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Post-polymerization modification of poly(vinyl ether)s: a Ru-catalyzed oxidative synthesis of poly(vinyl ester)s and poly(propenyl ester)s†

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Poly(vinyl ester)s were readily prepared *via* a ruthenium catalyzed C–H oxidation of the corresponding poly(vinyl ether)s under mild conditions. The transformations were efficient and in many cases proceeded without significant chain cleavage. The method was also successfully used to prepare high molecular weight poly(propenyl ester) for the first time as well as a polyester with a relatively high content (>50%) of γ -butyrolactone repeat unit from poly(tetrahydrofuran). The polymeric products were characterized *via* FT-IR spectroscopy, NMR spectroscopy, gel permeation chromatography, and other techniques.

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Introduction

Post-polymerization modification is a powerful method for gaining access to various types of functionally and structurally advanced macromolecules.^{1,2} Several industrially important polymers, such as poly(vinyl alcohol) and poly(vinyl butyral), are only accessible *via* post-polymerization modification since the corresponding monomers can not be isolated. For this reason, efforts have been directed toward utilizing reactive groups, such as activated esters and epoxides, as derivatization handles; as such, pre-installation of the requisite functional groups on the polymer precursor is generally required.^{1,3}

The direct transformation of relatively inert C–H bonds omnipresent in most synthetic polymers represents a potentially powerful post-polymerization modification strategy. Although there has been significant progress in the development of C–H bond functionalization methods for small molecules in recent years,^{4–9} only a few examples have been reported for the modification of polymeric materials.¹⁰ Elegant examples of such approaches include the regioselective functionalization of isotactic polypropylene and the main-chain modification of polysulfone *via* iridium or rhodium catalyzed C–H borylation.^{11–13}

Although poly(vinyl ester)s are often obtained *via* the free radical polymerization of the corresponding vinyl ester

monomer, the polymer produced often features ill-defined microstructures, including high degrees of head-to-head linkages and extensive branching.¹⁴ Moreover, some monomers, such as β -substituted vinyl esters and isopropenyl esters, are challenging to polymerize using free radical techniques due to steric hindrance and/or degradative chain transfer processes.^{15,16} For example, current methods for preparing high molecular weight ($M_w > 10$ kDa) poly(isopropenyl acetate) require high pressures and afford relatively low yields of polymer.¹⁷

In contrast, vinyl and propenyl ethers readily undergo cationic polymerization and well-defined polymeric materials are often obtained.^{18–20} Ruthenium tetroxide mediated oxidation of aliphatic ethers to their corresponding esters is a well-established and efficient transformation.^{21–23} We envisioned overcoming the aforementioned limitations associated with synthesizing poly(vinyl ester)s and poly(propenyl ester)s by taking advantage of established cationic polymerization process in conjunction with an efficient Ru catalyzed C–H oxidation methodology.²⁴

Herein, we describe the synthesis of various poly(vinyl ester)s and poly(propenyl ester)s *via* a Ru catalyzed oxidation of the corresponding poly(vinyl ether)s and poly(propenyl ether)s. In addition, we demonstrate that the method may also be used to access aliphatic polyesters *via* the main chain modification of poly(tetrahydrofuran).

Results and discussion

Oxidation of poly(vinyl ether)s

Initial efforts were directed toward the oxidation of poly(butyl vinyl ether) (PBVE) using various Ru based catalysts, including

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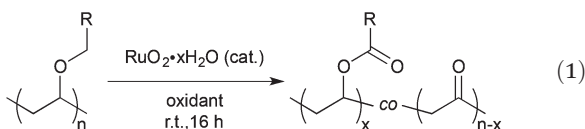
† Electronic supplementary information (ESI) available: ¹H NMR, ¹³C NMR, GPC, DSC, TGA and MS data. See DOI: 10.1039/c5py01409c

