Metal-Free Stereoselective Cationic Polymerization of Vinyl Ethers by Employing a Confined Brønsted Acid as the Catalyst

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Supporting Information Placeholder

ABSTRACT: The properties of poly(vinyl ether)s (PVEs) are highly dependent on their tacticity, and the appealing thermoplastics features of isotactic PVEs have drawn considerable efforts to develop stereoselective cationic polymerization methods to access this class of polymers. However, reported methods that could achieve a high degree of tacticity control are limited to process employing metal-based Lewis acids, and with various limitations on catalyst loading, monomer scope, etc. Here, we introduce a metal-free stereoselective cationic polymerization of vinyl ethers by employing a class of chiral confined Brønsted acids, imidodiphosphorimidates (IDPis), as the catalyst. This organocatalytic approach features its metal free conditions, high efficiency, high stereoselectivity, single catalyst system, operation simplicity, etc.

The tacticity of polymers being a critical factor affects the properties (e.g. mechanical strength, thermal performance, optical property etc.) of materials.[1] For example, atactic polypropylene is typically an amorphous fluid; in contrast, isotactic polypropylene is a crystalline, rigid thermoplastic, while syndiotactic polypropylene processes greater impact strength and better optical clarity than isotactic polypropylene.[2-3] Poly(vinyl ether)s also showed a significant tacticity-dependent properties,[4,5] and the earlier reports on stereoselective cationic polymerization of vinyl ethers (VEs) can even date back to the late 1940s.[6-8] However, in comparison to the coordination-insertion polymerizations that proceed at a non-planar chain-end with a relatively defined stereochemistry, the cationic polymerizations of vinyl ether monomers proceed with a planar sp^2-hydridized carbocation (Figure 1, A).[6,9-11] The planar configuration of this active carbocation with a large open space, together with the high polymerization rate, result in the difficulty in the development of a highly stereoselective cationic polymerization of vinyl ethers. Therefore, an additional stereochemical controls are normally required to set the stereochemistry at the planar, prechiral carbocationic center in the C-C bond formation step with the incoming vinyl ether monomer.

In the past seven decades, there are many attempts with a focus on the catalyst development, aiming to establish a stereoselective cationic polymerization of vinyl ethers to access (semi)crystalline poly(vinyl ether) products (Figure 1B, I).[6,7,12-24] In 1999, Sawamoto and co-workers reported high levels of tacticity by using $TiCl_4$/phenoate complexes as the catalyst,[15] and they later on found a combination of $SnCl_4$ Lewis acid with bulky phosphoric acid ligand was also effective.[17] Recently, Leibfarth et al. introduced chiral 1,1'-bi-2-naphthol (BINOL)-derived phosphoric acids into $TiCl_4$-based Lewis acids and achieved a remarkable high content of *meso* diads (up to 94% m).[5,21]
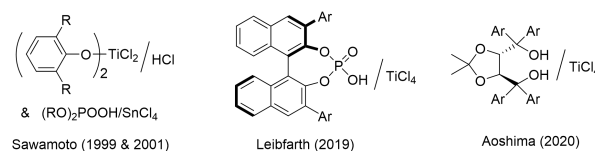
Very recently, Aoshima and co-workers disclosed a titanium complex bearing enantiopure α,α,α',α'-tetraaryl-2,2-disubstituted 1,3-dioxolane-4,5-dimethanol (TADDOL) ligands, which could provide poly(VE)s with isotacticity ranging from 83% to 94% m.[22] Whereas, the ever-increasing demand for metal-free polymer materials in metal-sensitive fields such as microelectronic and biomedical applications,[25,26] encouraged us to seek an organic catalyst to establish a metal-free stereoselective polymerization of vinyl ethers.
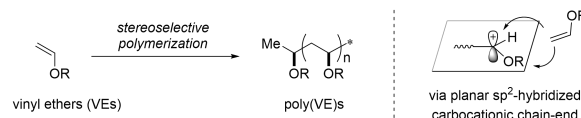
**Figure 1**. (A)Stereoselective polymerization of vinyl ethers. (B) The development of catalytic systems: metal-based Lewis catalysts (previous work) and metal-free confined acid catalysts (this work).

