

Fast and Regioselective Polymerization of para-Alkoxystyrene by Palladium Catalysts for Precision Production of High-Molecular-Weight Polystyrene Derivatives

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S Supporting Information

ABSTRACT: Polymerization of polar vinyl monomers by a coordinationinsertion approach is a topic of fundamental importance to the field of polymer synthesis. Herein, we initially report the coordination-insertion polymerization of para-alkoxystyrene (pAOS) monomers by the dibenzobarrelene-based α diimine palladium catalysts. The unprecedented polymerization characteristics including rapid initiation, fast chain growth, controlled chain transfer, and highmolecular-weight polymer with a narrow distribution ($M_w > 1000 \text{ kg/mol}$, PDI < 1.32) reflected previously unrecognized aspects of palladium-catalyzed pAOS polymerization. Chain-end analysis and characterization of palladium intermediates showed that the pAOS monomer was rapidly inserted into the primary palladium species in a full 1,2-regioselectivity, and the chain transfer took place by monomer-assisted β -H abstraction at high monomer concentrations. The resultant polymers showed improved mechanical properties and thermal stabilities and were also attractive candidates of hydrophilic styrenic resin.



INTRODUCTION

Coordination-insertion polymerization (CIP) is a powerful method to synthesize polymers with precisely designed macromolecular architecture, especially chain composition, molecular weight and distribution, and stereochemistry.^{1,2} In the modern "Plastic Age", CIP of ethylene and propylene is employed for the production of more than 100 million tons of polyolefins annually.³ However, CIP of polar vinyl monomers has remained elusive due to the deleterious side reactions that arise from heteroatom interactions with metal centers.⁴⁻⁶ In contrast to ethylene and α -olefins, polar vinyl monomers are predominately polymerized via radical and ionic methods. Therefore, polymerization of polar vinyl monomers by a coordination-insertion approach is a topic of fundamental importance to the field of polymer synthesis.^{7,8}

CIP of polar vinyl monomers using early metal catalysts is very difficult because of their high oxophilicity unless appropriate strategies, such as steric shielding or electronic protecting of the functional groups of the polar monomers.^{4,9} Late transition metal Ni/Pd catalysts are less oxophilic by comparison to early transition metal catalysts, and therefore can directly catalyze copolymerization of olefins and polar vinyl monomers.¹⁰⁻²³ Although late transition metal catalysts, especially palladium-based catalysts, are compatible with a broad scope of polar vinyl monomers, CIP of polar vinyl monomers normally suffers from the heavily reduced activity and a low molecular weight of the copolymer produced. The obtained copolymers usually contain low incorporation of polar monomers (<10 mol %), and no consecutive insertions of the vinyl monomer into the polymer chain are observed except for consecutive insertions of acrylate using phosphinesulfonato palladium catalysts till now.24,25 Consecutive units of polar vinyl monomers in Ni/Pd-catalyzed homo- and copolymerization of polar vinyl monomers with ethylene is currently inclined to ionic or radical polymerization.^{26–29} An alternative strategy of heteroatom-assisted olefin polymerization has been recently developed, and a new family of heteroatom-functionalized polyolefins is synthesized by rareearth metal catalysts.^{30–35} Despite these achievements, CIP of polar vinyl monomers has been far from successful.

para-Methoxystyrene (pMOS) is an electron-rich monomer because of a strong electron-donating effect of the methoxy group. pMOS is readily polymerized by cationic or radical method,³⁶⁻³⁸ and is also prone to coordinate to the metal center by a π -binding manner in metal-mediated catalysis. Although pMOS has been polymerized with titanium and palladium catalysts, the obtained homopolymers have low molecular weight (<30 kg/mol), and polymerization mechanisms are not clearly demonstrated.^{39–41} CIP of pMOS is only achieved by rare-earth metal catalytic systems.^{32,33,42,43}

In this paper, we initially report the coordination-insertion polymerization of polar para-alkoxystyrene (pAOS) monomers

Received: October 30, 2019 **Revised:** December 11, 2019



Figure 1. Molecular structures of dibenzobarrelene-based α -diimine palladium complexes.

(CH₂=CH(Ph-4-OR), R = Me, Et) using dibenzobarrelenebased α -diimine palladium catalysts. The bulky dibenzobarrelene backbone of α -diimine palladium catalysts markedly accelerated the chain growth rate and improved the 1,2regioselectivity of *p*AOS polymerization. At high monomer concentrations, chain transfer reaction occurred exclusively by monomer-assisted β -H abstraction, and narrowly dispersed poly(para-alkoxystyrene)s (PAOS) with high molecular weights up to 1000 kg/mol were precisely produced after only a few minutes.