Table 1 Summary of conditions used to oxidize various poly(vinyl ether)s^a

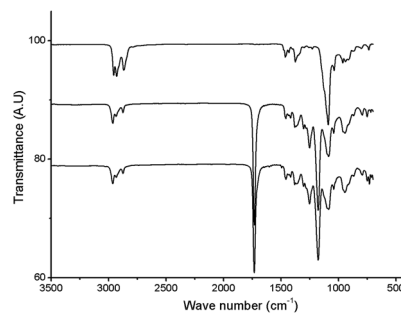
Entry	R	Solvent ^b	Oxidant	Conversion ^c (%)	Selectivity ^{c,d} (%)
1	Pr	EtOAc/H ₂ O	NaIO ₄	98	95
2	Pr	EtOAc/H ₂ O	NaBrO ₃	98	95
3	Pr	EtOAc/H ₂ O	NaClO	89	85
4	Pr	EtOAc/H ₂ O	Oxone	86	89
5 ^e	Pr	EtOAc/H ₂ O	NaBrO ₃	99	95
6 ^{e,f}	Pr	EtOAc/H ₂ O	NaBrO ₃	99	98
7 ^e	Pr	EtOAc/H ₂ O	NaClO	86	83
8	Pr	CH ₂ Cl ₂ /H ₂ O	NaBrO ₃	37	75
9	Pr	CH ₂ Cl ₂ /H ₂ O	NaIO ₄	35	80
10	Pr	CH ₂ Cl ₂ /H ₂ O ^g	NaIO ₄	97	88
11	Pr	EtOAc	NaIO ₄ /SiO ₂ ^h	96	91
12	i-Pr	EtOAc/H ₂ O	NaBrO ₃	99	97
13	Me	EtOAc/H ₂ O	NaBrO ₃	89	89
14 ⁱ	Me	EtOAc/H ₂ O	NaBrO ₃	30	89
15	H	EtOAc/H ₂ O	NaIO ₄	39	60

^a See eqn (1). Conditions: 1 mg RuO₂·xH₂O, 10 mg poly(vinyl ether) in 2 mL of the solvent indicated, oxidant (4 equiv. with respect to the polymer repeat unit), r.t., 16 h. ^b 1 : 1 (v/v) binary mixture. ^c Calculated *via* ¹H NMR spectroscopy. ^d Selectivity was defined as $(x/n) \times 100\%$. ^e RuCl₃·xH₂O was used as the catalyst. ^f [Ether repeat unit]₀ = 0.3 M, 2 mmol scale, 6.5 mg Ru catalyst, 2.1 equiv. NaBrO₃ with respect to the polymer repeat unit. ^g 0.5 mL acetonitrile was added to the reaction mixture. ^h 500 mg of NaIO₄/SiO₂ (20 wt% NaIO₄) was used as the oxidant. ⁱ The reaction was run for 1 h.

RuO₂·xH₂O and RuCl₃·xH₂O. As summarized in Table 1, various oxidants and solvent mixtures commonly used in RuO₄ mediated oxidation reactions were explored. Oxidants such as NaBrO₃ or NaIO₄ were found to be effective and resulted in high conversions of the starting materials and excellent selectivities (*vide infra*), as determined by NMR spectroscopy. In contrast, the use of oxone or aqueous NaClO resulted in rapid consumption of the oxidant, which may have limited the conversions observed. In addition, the use of binary mixtures of a chlorinated solvent and water gave poor results, presumably due to premature catalyst deactivation during the reaction.²² While the addition of CH₃CN improved the conversion of starting material, relatively low selectivities were observed. Ultimately, a 1 : 1 (v/v) mixture of ethyl acetate (EtOAc) : H₂O was determined to be the optimal solvent.



The structure of the polymer obtained from the aforementioned reaction using NaBrO₃ as the oxidant and EtOAc/H₂O as the solvent was elucidated using FT-IR and ¹H NMR spectroscopy. As shown in Fig. 1, the strong $\nu_{C=O}$ and ν_{C-O} signals recorded at 1176.6 and 1734.5 cm⁻¹, respectively, were consistent with the formation of ester functional groups; these signals were not observed in the poly(vinyl ether) starting material. In addition, the IR spectrum of the product matched that of an authentic sample of poly(vinyl butyrate) (PVB). As

**Fig. 1** FT-IR spectra of PBVE before (top) and after (middle) oxidation (Table 1, entry 6), and (bottom) an authentic sample of PVB.

shown in Fig. 2, the chemical shifts assigned to the C-H groups α to the ether repeat units in the main chain of the PBVE starting material (δ 3.2–3.7 ppm, CDCl₃) shifted downfield to approximately 4.8 ppm in the product. The poly(vinyl ester) product also exhibited a signal near 2.2 ppm, which was attributed to the side-chain methylene units adjacent to the ester carbonyl groups. Other recorded ¹H NMR signals were consistent with the structure of PVB.

