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A new family of syndiotactic polystyrene derivatives containing the methoxyl group was established successfully by employing an yttrium catalyst.
Syndioselective Coordination Polymerization of the Unmasking Polar Methoxystyrenes Using Pyridenylmethylenyl Fluorenyl Yttrium Precursor

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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 methylenyl 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, it than 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. 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 transition metals that are swiftly poisoned by the polar atoms with Lewis acidic metal followings the tendency of oxygen > nitrogen > halogen, it was amazing that the above methoxystyrene (pMOS) systems displayed moderate activity (0.3×10^5 g polymer·mol^{-1}·h^{-1}) for the polymerization of para-methoxystyrene (para-MOS), the polymerization became ten times faster than that of pMOS (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 7.4×10^7 g polymer·mol^{-1}·h^{-1} was achieved for the polymerization of meta-

![Chart 1](image-url)
methoxystyrene (mMOS) (entry 3) that, noteworthy, cannot be polymerized by cationic catalysts due to its particular electronic structure.\textsuperscript{25} The molecular weights of the resultant polymeric chains 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 15.9×10^4 (Figure S10), 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/AlBu3/[Ph3C][B(C6F5)4] could catalyze polymerization of mMOS but was inert to the other mMOS and pMOS 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.

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

<table>
<thead>
<tr>
<th>entry</th>
<th>Monomer</th>
<th>[M]/[Y]</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>Activity(^b) (10(^4))</th>
<th>M(_n)</th>
<th>M(_w)/M(_n) (\times 10^2)</th>
<th>T(_g)/T(_m) (°C)</th>
<th>WCA(^d) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pMOS</td>
<td>150</td>
<td>30</td>
<td>75</td>
<td>0.30</td>
<td>3.91</td>
<td>1.94 &gt;99</td>
<td>95/221</td>
<td>83.7</td>
</tr>
<tr>
<td>2</td>
<td>pMOS</td>
<td>300</td>
<td>30</td>
<td>58</td>
<td>0.46</td>
<td>5.50</td>
<td>1.85 &gt;99</td>
<td>96/221</td>
<td>83.7</td>
</tr>
<tr>
<td>3</td>
<td>mMOS</td>
<td>300</td>
<td>3</td>
<td>93</td>
<td>7.40</td>
<td>9.69</td>
<td>1.70 &gt;99</td>
<td>54/175</td>
<td>84.9</td>
</tr>
<tr>
<td>4</td>
<td>mMOS</td>
<td>600</td>
<td>5</td>
<td>65</td>
<td>6.24</td>
<td>15.9</td>
<td>1.74 &gt;99</td>
<td>54/176</td>
<td>84.9</td>
</tr>
<tr>
<td>5</td>
<td>pMOS</td>
<td>300</td>
<td>8</td>
<td>100</td>
<td>3.00</td>
<td>6.42</td>
<td>1.97 &gt;99</td>
<td>84/240</td>
<td>89.9</td>
</tr>
<tr>
<td>6</td>
<td>pMOS</td>
<td>600</td>
<td>15</td>
<td>60</td>
<td>1.92</td>
<td>8.21</td>
<td>2.11 &gt;99</td>
<td>85/240</td>
<td>89.9</td>
</tr>
</tbody>
</table>

\(^a\) General condition: 10\(^{-5}\) mol of Y complex; in toluene; [Al]/[Y] = 10; [Ph3C][B(C6F5)4] /[Y] = 1; [monomer]\(_0\) = 2.0 mol/L. \(^b\) Given in 10\(^3\) g polymer/mol. \(^c\) Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against polystyrene standard. \(^d\) Determined by 1H NMR and 13C NMR. \(^e\) Determined by DSC. \(^f\) Determined by static water contact angle.

Remarkably, the polymerization was extremely stereoselective despite the position of the polar substituent. The 1H NMR spectra of the resultant polymers give typical triplet-
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 $\text{m MOS} > \text{o MOS} > \text{p MOS}$ in agreement with the NBO charge of $\beta$-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

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

† The first two authors contributed equally to this paper.


Figure 3. WCA of syndiotactic PS (a), P(oMOS) (b), P(mMOS) (c) and P(pMOS) (d).

Figure 2. $^{13}$C NMR spectra of syndiotactic polymethoxystyrenes. (A) P(pMOS) (CDCl$_3$, 25°C); (B) P(mMOS) (CDCl$_3$, 25°C); (C) P(oMOS) (CDCl$_3$, 120°C).

These methoxyl functionalized polystyrenes have various transition temperatures strongly depending on substituent position that $\text{P(mMOS)}$ possessing the lowest $T_m$ around 54°C whilst $\text{P(pMOS)}$ having the highest $T_m$ around 96°C and the $T_g$ of 84°C for $\text{P(oMOS)}$. 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 $\text{P(oMOS)}$ (240°C) $\text{P(pMOS)}$ (221°C) $\text{P(mMOS)}$ (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(pMOS), poly(mMOS), and poly(oMOS) are 83.7°, 84.9° and 89.9°, respectively, while the WCA of PS is 95.1° (Figure 3).

This new type of stereoregular polar polystyrene materials via simple post polymerization modification such as transferring the methoxyl to hydroxyl are building blocks for functional styrene-based materials.