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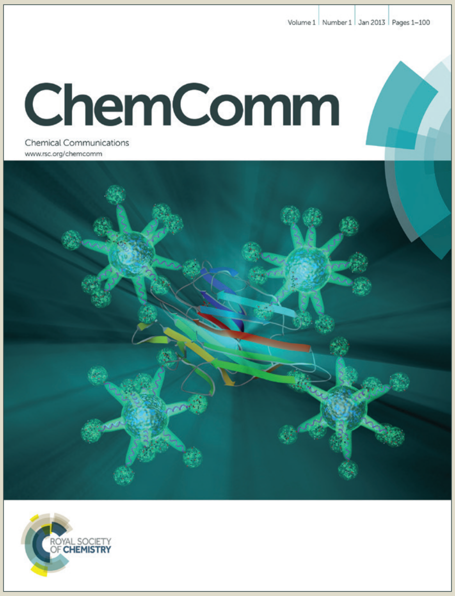

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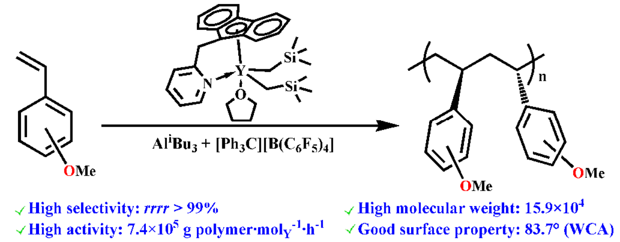

A new family of syndiotactic polystyrene derivatives containing the methoxyl group was established successfully by employing an yttrium catalyst.

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ARTICLE TYPE

Syndioselective Coordination Polymerization of the Unmasking Polar Methoxystyrenes Using Pyridenylmethylene Fluorenyl Yttrium Precursor

Dongtao Liu,[a#] Rong Wang,[b#] Meiyan Wang,[c] Chunji Wu,[a] Zichuan Wang,[a] Changguang Yao,[a] Bo Liu,[a] Xinhua Wan,*[b] Dongmei Cui*[a]

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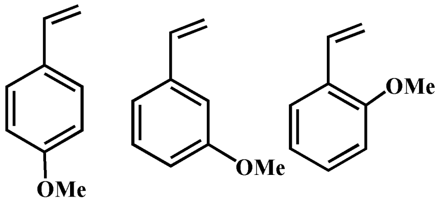
The unprecedented coordination-insertion polymerizations of the polar methoxyl substituted styrene derivatives, in despite of the position of the substituent, have been achieved by using the pyridyl methylene fluorenyl yttrium bis(alkyl) precursor with high activity to give polar polystyrenes of high molecular weight and perfect syndiotacticity.

No sooner the syndiotactic polystyrene (sPS) was discovered by Ishihara at Idemitsu in 1986[1,2] than it attracted a great interest from both industry and academic areas as a promising engineering plastics for many applications owing to its high tensile modulus, low dielectric constant, and excellent resistance to heat and chemicals endowed by its high melting temperature with relatively high crystallization rate.[3] For the past three decades, it has never been stopped to investigate the polymerization of styrene (St) in more highly active and syndioselective manner, which has stimulated the discovery of various homogeneous metallocene and half-metallocene and non-metallocene groups 3 and 4 based catalysts.[4–13] In contrast, the syndioselective polymerizations of styrene derivatives bearing polar group such as halogen, alkoxyl, aminoalkyl, *etc*, which provide polymers with improved surface property, adhesive property, affinity for dyes and compatibility with other polar polymers as compared to their sPS analogue, have been far from success.[14] The coordination polymerization of the polar monomers encounters the significantly challenging and long standing problem of academic research field, similar to other olefins bearing polar functional groups:[15–19] the efficient catalysts for St polymerization are based mainly on the hard Lewis-acidic groups 3 and 4 transition metals that are swiftly poisoned by the Lewis-basic polar groups to generate stable chelates via acid-base interaction. The *para*-dimethylamino styrene has been reported to be polymerized without masking by the half-titanocene Cp*Ti(TEA)/MMAO[20] and the half-scandocene Cp'Sc($CH_2C_6H_4NMe_2$-*o*)$_2$/[Ph_3C][$B(C_6F_5)_4$][21] in high activity and distinguished syndioselectivity albeit affording low molecular weight or insoluble products with broad molecular weight distribution. The polymerization of the strong coordinating *para*-methoxystyrene (*p*MOS) by the non-metallocene titanium-based catalytic system $Ti(CH_2Ph)_4$ / MAO[22] affords the atactic polymer although it provides perfect sPS. While the *meta*- and *para*-halostyrenes are hardly polymerized by the half-titanocene $CpTiCl_3$/MAO, although the polymerizations of alkyl substituted styrenes catalyzed by this system perform highly actively and syndioselectively.[2] Therefore, masking the polar atoms by bulky groups such as trialkylsilyl[23,24] or separating them with long spacer apart from the olefinic locus of the insertion[24] is a commonly adopted strategy, which, however, arouse the dramatic drop of the activity and the selectivity.