In fact, Brønsted acids (e.g. HCl, TfOH, Tf_2NH, etc.) are known capable to promote the cationic polymerization of vinyl ethers, but lack of effective stereochemical controls.[27-31] Our research experience[32] on the asymmetric catalysis with chiral confined Brønsted acids,[33-42] and particularly, the unprecedented high efficiency and stereoselectivity observed with the imidodiphosphorimidate (IDPi)-type confined acids in many transformations[33,35-42] encouraged us to explore the potential of these confined acids in polymer synthesis.[43] Inspiringly, the acid activation of aldehydes by protonation of the carbonyl oxygen of the aldehydes, for example, in the asymmetric [4+2]-cycloaddition of

dienes with aldehydes,[37] generated an oxocarbenium ion[36-38] that resembles the prechiral carbocationic chain-end of cationic polymerization of vinyl ethers (Figure 1B, II). We thus conceived, similar to the stereo-control in organic reactions, the chiral Brønsted acid anion[44-50] around this propagating carbocationic chain-end could also provide a stereochemical micro-environment to govern the trajectory of the incoming vinyl ether monomer, thus establish a stereoselective cationic polymerization. Here, we report our efforts toward this goal, and the first establishment of a stereoselective cationic polymerization of vinyl ethers by employing a confined Brønsted acid, IDPi, as the catalyst, which features its metal free condition, high stereoselectivity, and operational simplicity.[51]

We commenced our investigation with the cationic polymerization of isobutyl vinyl ether (IBVE) in toluene (0.4 M) at -78 °C with a series of imidodiphosphorimidates (**IDPi 1a-1h**) as the catalyst, which can be easily prepared from the corresponding 3,3'-substituted BINOLs[33] (Table 1). For comparison with the confined Brønsted acids, a small acid catalyst (Tf$_2$NH) was also examined under the same conditions (entry 1). As shown in Table 1, Tf$_2$NH delivered a rapidly polymerization, but the poly(isobutyl vinyl ether) (Mn = 13000 & Đ = 1.62) was obtained as a fluid, which is consistent with its low isotacticity (60% m) determined by ^{13}C NMR analysis of the backbone methylene resonances (δ 39 to 42 ppm). To our delight, the confined acid **IDPi 1a** provided the poly(IBVE) with a remarkable high degree of isotacticity (88% m, entry

Table 1. Optimization of Confined Brønsted Acid for the Stereoselective Cationic Polymerization of IBVE.[a]
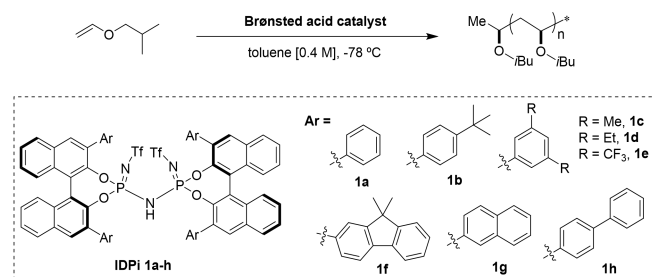
Entry	CAT	Mn (kg/mol)[b]	Đ[b]	m[c]
1	**Tf$_2$NH**	13.0	1.62	60%
2	**IDPi 1a**	12.1	1.71	88%
3	**IDPi 1b**	9.7	1.40	79%
4	**IDPi 1c**	15.7	2.15	88%
5	**IDPi 1d**	24.9	2.09	87%
6	**IDPi 1e**	18.9	2.38	91%
7	**IDPi 1f**	14.0	2.58	80%
8	**IDPi 1g**	18.1	2.92	88%
9	**IDPi 1h**	12.8	2.34	81%

[a] Polymerization conditions: [IBVE]$_0$/[Catalyst]$_0$ = 200/1, [IBVE]$_0$ = 0.4 M at -78 °C for 30 min. [b]Determined by GPC using polystyrene standards. [c]Determined by ^{13}C NMR analysis.