RESULTS AND DISCUSSION

Synthesis and Characterization of Palladium Complexes. A series of dibenzobarrelene-based α -diimine palladium complexes (Figure 1) was prepared by the complexation of dibenzobarrelene-based α -diimine ligands L1–L6 with different substituents and (COD)PdMeCl (COD: 1,5-cyclooctadiene) (Scheme S2 in Supporting Information).⁴⁵ Palladium complexes were fully confirmed and characterized by ¹H and ¹³C NMR spectroscopies (Figures S5–S28). Single crystal structures of palladium complexes 2–6 were previously reported, ^{19,44,45} and a single crystal of palladium complex 1 suitable for X-ray diffraction analysis was also obtained herein. Palladium complex 1 displays a distorted square planar coordination around the palladium center, and the rigid dibenzobarrelene backbone effectively shields the back space of the palladium center (Figure 2).

Polymerization of *para*-Alkoxystyrene. After treatment with sodium tetrakis(3,5-bis-trifluoromethyl)phenyl)borate (NaBArF), chloromethylpalladium complexes 1-6 were activated for olefin polymerization.²¹ It was reported that α -diimine palladium catalysts were usually inactive for polymer-



Figure 2. Crystal structure of palladium complex 1. The hydrogen atoms and 0.5 CH_2Cl_2 molecules are omitted for clarity.

ization of styrenic monomers through a coordinationinsertion mechanism. Styrene derivatives were previously used as chain quenching agents to quench ethylene polymerization by α -diimine palladium catalysts.^{46,47} For our dibenzobarrelene-based α -diimine palladium systems, styrene (St) polymerization also did not produce polymers (entry 1 in Table 1) because of the rapid benzyl transfer reaction (Scheme S4 and Figure S36). Strikingly, dibenzobarrelene-based palladium catalysts **1–6** were highly active for *p*MOS polymerization with high monomer conversions.

The influences of the catalyst structure on pMOS polymerization were first evaluated. Under the same conditions, a comparison of pMOS polymerization using catalysts 1-3clearly demonstrated the steric effects of o-aryl substituents. With increasing steric bulk of o-aryl substituents, polymerization activity and monomer conversion increased slightly. However, the polymer molecular weight was independent of the steric bulk of o-aryl substituents, and the least bulky palladium catalyst 1 without a substituent produced a highmolecular-weight poly(para-methoxystyrene) (PMOS) with a molecular weight of ~1000 kg/mol. This observation was different from the previously reported steric effect of o-aryl substituents on ethylene polymerization using α -diimine nickel and palladium catalysts.¹¹ Although the least bulky palladium catalyst 1 produced narrowly dispersed polymers, increasing the steric bulk of o-aryl substituents led to a decreased polydispersity index (PDI) of polymers. This observation indicated that bulky o-aryl substituents more effectively suppressed the chain transfer. The electronic effects of meta-/para-aryl substituents were also illuminated by pMOS polymerizations using palladium catalysts 1 and 4-6 (entries 5 and 17–19 in Table 1). The introduction of electron-donating methoxy groups on meta-/para-positions of aniline hardly affected pMOS polymerization, and catalysts 1 and 4-6 almost showed the same activity and produced the same polymers. As a comparison, a classic methyl-based α -diimine palladium catalyst 7 was also used to catalyze pMOS polymerization (entry 20 in Table 1).¹¹ Under the same conditions, methylbased α -diimine palladium catalyst 7 produced traces of polymers, indicating that the dibenzobarrelene backbone was a strategic substituent for pMOS polymerization.

Note that *p*MOS polymerizations using all 1-6 catalysts afforded narrowly dispersed polymers (PDI ≈ 1.2), suggesting living/controlled characteristics. Therefore, *p*MOS polymer-

Table 1. Polymerization Results of pAOS Catalyzed by Palladium Catalysts^a

entry	catalyst	monomer	time (min)	yield (g)	conv. (%)	act. ^b	$M_{\rm n}^{\ c} \ ({\rm kg/mol})$	PDI ^c
1	1-3	St	1440					
2	1	pMOS	5	0.1819	18.02	437	1011	1.15
3	1	pMOS	10	0.3432	31.82	412	987	1.16
4	1	pMOS	15	0.5126	50.80	410	962	1.16
5	1	pMOS	30	0.8014	79.43	321	853	1.21
6	2	pMOS	5	0.2082	20.63	500	933	1.11
7	2	pMOS	10	0.3912	38.77	469	923	1.12
8	2	pMOS	15	0.5839	57.87	467	902	1.14
9	2	pMOS	30	0.8943	88.63	358	909	1.17
10	3	pMOS	5	0.4788	47.45	1149	943	1.08
11	3	pMOS	10	0.6378	63.21	766	917	1.09
12	3	pMOS	15	0.8162	80.89	653	908	1.13
13	3	pMOS	30	0.9896	98.07	396	889	1.15
14 ^d	3	pMOS	30	0.3265	32.36	131	749	1.17
15 ^d	3	pMOS	60	0.7149	70.85	143	791	1.19
16 ^d	3	pMOS	90	0.9868	98.06	132	735	1.19
17	4	pMOS	30	0.8072	80.00	323	935	1.22
18	5	pMOS	30	0.7800	77.30	312	858	1.24
19	6	pMOS	30	0.7992	79.21	320	877	1.26
20	7^e	pMOS	30	traces				
21	3	pEOS	5	0.3924	39.64	942	900	1.09
22	3	pEOS	10	0.6019	60.80	722	886	1.10
23	3	pEOS	15	0.8085	81.67	647	881	1.11
24	3	pEOS	30	0.9767	98.66	391	824	1.17

