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Syndiospecific Living Copolymerization of Styrene with ε-Caprolactone by Scandium Catalysts

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The copolymerization of two or more different monomers into a well-defined copolymer is an important strategy for the preparation of novel polymer materials having advanced properties. In this context, the precise control of the macromolecular architecture such as stereoregularity, molecular weight, molecular weight distribution, and comonomer composition is of significant importance. In endeavors toward this goal, the search for efficient, selective catalysts plays a critically important role. So far, extensive studies on the copolymerization of two monomers with similar properties (e.g., olefins) have been carried out, whereas the copolymerization of monomers with distinctly different properties (such as polar and nonpolar monomers) remained limited.[1] Several catalyst systems based on lanthanide or transition metals such as Sm,[2] Zr,[3] Ni,[4] Pd,[5] etc.,[6] were reported to copolymerize ethylene or propylene with polar monomers such as alkyl acrylates or functionalized vinyl monomers. However, the copolymerization of styrene with a polar monomer was limited mostly to anion or radical initiators,[7] which usually show poor stereoselectivity. Although titanium-based catalysts were known to show excellent syndiospecific selectivity for the homopolymerization of styrene,[8] attempts to copolymerize styrene with a polar monomer by a titanium-based catalyst did not produce any syndiotactic styrene−styrene sequences in the resulting copolymers.[9−11] As far as we are aware, the stereospecific copolymerization of styrene with a polar monomer has never been achieved previously. The search for a novel catalyst system suitable for the stereospecific copolymerization of styrene and a polar monomer is therefore of obvious interest and importance.

We previously demonstrated that cationic half-sandwich scandium alkyls can serve as excellent catalysts for the polymerization and copolymerization of a wide range of olefins, including syndiospecific polymerization of styrene and copolymerization of styrene with isoprene and ethylene.[12,13] In this study, we examined the potential of scandium catalysts for the copolymerization of styrene and polar monomers. We report here the first example of syndiospecific, living copolymerization of styrene with ε-caprolactone (CL), which gives efficiently well-defined block copolymers consisting of a perfectly stereoregulated syndiotactic polystyrene (*s*PS) block (which is hard and hydrophobic) and a flexible, hydrophilic polycaprolactone (PCL) block with controllable *s*PS/PCL contents. A preliminary stress−strain study revealed that these novel block copolymers can show excellent unique properties which are not seen in either of the homopylymers or their blends.

To probe the potential of the scandium catalysts for the copolymerization of styrene and CL, the homopolymerization of these two monomers under similar conditions was first examined. As shown in Table 1, both complexes **1** and **2** (Chart 1) showed excellent activity and living character for the syndiospecific polymerization of styrene and the ring-opening polymerization of CL at room temperature in the presence of an equivalent of $[Ph_3C][B(C_6F_5)_4]$. When the monomer/catalyst ratio was doubled, the molecular weight of the resulting polymers also double increased while the molecular weight distribution remained rather narrow.

The block copolymerization of styrene and ε-CL was then carried out in one-pot by addition of CL to a completed styrene polymerization reaction mixture in toluene at room temperature. Some representative results are summarized in Table 2. Well-defined AB-type styrene−CL diblock copolymers containing a perfect *s*PS block were obtained by use of either **1** or **2** activated with $[Ph_3C][B(C_6F_5)_4]$. A small amount of homo-PCL was formed as a minor product, which could be easily removed by washing with acetone. The copolymers are insoluble in acetone at room temperature but have certain solubility suitable for GPC analysis in hot THF (40 °C).[14] A sharp peak shift of the GPC traces to a higher molecular weight was observed after addition of CL, suggesting that all of the preformed *s*PS−Sc species initiated the PCL chain growth (Figure 1). The ^1H and ^{13}C NMR spectra showed typical signals of *s*PS, in addition to those of PCL (see Supporting Information). Compared to **1**, complex **2** showed higher activity and selectivity for the copolymerization with CL, leading to formation of copolymers with higher PCL content (higher molecular weight) under the same conditions (Table 2, runs 1−4), although a significant difference between **1** and **2** was not observed in the homopolymerization of CL under similar conditions. When the monomer/catalyst ratio was raised, the block copolymers with higher molecular weights were obtained. The increase of the CL/styrene ratio resulted in increase of the PCL content (block length) in the copolymers. The molecular weight distribution of the copolymer products remained narrow ($M_w/M_n = 1.13-1.34$) in all the cases.