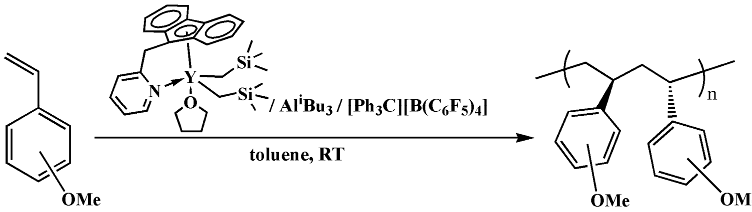
***p*MOS *m*MOS *o*MOS**

Chart 1

Herein we report by using the constrain-geometry-configuration catalyst (CGC), [(Py-CH_2-Flu)Y((CH_2SiMe_3)$_2$-(THF))] (**1**),[12] the polymerizations of unmasked strong Lewis-basic *para-*/*meta-*/*ortho-* methoxyl functionalized styrenes (chart 1) have been realized for the first time with a moderate to high activity and an excellent syndioselectivity to afford polar polystyrenes having high molecular weights.

The yttrium alkyl complex **1** combined with Al^iBu_3 and [Ph_3C][$B(C_6F_5)_4$] established a cationic homogeneous catalyst system, which has been reported to show an excellent syndio-specific selectivity for the polymerization of styrene in a top-recorded high activity.[12] Known that the coordination strength of the polar atoms with Lewis acidic metal followings the tendency of oxygen > nitrogen > halogen,[15] it was amazing that the above system displayed moderate activity (0.3×10^5 g polymer·mol_Y^{-1}·h^{-1}) for the polymerization of *para*-methoxyl substituted styrene (entry 1, Table 1), although much lower than that of St polymerization.[12] To our surprise, switching to *ortho*-methoxystyrene (*o*MOS), the polymerization became ten times faster than that of *p*MOS (entry 5), since the polar group is so close to the vinyl group that its coordination to the active metal center is unavoidable. The highest activity of 7.4×10^5 g polymer·mol_Y^{-1}·h^{-1} was achieved for the polymerization of *meta*-

Table 1. Syndiotactic Polymerization of Methoxyl Functionalized Styrenes with Yttrium Precursor **1**



entry	Monomer	[M]/[Y]	Time (min)	Conv. (%)	Activity[b]	M_n[c] (/10^{-4})	M_w/M_n[c]	rrrr[d] (%)	T_g/T_m[e] (°C)	WCA[f] (°)
1	*p*MOS	150	30	75	0.30	3.91	1.94	>99	95/221	83.7
2	*p*MOS	300	30	58	0.46	5.50	1.85	>99	96/221	83.7
3	*m*MOS	300	3	93	7.40	9.69	1.70	>99	54/175	84.9
4	*m*MOS	600	5	65	6.24	15.9	1.74	>99	54/176	84.9
5	*o*MOS	300	8	100	3.00	6.42	1.97	>99	84/240	89.9
6	*o*MOS	600	15	60	1.92	8.21	2.11	>99	85/240	89.9

[a] General condition: 10^{-5} mol of Y complex; in toluene; [Al]/[Y] = 10; [Ph$_3$C][B(C$_6$F$_5$)$_4$] / [Y] = 1; [monomer]$_0$ = 2.0 mol/L. [b] Given in 10^5 g polymer·mol$_Y^{-1}$·h^{-1}. [c] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard. [d] Determined by ^{1}H NMR and ^{13}C NMR. [e] Determined by DSC. [f] Determined by static water contact angle.