^{*a*}Reaction conditions: 5 μ mol of Pd, 1.2 equiv of NaBArF, 10 mL of CH₂Cl₂, 1 mL of monomer, 30 °C. ^{*b*}Activity, in the unit of kg PAOS/(mol·Pd·h). ^{*c*}Determined by GPC using THF as the eluent. ^{*d*}Polymerization proceeded under air with RH of 45%. ^{*e*}7 is a conventional methyl-based α -diimine palladium complex, and traces of polymer was produced.

Table 2. p.	AOS Pol	ymerizations	by Sec	juential	Monomer	Addition	Using	Catalyst	3 "
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entry	M/t_1 (min)	M/t_2 (min)	yield (g)	conv. (%)	act. ^b	$M_{\rm n}^{\ c} \ ({\rm kg/mol})$	PDI ^c
1	pMOS/30		0.4894	97.01	195	668	1.29
2	pMOS/30	pMOS/10	0.7504	74.37	180	684	1.33
3	pMOS/30	pMOS/20	0.8676	85.99	174	716	1.29
4	pMOS/30	pMOS/30	0.9629	95.43	144	711	1.30
5	pMOS/30	pEOS/10	0.7335	73.72	176	705	1.32
6	pMOS/30	pEOS/20	0.8887	88.91	177	751	1.27
7	pMOS/30	pEOS/30	0.9572	95.77	164	720	1.29

^{*a*}Reaction conditions: 5 μmol of palladium catalyst **3**, 1.2 equiv of NaBArF, 10 mL of CH₂Cl₂, 30 °C, 0.5 mL of monomer for each stage. ^{*b*}Activity in kg PAOS/(mol·Pd·h). ^{*c*}Molecular weight and PDI were determined by GPC using tetrahydrofuran as the eluent.

izations at different times were performed to gain deep insight into polymerization characteristics. As shown in Table 1, catalysts 1–3 showed the same trend within the nearly full conversion of monomers. Polymer molecular weight reached ~1000 kg/mol at a short time of 5 min, indicating a very fast chain growth rate. With prolonging polymerization time from 5 to 30 min, the monomer conversion increased consistently, whereas the M_n of polymer slightly decreased. This finding strongly indicated that dibenzobarrelene-based α -diimine palladium catalysts were not living systems for pMOS polymerization. During polymerization, chain termination typically occurred to produce a high-molecular-weight polymer chain and new active species that was able to reinitiate pMOS polymerization.

Catalyst **3** was in fact able to catalyze pMOS polymerizations under mild reaction conditions. pMOS polymerizations smoothly proceeded under an atmosphere of air with relative humidity (RH) of 45% instead of nitrogen. Under air, catalyst **3** showed reduced activity and still produced narrowly dispersed PMOS (entries 14–16 in Table 1). However, the monomers were fully consumed after 90 min, indicating that the moisture and the oxygen in air only reduced the chain growth rate, and did not poison the palladium species and quench the polymerization. Palladium catalyst **3** was also highly active for polymerization of *para*-ethoxystyrene (*p*EOS) and produced narrowly dispersed poly(*para*-ethoxystyrene) (PEOS) with high molecular weight. As observed, the *p*EOS polymerization behavior was the same as that of *p*MOS (entries 21–24 in Table 1).

The polymerization of *p*AOS using catalyst **3** was further studied by sequential monomer addition. As shown in Table 2, polymerization of half an amount of *p*MOS (0.5 mL) was first performed for 30 min to ensure full conversion of the *p*MOS monomer and resulted in the formation of the PMOS with M_n of 668 kg/mol and PDI of 1.29. Additional half an amount of *p*MOS monomer was sequentially added into the system, and the polymerization was reinitiated. After 10 min, the molecular weight of the final PMOS was slightly increased to 684 kg/mol,



Figure 3. ¹H and ¹³C NMR spectroscopy of low-molecular-weight PMOS.

and the PDI remained narrow (PDI = 1.33). When *p*EOS was used as an additional monomer instead of *p*MOS, the same trend was observed. Despite narrow distribution, the polymeric products were a blend of two homopolymers rather than a block copolymer because of almost no increase in polymer molecular weight and a tiny discrepancy of the molecular weight between two homopolymers (Figure S35).