All of the block copolymers obtained above showed two melting points (271−274 and 51−54 °C) originating from a *s*PS block and a PCL block, respectively (Table 2). It is well-known that *s*PS is a semicrystalline engineering plastic,[8] showing excellent thermal stability and dimensional stability, but having a drawback of brittleness. In contrast, PCL is a well-known flexible, biocompatible polymer, showing relatively low melting point (<60 °C) and weak strength.[15] To see if the present block copolymers could show superior or synergistic properties, the stress−strain measurement of solution casting films of various polymer samples was carried out. It was found that the mechanical properties of the block copolymers depend significantly on the comonomer content (or relative block length).

The copolymers with CL content less than 50 mol % are too brittle to give a measurable stress−strain value, similar to homo-*s*PS. However, when the CL content was raised to more than 50 mol %, a dramatic improvement in toughness was observed. As expected, when the CL content increased from 52 to 82 mol %, the Young's modulus of the copolymers decreased gradually from a peak value of 782.9 to 497.4 MPa (Table 3, runs 3−5). However, these values are still higher than that of the homopolymers or their blend in all the cases. As the CL content increased from 52 to 82 mol %, the flexibility (elongation at break) of the copolymers increased significantly, reaching as high as 1359% (Table 3, run 5). This value is higher by more than

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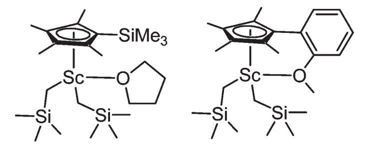
Table 1. Sc-Catalyzed Syndiospecific Homopolymerization of Styrene and Homopolymerization of ε-Caprolactone[a]

run	cat.	monomer[b]	time (min)	yield (%)	M_n[d] ($\times 10^{-3}$)	M_w/M_n[d]	T_m[e] (°C)	efficiency[f] (%)
		St						
1	**1**	100	1	100[c]	23.7	1.24	272	44
2	**1**	200	1	100[c]	46.5	1.33	272	45
3	**2**	100	1	100[c]	20.0	1.26	273	52
4	**2**	200	1	100[c]	41.3	1.36	274	51
5[g]	**2**	500	1	100[c]	98.2	1.25	274	53
		CL						
6	**1**	100	5	100	17.0	1.14	54	40
7	**1**	200	5	100	34.2	1.11	54	40
8	**2**	100	5	100	12.5	1.21	55	55
9	**2**	200	5	100	24.2	1.23	55	56
10[g]	**2**	700	5	100	85.6	1.18	55	56

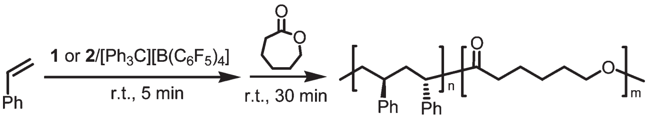
[a] Conditions: [Sc] = 21 μmol, $[Ph_3C][B(C_6F_5)_4]$ = 21 μmol, toluene V = 6 mL, 25 °C, unless otherwise noted. [b] Molar ratio to [Sc]. [c] Sydiospecific PS > 99% as shown by ^{13}C NMR. [d] Determined by GPC against PS standards in THF at 40 °C. [e] Measured by differential scanning calorimeter (DSC). [f] Catalyst efficiency = M_n(calculated)/M_n(measured). [g] [Sc] = 42 μmol, $[Ph_3C][B(C_6F_5)_4]$ = 42 μmol, toluene = 20 mL.

Chart 1



1 **2**

Table 2. Sc-Catalyzed Syndiospecific Block Copolymerization of Styrene with ε-CL[a]



run	cat.	St/CL[b]	yield[c] (g)	sel[d] (%)	sPS/PCL[e]	M_n[f] ($\times 10^{-3}$)	PDI[f]	T_m[g] (°C)
1	**1**	100/50	0.26	84	81/19	26.5	1.32	274; 51
2	**1**	100/400	0.36	83	57/43	54.3	1.29	273; 54
3	**2**	100/50	0.31	97	71/29	30.4	1.17	272; 54
4	**2**	100/400	1.00	89	22/78	97.6	1.13	271; 54
5[h]	**2**	200/250	1.80	94	48/52	76.4	1.22	273; 54
6[h]	**2**	200/500	2.70	89	33/67	117.8	1.23	273; 54
7[h]	**2**	200/1000	4.85	88	18/82	165.2	1.34	272; 55

[a] Conditions: [Sc] = 21 μmol, $[Ph_3C][B(C_6F_5)_4]$ = 21 μmol, toluene V = 20 mL, unless otherwise noted. [b] Molar ratio to [Sc]. [c] Copolymer yield (g) after washing with acetone. [d] Copolymer selectivity = [(weight of copolymer)/(weight of all crude products)] × 100%. [e] Composition (mol) of the copolymer determined by ^1H NMR. [f] PDI = M_w/M_n, determined by GPC against PS standards in THF at 40 °C. [g] Measured by DSC. [h] [Sc] = 42 μmol, $[Ph_3C][B(C_6F_5)_4]$ = 42 μmol, toluene V = 40 mL.

