by ¹³C NMR in the carbonyl region, has never been seriously tackled. It has always been tacitly assumed that regioirregular tail-to-tail and head-to-head enchainments should be easily recognizable in that region due to relatively large differences in chemical shift, as in the case of aliphatic 1-alkenes such as propene.^{26,28} Model compounds²⁹ as well as alternating terpolymers containing also ethene³⁰ show that probably this is not the case.

Pursuing our investigation of the highly enantioselective styrene–carbon monoxide copolymerization catalyzed by [(P \wedge N)-Pd(H₂O)₂](SO₃CF₃)₂ complexes,¹⁹ we have synthesized the corresponding compounds modified by (*S*)-2-[2-(diarylphosphino)phenyl]-4-benzyl-4,5-dihydrooxazole **2a–d**³¹ and we have used



them as catalyst precursors. Table 1 reports the results of the polymerization experiments. The parallel decrease of the melting point and of the rotatory strength of the CD band in the $n \rightarrow \pi^*$ transition region of the carbonyl chromophore for **1a** by changing ligand in the order phenyl > *p*-anisyl > *o*-anisyl > *o*-tolyl is clear evidence of a loss of regularity. This is confirmed by the

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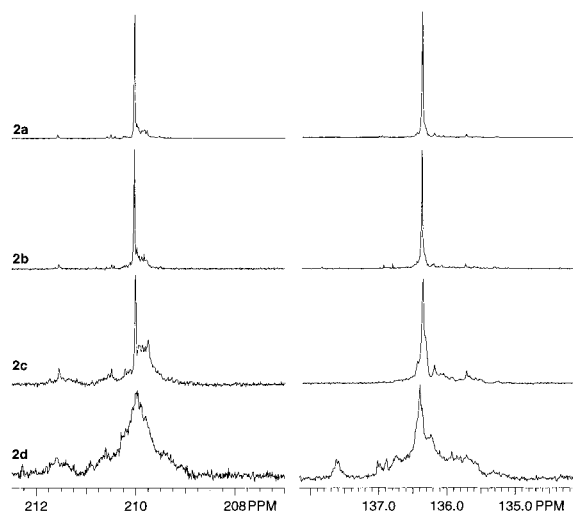


Figure 1. ^{13}C NMR (HFIP- d_2 /CDCl $_3$ 1:1, 125 MHz) of the poly(styrene-*alt*-CO) copolymers prepared with **2a–d** catalyst precursors (carbonyl- and *ipso*-C-regions).

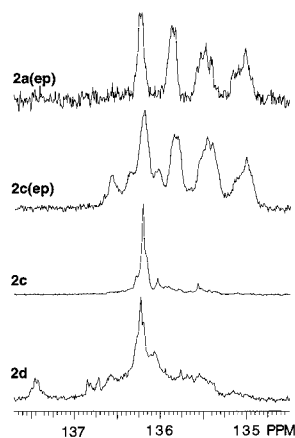
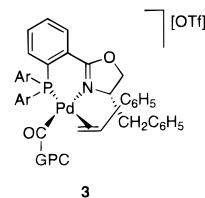


Figure 2. ^{13}C NMR (HFIP- d_2 /CDCl $_3$ 1:1, 125 MHz, *ipso*-C-region) of the poly(styrene-*alt*-CO) copolymers prepared with **2a** (after epimerization), with **2c** (native and after epimerization), and with **2d** catalyst precursors.

^{13}C NMR spectrum of the carbonyl region and of the *ipso*-carbon atom region (Figure 1) of the polymeric materials produced.

Considering that atactic poly[1-oxo-2-phenylpropane-1,3-diyl] shows in the latter region four bands (associated with the presence of the four possible triads *ll*, *ul*, and/or *lu*, and *uu* within 1.6 ppm, compare Figure 2, 2a(ep)) and a broad band spanning 1.2 ppm in the former region^{2,32} it is clear that, particularly with ligands **2c** and **d**, the regiospecificity of the copolymerization process is lost. Specifically for **2d** regioregularity seems quite low.

Lower $\Delta\epsilon$ values for the products having lower regioregularity are in keeping with a change of enantioface associated with a change in regioselectivity.³³ Unfortunately a quantification of regioirregular head-to-head and tail-to-tail diads, as in the case of the copolymers of aliphatic olefins,^{9,26,27,34} is at the moment very difficult. Nevertheless, the question arises about the factors causing increasing primary insertion for the catalyst precursors **2a–d**. Electronic factors for regioselectivity control appear to be of minor importance (compare **2b** vs. **2c**, Figure 1) with respect to steric factors. Model as well as catalysis studies^{19,21} suggest **3** as the propagating species for the regiospe-



cific enantioselective copolymerization. It seems reasonable to assume that high regioselectivity associated with high enantioface discrimination (trans to P) would be maintained independently from the ligands used.¹⁹ On the other hand, change (trans to N) of the olefin coordination site, which might be sterically forced by the interaction between the phosphorus substituents and the growing polymer chain, should not cause a change of regiochemistry of the insertion as a consequence of the changed electronic situation.^{4,15,16} Maintaining regiochemistry, however, would imply a steric repulsion of the phenyl substituent of the double bond with the aryl substituent on the phosphorus. Of course, this interaction would increase by increasing the steric requirements of the phosphorus ligand. Site-selective coordination of the olefin substrate forced by interactions of the growing chain with the ancillary ligands has also been proposed for propene polymerization with homogeneous C_1 -symmetric metallocene catalysts.³⁵

Supporting Information Available: Experimental procedure for the epimerization of polymers obtained with **2a** and **c** and XRD profiles of the copolymers prepared with **2a**, **c** and **d** (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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