Generally, the *para*-alkoxystyrene (*p*AOS) polymerization using dibenzobarrelene-based α -diimine palladium catalysts showed unique characteristics including rapid initiation, fast chain growth, controlled chain transfer, nearly quantitative conversion of monomer and high activity, and high molecular weight. The active species was long-lived and showed good tolerance toward polar groups and high atomic economics because the polymerization of newly added *p*AOS monomers could be reinitiated to produce new polymer chains.

Mechanistic Study. Currently, a crucial polymerization mechanism involving the nature of the active species and the chain transfer manner for pAOS polymerization remains unanswered. Typically, pAOS could be polymerized by a cationic method because of the strong electron-donating effect of the alkoxy group.^{48–50} However, the cationic polymerization of pAOS usually produced well-defined polymers (PDI < 1.2) with lower than 100 kg/mol molecular weight under harsh conditions. The control pMOS polymerization using NaBArF as a cationic initiator produced a trace of polymer with a relatively low molecular weight ($M_n = 61 \text{ kg/mol}$, PDI = 2.45) under adopted conditions (Table S6 in SI). Therefore, the influence of NaBArF should be excluded in pMOS polymerizations. Besides, pMOS polymerizations exposed to air produced high-molecular-weight polymers with a narrow distribution in our palladium system. No palladium black (Pd(0)) was observed during the *p*MOS polymerization, but it was previously reported that palladium black was closely related to the cationic polymerization of vinyl ethers with a classic methyl-based α -diimine palladium catalyst.²⁸ Furthermore, the copolymerization of pMOS with ethylene using catalyst 3 produced the copolymer with low ethylene incorporation of 5.4 mol % because of the slow ethylene insertion rate. The sequential addition copolymerization produced a blend of two homopolymers because of fast chain growth and controlled chain transfer of pMOS polymerization (Table S4 in SI). These copolymerization results of pMOS with ethylene strongly indicated a coordination-insertion mechanism. In combination with the

catalyst structure-polymerization activity relationship, it was deduced that palladium-catalyzed polymerization of pAOS should obey a coordination—insertion mechanism, and the cationic mechanism was ruled out.

Chain-End Analysis. The polymer chain-end analysis can provide more information on the chain initiation and termination and further elucidates the polymerization mechanism. The low-molecular-weight PMOS ($M_{\rm p}$ = 5200, Figure \$68) was prepared at a very low monomer concentration for NMR analysis. The polymer exhibited weak signals H_h at 5.2-5.7 ppm in ¹H NMR spectroscopy (Figure 3A), which was indicative of the vinyl end group $(CH_2 = CH(4-MeO-Ph) -)$ produced by β -H elimination or monomer-assisted β -H abstraction. ¹³C NMR spectrum of the polymer also proved the existence of the vinyl end group (Figure 3B) on the basis of the assignment of the weak peak C_h at 110.1 ppm. The peaks C1 and Cm at 134.6 and 126.5 ppm were safely assigned to ortho- and meta-phenyl protons of the chain end, not to the doubt bond of the vinylene end group (CH(4-MeO-Ph)= CH-) according to previous assignments.^{51,52} No signals were observed at 5.8-6.0 ppm in ¹H NMR spectroscopy, suggesting no existence of the vinylene end group (CH(4-MeO-Ph)= CH-) in the polymer chain end.⁵³ The major 4-MeO-benzyl terminal (CH₂(4-MeO-Ph)-CH₂-) was also confirmed by the peak at 32.74 ppm in ¹³C NMR spectroscopy. The minor methyl terminal (CH₃CH(4-MeO-Ph)-CH₂-) generated at the chain initiation step was also confirmed by the weak peak at 0.84 ppm in ¹H NMR spectroscopy.

The polymer chain structure of the low-molecular-weight PMOS was further demonstrated by MALDI-TOF mass analysis. As shown in Figure 4, two series of polymers with a molecular weight difference of 14 were observed, which were separately attributed to the vinyl-end polymer I with a 4-MeObenzyl terminal and polymer II with a methyl terminal. This result was well consistent with NMR analysis.

The appearance of the vinyl end group (CH₂=CH(4-MeO-Ph)-) proved that the *p*MOS polymerization did not obey a cationic mechanism, which typically produced a vinylene end group because of the 2,1-insertion of the monomer.⁴⁸⁻⁵⁰ Therefore, the vinyl end group (CH₂=CH(4-MeO-Ph)-) was originated from the chain transfer by β -H elimination or/ and monomer-assisted β -H abstraction in the aprotic CH₂Cl₂ solvent.^{54,55} A direct way to discriminate between the two mechanism is through the study of the effects of monomer concentrations [M] on the degree of polymerization (DP).⁵⁶



Figure 4. MALDI-TOF mass spectrum of low-molecular-weight PMOS.