Table 2. Stereoselective Cationic Polymerization of Vinyl Ethers with IDPi 1e.[a]
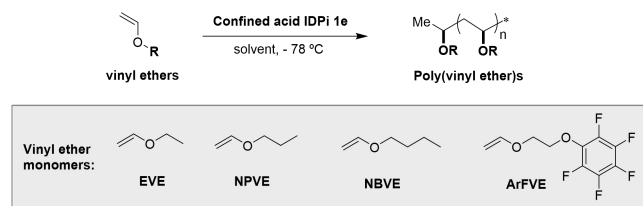
| Entry	VE	Solvent	$M_{n,GPC}$[b] (kg/mol)	Đ[b]	m[c]
1	IBVE	toluene	18.9	2.38	91%
2	IBVE	hex/tol = 4:1	21.5	1.46	82%
3	IBVE	hex/tol = 1:1	20.8	1.65	85%
4	IBVE	hex/tol = 1:4	28.1	2.33	87%
5[d]	IBVE	toluene	19.3	1.74	90%
6[e]	IBVE	toluene	16.9	1.62	90%
7[f]	IBVE	toluene	58.4	1.79	89%
8[g]	IBVE	toluene	101.0	1.68	86%
9	EVE	toluene	10.2	1.57	85%
10	NPVE	toluene	14.0	1.74	90%
11	NBVE	toluene	24.9	1.68	88%
12	ArFVE	toluene	34.8	1.79	89%

[a]Polymerization conditions: [IBVE]$_0$/[**IDPi 1e**]$_0$ = 200/1 at -78 °C for 30 min. hex = hexane; tol = toluene. [b]Determined by GPC using polystyrene standards. [c]Determined by ^{13}C NMR analysis. [d]0.2 M of IBVE was used. [e]0.1M of IBVE was used. [f]Polymerization carried out at [IBVE]$_0$/[**IDPi 1e**]$_0$ = 500/1. [g]Polymerization carried out at [IBVE]$_0$/[**IDPi 1e**]$_0$ = 1200/1.

2). This result demonstrated that the confined IDPi counterion could indeed control the stereoselectivity in the polymer chain growth. Inspired by this initial result, a series of IDPi acids were prepared and evaluated in the polymerization of IBVE. **IDPi 1b** with a *tert*-butyl substituent at the *para* positions of the phenyl groups was tested, but lower isotacticity (79% m) was observed (entry 3). We thus decided to modify the 3,5-positions of the phenyl groups, which unveiled a high stereoselectivity with **IDPi 1c** (entry 4). Even though increasing the steric hindrance (**IDPi 1d**) led no further improvement in isotacticity (entry 5), the introduction of an electron-withdrawing trifluoromethyl group could enhance the isotacticity to a remarkable level of above 90% m (entry 6). Further variation on the aryl groups, including 9,9-dimethylfluorene (**IDPi 1f**), naphthyl group (**IDPi 1g**), as well as an extended arm (**IDPi 1h**) afforded good stereoselectivities (80-88% m, entries 7-9), but **IDPi 1e** remains the best, giving the highest isotacticity (91% m, entry 6).

With **IDPi 1e** giving the highest isotacticity in the stereoselective cationic polymerization of IBVE, we further investigated its

performance under other polymerization conditions (Table 2). The effect of adding non-polar solvent hexane was first examined by varying the hexane/toluene ratio. As shown in Table 2 (entries 1-4), the addition of hexane led to a lower isotacticity, while narrower dispersities were observed when compared with the polymerization conducted in toluene (entry 1). Decreasing the monomer concentration from 0.4 M to 0.1 M gradually narrowed down the molecular weight distributions of the obtained poly(IBVE)s, while maintaining the tacticity (entries 5-6). Further, poly(IBVE) with high molecule weights can be prepared with this method (M_n = 58.4 kg/mol, 101.0 kg/mol, entry 7 & 8). This confined acid-catalyzed cationic polymerization method can also be applied to the polymerization of other vinyl ether monomers with high degrees of isotacticity (Table 2, entries 9-12). Under the optimized reaction conditions with **IDPi 1e** as the catalyst, the polymerization of small ethyl vinyl ether (EVE) could afford the corresponding poly(EVE) with good isotacticity (85% m, entry 9). The polymerization of other alkyl vinyl ethers, *n*-propyl vinyl ether (NPVE) and *n*-butyl vinyl ether (NBVE), gave poly(NPVE) and poly(NBVE) with 90% m and 88% m, respectively (entry 10 & 11). To our delight, a fluorinated vinyl ether monomer, 1,2,3,4,5-pentafluoro-6-(2-(vinyloxy)ethoxy)benzene (ArFVE) can also be polymerized with this confined acid-catalyzed polymerization method, to give the fluorinated poly(vinyl ether) product with high isotacticity (89% m).