methoxystyrene (*m*MOS) (entry 3) that, noteworthy, cannot be polymerized by cationic catalysts due to its particular electronic structure.[25] The molecular weights of the resultant polar polystyrenes were higher than the calculated values, reflecting moderate initiation efficiencies; while the molecular weight distributions were rather narrow ranging from 1.70 to 2.11, indicative of the single-sited nature of the catalyst system (Figures S11~S13, ESI†). Increasing the monomer loading aroused the increase of the molecular weight up to M_n 15.9×10^4 when the monomer-to-catalyst ratio was 600:1 albeit with minor drop of the activity (entry 4). This is contrary to the coordination (co)polymerization of polar monomers that a higher polar monomer loading arouses dramatic drop of both activity and molecular weight, because the congregation of the polar groups under higher monomer concentration leads to poison of the active metal centers.[26] The methoxyl group, a strong Lewis-base, is more favoured than the vinyl group by the Lewis-acidic metal center. Therefore in the *o*MOS polymerization system, due to the geometry convenience, the interaction between the σ-methoxyl group and the active yttrium center should be peacefully coexistent with the vinyl groups repeatedly π-coordinating to the active yttrium center and their following insertion to propagate to macromolecule. In both *m*MOS and *p*MOS polymerization systems, the methoxyl groups have privilege of bonding to the active yttrium centers in σ-mode, leaving no chance for the vinyl group π-coordinating to the active yttrium centers, as usual the polymerization shouldn't take place. Fortunately, the chelating pyridine side arm of this CGC system reduces the oxophilicity of the yttrium active center. Thus the interaction between the polar methoxyl group and the active yttrium center was weakened, which affected but not block the coordination-insertion of the *ortho*- vinyl group and the propagation of the macromolecular chain (Figure S8a); meanwhile the interaction could be reversible and replaced by the *para*- or *meta*- vinyl group, whenever this took place, the polymerization of *m*MOS or *p*MOS started (Figures S8b and S8c). The activity related mainly the electronics of the monomers following the trend of St > *m*MOS > *o*MOS > *p*MOS, in consistence with the NBO charge of β-CH$_2$ of these styrene derivatives that St and *m*MOS have the same electron negativity (−0.345) lower than *o*MOS (−0.349) and *p*MOS (−0.360) (Figure S9). Thus the former two are easier to be anionically attacked by the metal-alkyl species via 2,1-insertion (Figure S10),[27] providing high activity. To confirm further the effect of the side arm, we synthesized an yttrium precursor (**2**) supported by phenyl substituted fluorenyl ligand without side-arm. The ternary system of **2**/Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] could catalyze polymerization of *o*MOS but was inert to the other *m*MOS and *p*MOS monomers (Table S1), because lacking of side-arm arouses strong interaction between the oxophilic yttrium active species and the methoxyl groups at *para*- or *meta*-positions to completely inhibit the coordination of the vinyl groups.

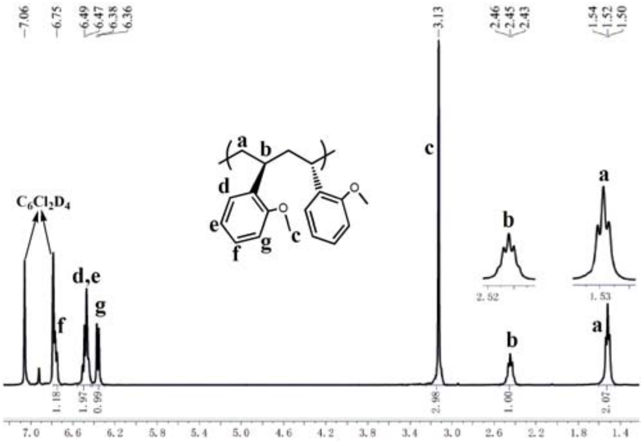


Figure 1. ^{1}H NMR spectrum of syndiotactic P(*o*MOS) (C$_2$Cl$_4$D$_2$, 120 °C).

Remarkably, the polymerization was extremely stereoselective despite the position of the polar substituent. The ^{1}H NMR spectra of the resultant polymers give typical tripletquintet resonances for the methylene/methine protons[1] of the syndiotactic regularity centered at δ 1.52/2.45 ppm for P(*o*MOS), δ 1.30/1.77 ppm for P(*m*MOS), and δ 1.23/1.72 ppm for P(*p*MOS), respectively (Figure 1, Figures S1 and S4). Correspondingly, in the ^{13}C NMR spectrum, the *ipso* carbon gives a sharp singlet at δ 135.4 ppm for P(*o*MOS), δ 146.9 ppm for P(*m*MOS) and δ 137.5 ppm for P(*p*MOS) assignable to the *rrrr* pentads, and no stereo-error resonances were visible (Figure 2, Figures S3, S6 and S7). These results indicated that the electronics and sterics as well as location of the polar methoxyl substituent influenced significantly the activity of the system but not the stereoselectivity.