Chain transfer constants have been determined using variations of the Mayo equation from theoretical considerations of polymerization kinetics,^{57,58} a form of it is given below on the basis of the omission of the chain transfer to the cocatalyst and solvent:

$$\frac{1}{\text{DP}} = \frac{k_{\text{trM}}}{k_{\text{p}}} + \frac{k_{\text{tH}}}{k_{\text{p}}[\text{M}]}$$

where DP is the number-average degree of polymerization, $k_{\rm p}$ is the propagation rate coefficient, $k_{\rm trM}$ is the rate coefficient of monomer-assisted β -H abstraction, $k_{\rm tH}$ is the rate coefficient of β -H abstraction, and [M] is the monomer concentration.

A series of polymerization experiments at different monomer concentrations were performed (Table S2), and polymerizations were quenched at short times to assure low monomer conversion (<20%) and to reduce the influence of monomer concentration change. The effect of [M] on the DP of the resultant polymer is shown in Figure 5. Two linearities and a



Figure 5. Plot of 1/DP versus 1/[M] for pMOS polymerizations catalyzed by palladium catalyst 3 with low monomer conversions.

critical point corresponding to critical [M] of ca. 0.59 mol/L were clearly observed. DP is independent of [M] above critical [M], strongly indicating the occurrence of monomer-assisted β -H abstraction in *p*MOS polymerization. Below critical [M], chain transfer took place by β -H elimination and monomerassisted β -H abstraction. Generally, the two transfer constants (k_{trM}/k_p and k_{tH}/k_p) were small (10⁻⁴ order of magnitude); therefore, high-molecular-weight polymers were formed.

Palladium Intermediate Analysis. To gain a deep insight into the palladium-active species for coordination–insertion polymerization of *p*MOS, *p*MOS-chelated palladium complex

was prepared by treatment of chloromethylpalladium complex 3 with NaBArF and 10 equiv pMOS in CH₂Cl₂ (Scheme S5).⁵⁹ pMOS-treated palladium complexes were obtained in high yield after the removal of polymeric product. The obtained palladium products showed two sets of peaks in ¹H NMR spectroscopy in a ratio of ~10/1 (Figure 6). H-H COSY



Figure 6. ¹H NMR spectrum of pMOS-treated palladium mixture (Pd-MOS1 and Pd-MOS2).

analysis (Figure S37) further confirmed that the isolated palladium products were a mixture of two π -benzyl palladium complexes **Pd-MOS1** [(L3)Pd(η^3 -CH(CH₂CH₃)-C₆H₅]⁺BArF⁻ and **Pd-MOS2** [(L3)Pd(η^3 -CH(CH₃)-C₆H₅]⁺BArF⁻ but not diastereomers (*anti-* and *syn-*isomers) of the π -benzyl palladium complex on the basis of previous assignment.⁶⁰ No *syn-*isomer was observed by NMR spectroscopy because of unfavorable interactions of the anti-methyl group and the bulky dibenzobarrelene-based α -diimine ligand. These interactions were also observed for *anti-*isomer of palladium on the basis of great shift of the proton of the methylene toward the high field (-0.21 ppm) because of extremely bulky ligand.⁶⁰

A single crystal of the major palladium product **Pd-MOS1** suitable for X-ray analysis was obtained and depicted in Figure 7. The single-crystal structure confirmed that **Pd-MOS1** was



Figure 7. Crystal structure of η^3 - π -benzyl palladium complex Pd-MOS1.

an η^3 - π -benzyl complex with *anti*-configuration. Palladium complex **Pd-MOS1** was formed by the insertion of *p*MOS into a Pd–Me bond in a 2,1-mode and followed methyl migration to the methylene carbon (Scheme 1). Palladium complex **Pd-MOS2** was produced by the benzyl transfer reaction of **Pd-MOS1** with excess *p*MOS.⁵⁹ The isolated palladium mixture was stable and inactive for *p*MOS polymerization, which indicated that the π -benzyl palladium complexes were inert





Figure 8. ¹³C NMR of high-molecular-weight PMOS (A) and PEOS (B) (entries13 and 24 in Table 1).

species for pMOS polymerization. The true active species was not isolated and afforded polymer because of the fast chain growth rate.

In combination with the above chain-end analysis, the methyl terminal was originated from the pMOS monomer insertion into the Pd-Me in a 1,2-fashion at the initiation step and the 4-MeO-benzyl terminal (CH₂(4-MeO-Ph)-CH-) came from the monomer-assisted β -H abstraction in 1,2regioselectivity. ¹³C NMR spectrum of low-molecular-weight polymer also showed regioregular head-to-tail enchainment and no detectable head-to-head and tail-to-tail enchainments (Figure 3B). These results showed that the pMOS monomer inserted into the Pd-R bond in a 1,2-mode with full regioselectivity. It is reported that an electron-rich ethyl vinyl ether is majorly inserted into the Pd-R bond with a 52% 1,2selectivity in the copolymerization of ethylene and ethyl vinyl ether by a phosphine-sulfonato palladium catalyst.⁶¹ 1,2-Selective insertion of styrenic monomers has been rarely observed for phosphine-ligated Pd-catalyzed copolymerizations of CO and styrene, while the 2,1-insertion of styrenic monomers is only observed for [N,N] bidentate palladium catalysts with 1,10-phenanthroline, 2,2'-bipyridyl, bisoxazoline, and conventional α -diimine ligands.^{59,62} To the best of our knowledge, this is the first report on 1,2-regioselective Pd-catalyzed homopolymerization of styrenic monomers in sharp contrast to the predominant 2,1-selectivity by radical and ionic polymerization.