As shown in Figure 2, this chiral confined Brønsted acid-catalyzed stereoselective polymerization afforded the poly(IBVE) (M_n 99.3 kg/mol, 90% m) as semi-crystalline, white solids. In contrast, Tf$_2$NH-catalyzed polymerization gave a fluid with a glass transition temperature below 0 ºC. The poly(vinyl ether) products were further evaluated using differential scanning calorimetry (DSC). Poly(NPVE) (90% m) displayed single melting transitions at 52 ºC, while poly(IBVE) (90% m) showed two melting transitions at 113 and 127 ºC.
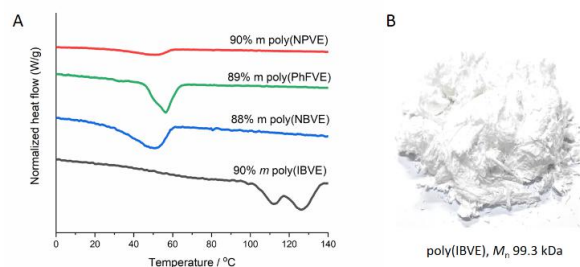
Figure 2. (A) DSC scan curves. (B) Photo of the poly(IBVE) product.

The IDPi-catalyzed stereoselective polymerization of vinyl ethers can also be employed in the one-pot synthesis the poly(vinyl ether)s with a chain-end functionalization by trapping the carbocationic chain-
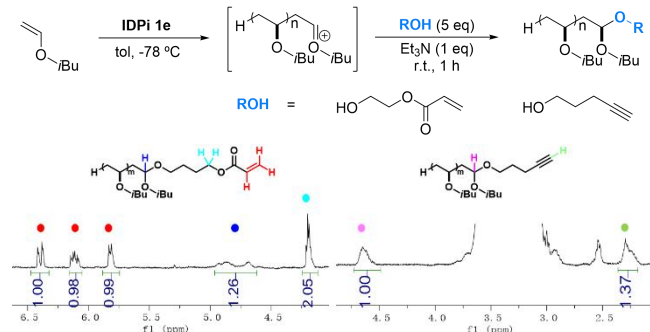
Figure 3. In situ chain-end functionalization and NMR characterization.

ends in situ. As shown in Figure 3, upon full conversion of the IBVE monomers, functionalized alcohols and trimethylamine (Et$_3$N) were added under argon. After stirred for one hour at room temperature, the corresponding alcohol-trapped poly(vinyl ether)s can be obtained by precipitation in methanol. In this approach, poly(IBVE)s attached with an acrylate or alkyne functionality can be synthesized, which could allow further modifications at the chain ends.

In conclusion, a metal-free highly stereoselective cationic polymerization of vinyl ethers have been developed by employing IDPi-type chiral confined Brønsted acids as the catalyst. This organocatalytic approach could afforded poly(vinyl ether)s with high molecular weights and isotacticity, featuring its high efficiency, high stereoselectivity, single catalyst system, and operation simplicity. Moreover, a one-pot chain-end modification via *in situ* trapping of the oxocarbenium was also demonstrated. Further application of the confined Brønsted acids in other stereoselective cationic polymerizations can be expected.

ASSOCIATED CONTENT

Supporting Information

Synthesis of IDPi catalysts, experimental procedures, characterization data, copies of NMR spectra. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no conflict of interests.

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(51) A patent has been filed on this stereoselective polymerization method employing chiral confined Brønsted acids as the catalyst.

Table of Content

Confined Acid-Catalyzed Stereoselective Cationic Polymerization of Vinyl Ethers:

vinyl ethers (VEs)

isotactic PVEs

IDPi-Confined Brønsted Acids
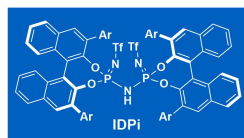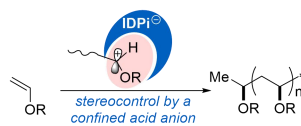
• *metal free* • *high stereoselectivity* • *crystalline PVE products* • *simple operation*