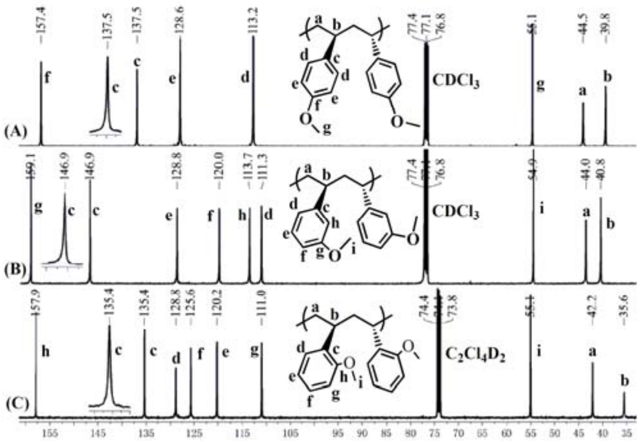


Figure 2. ^{13}C NMR spectra of syndiotactic polymethoxystyrenes. (**A**) P(*p*MOS) ($CDCl_3$, 25 °C); (**B**) P(*m*MOS) ($CDCl_3$, 25 °C); (**C**) P(*o*MOS) ($C_2Cl_4D_2$, 120 °C).

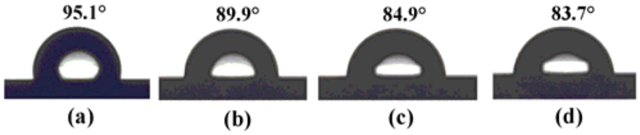


Figure 3. WCA of syndiotactic PSt (a), P(*o*MOS) (b), P(*m*MOS) (c) and P(*p*MOS) (d).

These methoxyl functionalized polystyrenes have various transition temperatures strongly depending on substituent position that P(*m*MOS) possessing the lowest T_g around 54 °C whilst P(*p*MOS) having the highest T_g around 96 °C and the T_g of 84 °C for P(*o*MOS). Unmatched to their perfect stereo-regularity, these functional polymers have much lower melting temperatures compared to their non substituted sPS analogue (T_m = 270 °C) in the order of P(*o*MOS) (240 °C)>P(*p*MOS) (221 °C)>P(*m*MOS) (175 °C) (Figures S14~S16). This might be attributed to the presence of the substituent that interrupts the high crystallization rate as well as the crystallization degree. To confirm the polarity of the methoxyl functionalized syndiotactic polystyrenes, the surface property of these new polymers were characterized by the static water contact angle (WCA), which was measured by using the sessile drop method. The results showed that the WCA of the poly(*p*MOS), poly(*m*MOS), and poly(*o*MOS) are 83.7°, 84.9° and 89.9°, respectively, while the WCA of sPS is 95.1° (Figure 3). These new type of stereoregular polar polystyrene materials via simple post polymerization modification such as transferring the methoxyl to hydroxyl,[28] are building blocks for functional styrene-based materials.

In summary, we have demonstrated that by using a cationic CGC yttrium catalyst, the unprecedented coordination-insertion polymerizations of polar methoxyl substituted styrene derivatives have been achieved with moderate to high activity to give polar polystyrenes of high molecular weight and perfect syndiotacticity. This is partly attributed to the extremely high activity of this catalyst system to styrene polymerization and the presence of pyridine side arm in the CGC yttrium catalyst that reduces the oxophilicity of the metal center. Therefore the coordination of methoxyl to the metal center is weak, and the competitive coordination of vinyl group to the metal center results in rapid insertion of methoxystyrenes. The position of the substituent methoxyl group on the aromatic ring strongly affects the polymerization activity in the order of *m*MOS > *o*MOS > *p*MOS in agreement with the NBO charge of β-CH_2 of the vinyl group, which seems to have no influence on the syndioselectivity. The polymerization of other polar styrenes and copolymerization with styrene to prepare random copolymers, are under investigation.