Building on the above experimental results, the *p*MOS polymerization mechanism catalyzed by dibenzobarrelenebased α -diimine palladium catalysts is proposed (Scheme 1). In the presence of NaBArF, the chloromethylpalladium complex is activated to form a methylpalladium complex with a vacant orbit. The *p*MOS monomer majorly inserted a Pd–Me bond in 2,1-fashion, *anti-η*³- π -benzyl palladium complex **Pd-MOS1** is obtained by the methyl migration to the methylene carbon. Palladium complex **Pd-MOS1** is further produced by the benzyl transfer reaction of **Pd-MOS1** with an excess *p*MOS monomer. η ³- π -Benzyl palladium complexes are stable and inert for *p*MOS polymerization. When the 1,2-insertion of *p*MOS into a Pd–Me bond occurs, the palladium



Figure 9. DSC curves (A) and WAXD patterns (B) of PMOS and PEOS (entries13 and 24 in Table 1).



Figure 10. Comparison of mechanical, thermal, and hydrophilic properties for PS, CPMOS, and PMOS samples.

species for pMOS polymerization is produced. The chain is rapidly propagated by 1,2-insertion of pMOS. The 1,2regioselectivity can be reasonably explained by the enantioselectivity of the α -olefin in a coordination-insertion mechanism. It is widely acceptable that steric factors instead of electronic factors determined the enantioface of α -olefin, thereby the bulky and rigid dibenzobarrelene backbone leads to high 1,2-regioselectivity (Scheme S6).^{53,62-66} This is well consistent with the experimental observation that the dibenzobarrelene-based palladium catalyst is much more active than the methyl-based analogue for pMOS polymerization. The chain transfer takes place by monomer-assisted β -H abstraction to produce Pd-CHCH₂(Ph-4-OMe) species with the Pd…phenyl interaction, which can reinitiate pMOS polymerization by 1,2-insertion. In the whole process, the chain growth rate is much faster than the chain transfer rate, thereby producing a high-molecular-weight polymer with a narrow distribution.

Polymer Characterization and Properties. All highmolecular-weight poly(*para*-alkyloxystyrene)s produced by dibenzobarrelene-based palladium catalysts showed low stereoregularity. ¹³C NMR analysis confirmed that the obtained PMOS and PEOS were atactic polymers, which was a result of poor stereoselectivity of Ni/Pd catalysts (Figure 8). In the carbon atom C1 region, three peaks at 138.3, 137.7, and137.4 ppm were assigned to isotactic triad (mm), heterotactic triad (mr), and syndiotactic triad (rr), respectively, indicating that the obtained PMOS (rr = 52%) and PEOS (rr = 62%) was a syndio-rich polymer. DSC curves of the poly(*para*alkyloxystyrene)s exhibited a single glass transition temperature ($T_g = 110$ °C for PMOS and 90 °C for PEOS) without a melting point (Figure 9A). The wide-angle X-ray diffraction (WAXD) analysis of the PAOS showed a broad peak ($2\theta =$ 18.6° for PAOS and 23.1° for PEOS), indicating that PMOS and PEOS were amorphous (Figure 9B).

High molecular weight was expected to endow polymeric materials with improved properties. Commercial polystyrene (PS) purchased from SINOPEC ($M_n = 110 \text{ kg/mol}$, PDI = 2.47, Figure S71) and PMOS prepared by a cationic polymerization using BF₃·(OEt)₂ as an initiator ($M_n = 130$ kg/mol, PDI = 2.81, Figure S72) (CPMOS) were chosen for a comparison. The stress-strain curves of three samples showed plastic deformation behavior of typical thermoplastics. The mechanical properties of high-molecular-weight PMOS, including tensile strength and breaking elongation, are somewhat improved by a factor of $\sim 15\%$ (Figure 10). High molecular weight also enhanced the thermal stability of polymeric materials. The thermogravimetric analysis (TGA) of three samples showed that PMOS catalyzed by palladium catalysts had the highest decomposition onset temperature (temperature at 5% weight loss, $T_{d,5\%}$) up to 392 °C. The water surface contact angle (WSCA) was tested to evaluate the hydrophilic properties of these three samples. The PMOS showed a contact angle of $61.6 \pm 0.6^{\circ}$, substantially lower than that observed for commercial PS (98.6 \pm 0.5°), CPMOS (80.9 \pm 0.3°, $M_{\rm n}$ =130 kg/mol) produced by a cationic method, and syndiotactic PMOS produced by yttrium catalysts (83.7°, $M_{\rm p}$ = 55 kg/mol).⁴² Therefore, the PMOS should display superior adhesion to polar surfaces. The enhanced hydrophilic properties might be mainly ascribed to the high-density polar methoxy group existing in the long polymer chains. Collectively, high-molecular-weight PMOS prepared by our palladium systems showed improved mechanical properties and thermal stability, and the polarity of methoxy groups substantially enhanced the adhesion of materials to polar surfaces relative to hydrophobic PS.