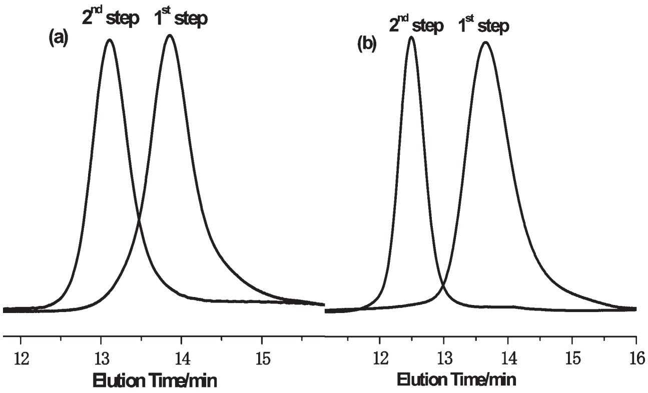


Figure 1. GPC profiles of sequential styrene−CL block copolymerization: (a) by **1** (Table 2, run 2); (b) by **2** (Table 2, run 4). First step, styrene (2.1 mmol), 5 min; second step, ε-CL (8.4 mmol), 30 min.

Table 3. Mechanical Properties of *s*PS-*b*-PCL Diblock Copolymers[a]

run	sample	M_n ($\times 10^{-3}$)	PDI	sPS/PCL[b]	E[c] (MPa)	σ[d] (MPa)	ε[e] (%)
1	*s*PS	98.2	1.25	100/0	–[f]	–[f]	–[f]
2	PCL	85.6	1.18	0/100	254.5	14.7	784
3	$s\mathrm{PS}_{48}$-b-PCL_{52}	76.4	1.22	48/52	782.9	31.4	884
4	$s\mathrm{PS}_{33}$-b-PCL_{67}	117.8	1.23	33/67	768.5	25.0	941
5	$s\mathrm{PS}_{18}$-b-PCL_{82}	165.2	1.34	18/82	497.4	51.4	1359
6[g]	$s\mathrm{PS}_{18} + \mathrm{PCL}_{82}$			18/82	420.4	18.2	200

[a] Samples (ca. 300 μm thick) were prepared via solution casting and were measured at an extension rate of 20 mm/min. [b] Molar ratio calculated from ^1H NMR. [c] Young's modulus. [d] Tensile strength. [e] Elongation at break. [f] A homo-*s*PS sample was too brittle to give a measurable value. [g] A blend of *s*PS (run 1) and PCL (run 2) with a molar ratio of 18/82.

6 times than that of a homopolymer blend with the same ratio (200%) (Table 3, run 6). More remarkably, all of the copolymers showed much higher flexibility even than that of homo-PCL. Similarly, the tensile strength of the copolymers with CL content of 52−82 mol % is also much improved (up to about 3 times) compared to either homopolymers or their blend. Such significant improvement in both flexibility and stiffness observed in the present copolymers is perhaps unprecedented, as far as we are aware. This is probably owing to possible strain hardening resulting from a high degree of orientation of the two different crystalline blocks with chain axes parallel to the stretching direction.[16] However, further studies are certainly needed to clarify the physical mechanism.

In summary, we have demonstrated that cationic half-sandwich scandium alkyls can serve as excellent catalysts not only for the homopolymerization of styrene and ε-caprolactone but also for the copolymerization of these two distinctly different monomers, affording for the first time styrene−CL diblock copolymers with well-controlled molecular weight and molecular distribution and a wide range of *s*PS/PCL contents. The copolymers obtained contain two unique crystalline blocks (hydrophobic hard *s*PS and hydrophilic soft PCL) and exhibit unique synergistic mechanical properties.

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Supporting Information Available: Polymerization procedures, GPC traces, DSC curves, ^1H NMR and ^{13}C NMR spectra, and details on the mechanical analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The block copolymers with a relatively short *s*PS block were deliberately prepared, so that they could have certain solubility in THF for easy GPC analysis. Copolymers with a long *s*PS block are poorly soluble and have to be characterized by high-temperature GPC using *o*-dichlorobenzene as a solvent, which, however, is not suitable for the analysis of styrene−ε-CL copolymers because of the distinctly different refraction properties of styrene and ε-CL in *o*-dichlorobenzene.

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