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Notes and references

[a] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. Fax: 0431-85262774; Tel: 0431-85262773; E-mail: dmcui@ciac.ac.cn*

[b] *Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. E-mail: xhwan@pku.edu.cn*

[c] *Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130022, People's Republic of China.*

† Electronic Supplementary Information (ESI) available: Experimental procedures; NMR spectra of P(*p*MOS), P(*m*MOS) and P(*o*MOS); Polymerization of methoxystyrenes by complex **2**; GPC and DSC curves of P(*p*MOS), P(*m*MOS) and P(*o*MOS); and NBO charge of the monomers. See DOI: 10.1039/b000000x/

[#] The first two authors contributed equally to this paper.

1 N. Ishihara, T. Seimiya, M. Kuramoto and M. Uoi, *Macromolecules*, 1986, **19**, 2464.
2 N. Ishihara, M. Kuramoto and M. Uoi, *Macromolecules*, 1988, **21**, 3356.
3 Malanga, M. *Adv. Mater.*, **2000**, *12*, 1869.
4 J. Schellenberg and N. Tomotsu, *Prog. Polym. Sci.*, 2002, **27**, 1925.
5 A.-S. Rodrigues, E. Kirillov and J.-F. Carpentier, *Coord. Chem. Rev.*, 2008, **252**, 2115.
6 C. Pellecchia, D. Pappalardo, L. Oliva and A. Zambelli, *J. Am. Chem. Soc.*, 1995, **117**, 6593.
7 A. Zambelli, L. Oliva and C. Pellecchia, *Macromolecules*, 1989, **22**, 2129.
8 C. Capacchione, A. Proto, H. Ebeling, R. Mullhaupt, K. Moller, T. Spaniol and J. Okuda, *J. Am. Chem. Soc.*, 2003, **125**, 4964.
9 E. Kirillov, C. W. Lehmann, A. Razavi and J.-F. Carpentier, *J. Am. Chem. Soc.*, 2004, **126**, 12240.
10 Y. Luo, J. Baldamus and Z. Hou, *J. Am. Chem. Soc.*, 2004, **126**, 13910.
11 Z. Jian, S. Tang and D. Cui, *Chem. Eur. J.*, 2010, **16**, 14007.
12 Y. Pan, W. Rong, Z. Jian and D. Cui, *Macromolecules*, 2012**, 45**, 1248.
13 M. Nishiura, T. Mashiko and Z. Hou, *Chem. Commun.*, **2008**, 2019.

14 P. Zinck, F. Bonnet, A. Mortreux and M. Visseaux, *Prog. Polym. Sci.*, 2009, **34**, 369, and references therein.

15 L. S. Boffa and B. M. Novak, *Chem. Rev.*, 2000, **100**, 1479.

16 N. M. G. Franssen, J. N. H. Reek and B. de Bruin, *Chem. Soc. Rev.*, 2013, **42**, 5809.

17 X.-H. Yang, C.-R. Liu, C. Wang, X.-L. Sun, Y.-H. Guo, X.-K. Wang, Z. Wang, Z. Xie and Y. Tang, *Angew. Chem., Int. Ed.*, 2009**,** **48**, 8099.

18 Z. Chen, J.-F. Li, W.-J. Tao, X.-L. Sun, X.-H. Yang and Y. Tang, *Macromolecules*, 2013, **46**, 2870.

19 H. Hagihara, K. Tsuchihara, J. Sugiyama, K. Takeuchi and T. Shiono, *Macromolecules*, 2004**, 37,** 5145.

20 Y. Kim, S. Park, Y. Han and Y. Do, *Bull. Korean Chem. Soc.*, 2004, **25**, 1648.

21 Z. Shi, F. Guo, Y. Li and Z. Hou, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 5.

22 A. Grassi, P. Longo, A. Proto and A. Zambelli, *Macromolecules*, 1989, **22**, 104.

23 K. H. Kim, W. H. Jo, S. Kwak**,** K. U. Kim, S. S. Hwang and J. Kim, *Macromolecules*, 1999, **32**, 8703.

24 G. Xu and T. C. Chung, *Macromolecules*, 2000, **33**, 5803.

25 G. Natta, G. Dall'Asta, G. Mazzanti and A. Casale, *Makromol. Chem.*, 1962, **58**, 217.

26 H. Terao, S. Ishii, M. Mitani, H. Tanaka and Fujita, T. *J. Am. Chem. Soc.*, 2008, **130**, 17636.

27 Y. Luo, Y. Luo, J. Qu and Z. Hou, *Organometallics*, 2011, **30**, 2908.

28 A. Isakova, P. D. Topham and A. J. Sutherland, *Macromolecules*, 2014, **47**, 2561.