CONCLUSIONS

In summary, we have reported fast and regioselective coordination-insertion polymerization of polar para-alkoxystyrene ($CH_2 = CH(Ph-4-OR)$, R = Me, Et) by dibenzobarrelene-based α -diimine palladium catalysts. The bulky dibenzobarrelene backbone markedly accelerated the chain growth rate, and narrowly dispersed polymers with high molecular weight ($M_w > 1000 \text{ kg/mol}$, PDI < 1.3) were produced after only 30 min with nearly quantitative monomer conversions. Chain-end analysis of the polymer confirmed that palladiumcatalyzed pAOS polymerization obeyed a coordinationinsertion mechanism rather than a cationic method. The mechanistic study demonstrated that the primary palladium species was highly active and catalyzed pAOS polymerization in a full 1,2-regioselectivity. The chain transfer occurred by the monomer-assisted β -H abstraction at high monomer concentrations to produce a high-molecular-weight polymer with a narrow distribution. The resulting atactic PMOS showed improved mechanical properties, thermal stability, and hydrophilicity, and had a high potential for applications as highperformance styrenic resins.

EXPERIMENTAL SECTION

General Procedures. All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard vacuum-line, Schlenk, or glovebox techniques.

Materials. Dichloromethane was distilled from P_2O_5 , tetrahydrofuran was distilled from CaH₂, and toluene and hexane were from Na/K alloy under nitrogen. Anthracene, vinylene carbonate, and trifluoroacetic acid were purchased from Energy Chemical. 2,6-Diisopropylaniline was purchased from Aldrich Chemical and was distilled under reduced pressure before use. ZnCl₂ was purchased from TCI and stored in an oven at 110 °C overnight before use. Methyltriphenylphosphonium bromide, BF₃·(OEt)₂, potassium *tert*butoxide, *para*-methoxybenzaldehyde, *para*-ethoxybenzaldehyde, *ortho*-methoxybenzaldehyde, aniline, 2,6-dimethylaniline, 2,6-diisopropylaniline, and potassium oxalate were also purchased from Energy Chemical. All α -diimine palladium complexes were prepared by the reaction of Pd(COD)MeCl with the corresponding α -diimine ligand according to the previously reported method.⁴⁵ The ligands and palladium complexes were fully characterized by ¹H and ¹³C NMR (Figures S5–S28 in the Supporting Information).

Measurements. Elemental analyses were performed on a Vario EL microanalyzer. NMR spectra of all samples were carried out on Bruker 400 or 600 MHz instruments in CDCl₃ using TMS as a reference. MALDI-TOF spectroscopy was performed on a Bruker ultrafleXtreme. GPC analyses of the molecular weights and molecular weight distributions (PDI = M_w/M_p) of the polymers were performed on an Agilent technologies 1260 infinity equipped with a differential refractive-index detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. DSC analyses were conducted with a Perkin-Elmer DSC-4000 system. The DSC curves were recorded as second heating curves from 30 to 200 °C at a heating rate of 10 °C/min and a cooling rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-7 thermal gravimetric analyzer at a heating rate of 10 °C/min from 30 to 800 °C under a nitrogen flow. The mechanical properties were determined by stress/strain measure under uniaxial tension (5 mm/min) using CMT4104. The water surface contact angle (WSCA) test was conducted on a goniometer (Krüss, DSA100S).

Crystal Structure Determination. The crystals of palladium complexes were mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. Data obtained with the ω -2 θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Cu K α radiation (λ = 1.54184 Å) or Mo K α radiation (λ = 0.71073 Å). The structures were solved using

direct methods, while further refinement with full-matrix least-squares on F^2 was obtained with the SHELXTL program package. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Synthesis of para-Alkoxystyrene. para-Methoxystyrene (pMOS) and para-ethoxystyrene (pEOS) were synthesized by Wittig reactions according to the related literature (Scheme S1).42,70 Å typical synthetic route of pMOS was shown as follows. In a dry 250 mL three-necked round-bottom flask, the methyltriphenylphosphonium bromide (10.6004 g, 29.7 mmol), potassium tert-butoxide (3.0485 g, 27.2 mmol), and dry THF (100 mL) were added with stirring at 0 °C under a nitrogen atmosphere. After stirring for 30 min, para-methoxybenzaldehyde (24.7 mmol, 3 mL), which dissolved in 20 mL dry THF, was added dropwise into the flask. The reaction was stirred for 24 h, and then 10 mL deionized water was added to the flask to terminate the reaction. The mixture was extracted with petroleum ether 6 times (6 \times 20 mL), and the organic layer was collected and dried with anhydrous Na2SO4 overnight. The solution was filtered, evaporated to remove the solvents, and then was purified by column chromatography using pure petroleum ether as the solvent. The solution was evaporated to remove the solvents and finally distilled under reduced pressure over CaH₂ to obtain a colorless liquid (yield: 80%). The pEOS were also synthesized by a similar method.

pMOS, ¹H NMR (400 MHz, CD₃OD), δ (ppm): 7.37–7.32 (m, 2H, Ar-H), 6.89–6.83 (m, 2H, Ar-H), 6.70–6.60 (q, 1H, CH), 5.64– 5.57 (dd, 1H, CH₂), 5.15–5.09 (dd, 1H, CH₂), 3.80 (s, 3H, OCH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 159.28 (Ar-C), 136.14 (CH), 130.30 (Ar-C), 127.27 (Ar-C), 113.79 (Ar-C), 111.37 (CH₂), 55.04 (OCH₃).

pEOS, ¹H NMR (400 MHz, CD₃OD), δ (ppm): 7.36–7.31 (m, 2H, Ar-H), 6.88–6.82 (m, 2H, Ar-H), 6.70–6.60 (q, 1H, CH), 5.63– 5.57 (dd, 1H, CH₂), 5.13–5.08 (dd, 1H, CH₂), 4.07–4.00 (q, 2H, OCH₂CH₃), 1.44–1.38 (t, 3H, OCH₂CH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 158.64 (Ar-C), 136.17 (CH), 130.10 (Ar-C), 127.08 (Ar-C), 114.20 (CH₂), 111.12 (Ar-C), 63.09 (OCH₂CH₃), 14.69 (OCH₂CH₃).

Polymerization Procedure. A detailed polymerization procedure of *p*AOS was described as follows. A round-bottom Schlenk flask with a stirring bar was heated for 1 h at 150 °C under vacuum and then cooled to room temperature. Next, 1 mL of *p*MOS and 9 mL of CH₂Cl₂ were injected into the round-bottom Schlenk flask at 30 °C. Then, 1 mL of palladium catalyst solution consisting of palladium complexes (5 μ mol) and NaBArF (6 μ mol) in CH₂Cl₂ was then injected into the round-bottom Schlenk flask at 30 °C. The reaction mixture was continuously stirred at a polymerization temperature of 30 °C. After a certain polymerization time, the reaction was quenched with 100 mL mixture of 10% HCl solution of methanol. The resulting precipitated polymers were collected and treated by filtration, washed with methanol three times, and dried in a vacuum at 40 °C to a constant weight.

Synthesis of Low-Molecular-Weight PMOS. Following the polymerization procedure, 0.01 mL of *p*MOS monomer was used for polymerization. The low-molecular-weight PMOS was obtained, and its molecular weight was analyzed by GPC analysis ($M_n = 5200$, PDI = 2.27).

Synthesis of CPMOS by Cationic Polymerization. A detailed synthesis procedure of CPMOS by cationic polymerization³⁸ was described as follows. A round-bottom Schlenk flask with a stirring bar was heated for 1 h at 150 °C under vacuum and then cooled to room temperature. Next, 1 mL of *p*MOS and 10 mL of toluene were injected into the round-bottom Schlenk flask at 0 °C. Then, 0.1 mL of BF₃·(OEt)₂ was injected into the round-bottom Schlenk flask at 0 °C for 0.5 h. The reaction was initiated and continuously stirred at 0 °C. After 0.5 h, the reaction was quenched with 100 mL mixture of 10% HCl solution of methanol. The resulting precipitated polymers were collected and treated by filtration, washed with methanol several times, and dried in a vacuum at 40 °C to a constant weight. The molecular weight and distribution were analyzed by GPC ($M_n = 130.631$, PDI = 2.81).

Preparation Process of Polymer Films. A detailed procedure of polymer films was described as follows. The polymer (10 mg) was dissolved in 10 mL of CH_2CL_2 , and then it was subjected to ultrasound for 1 h. Subsequently, the homogeneous polymer solution was cast onto a level glass plate for 12 h, and polymer films were successfully prepared.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.9b02274.

NMR spectra of ligands and palladium complexes, crystallographic data of palladium complexes, and NMR, DSC, GPC, and XRD of polymers (PDF)

Crystallographic data (cif) (cif)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grants from the National Natural Science Foundation of China (Project 51873234 and 21674130).

DEDICATION

Dedicated to Professor Qing Wu on the occasion of his 65th birthday.

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