The formation of a side product comprising main-chain ketones (*i.e.*, the structures shown in the brackets indicated by the subscripted $n-x$ in eqn (1)) was also observed upon close inspection of the NMR data. As shown in Fig. 2 (bottom, inset), the signal recorded at δ 2.6 ppm was attributed to the main chain methylene units adjacent to the ketone groups, which presumably formed *via* C–O bond cleavage followed by oxidation. Similarly, the signal recorded at 5.2 ppm was assigned to main chain methine units positioned β to the ketone groups. The assignments were further supported by a nearly constant integral ratio of the two signals ($I_{2.6 \text{ ppm}}/I_{5.2 \text{ ppm}} \approx 2$) among the various samples analyzed as well as by a ¹H–¹H COSY experiment (see the ESI†). It has been previously shown that the oxidation chemistry displayed by RuO₄ can be strongly influenced by the solvent.²⁶ Indeed, the quan-

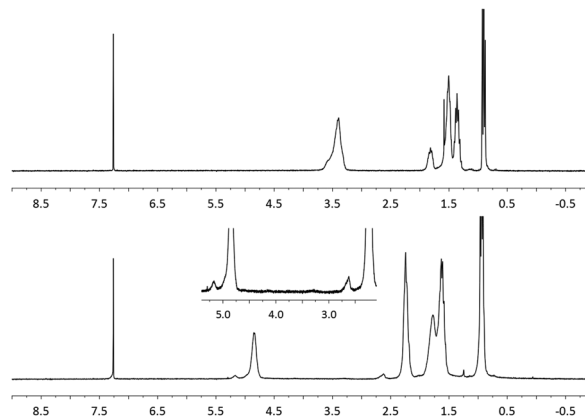
**Fig. 2** ¹H NMR spectra of PBVE before (top) and after (bottom) oxidation (Table 1, entry 6) (CDCl₃, 400 MHz).

Table 2 Evaluation of chain degradation upon oxidative modification^a

Starting material	Oxidant	M_n^b (kDa)		D^b	
		Pre-oxidation		Post-oxidation	
PBVE	NaBrO ₃	21.9	1.3	19.6	1.4
PBVE	NaIO ₄	21.9	1.3	14.1	1.6
PIBVE	NaBrO ₃	10.4	1.4	10.1	1.4
PIBVE	NaIO ₄	10.4	1.4	7.7	1.7

^a Reaction conditions: [ether repeat unit]₀ = 0.1 M, 4 equiv. of oxidant (indicated) with respect to the polymer repeat unit, 5 wt% RuO₂·xH₂O, r.t., 24 h. ^b Determined *via* GPC against polystyrene standards (THF, 35 °C).

tivity of ketone groups observed in the products appeared to depend on the reaction conditions employed. For example, we observed up to 37% of the repeat units contained ketone units when a chlorinated solvent was used; in contrast, the use of EtOAc/H₂O as the reaction medium was found to reduce ketone formation to less than 5%.

Using the optimized reaction conditions described above, a variety of poly(vinyl ether)s were explored as starting materials. As summarized in Table 1, poly(vinyl isobutyrate) and poly(vinyl acetate) were obtained from the corresponding poly(vinyl ether)s in excellent yield and selectivity. However, attempts to oxidize poly(methyl vinyl ether) resulted in relatively limited selectivity as well as incomplete conversion. Poly(*tert*-butyl vinyl ether) was found to be inert toward oxidation under the conditions explored (see the ESI†).

To probe whether the aforementioned oxidation reactions resulted in chain cleavage, a series of poly(vinyl ether)s and their corresponding poly(vinyl ester)s were analyzed *via* gel permeation chromatography (GPC). While slight changes in the polymer molecular weights were observed when NaBrO₃ was used as the oxidant, no significant changes in the respective polydispersity indices (D) were measured. Since PVB is more polar than poly(butyl vinyl ether) (PBVE), it was expected that the former should display stronger intramolecular interactions and therefore exhibit a relatively longer retention time (and thus a low molecular polystyrene standard equivalent molecular weight) when measured by GPC.²⁷ Nevertheless, the nearly unchanged D indicated that significant chain cleavage did not occur over the course of the oxidation reaction. In comparison, performing a reaction with NaIO₄ as the oxidant resulted in a more pronounced reduction in molecular weights and relatively larger D values under otherwise identical conditions. Similar results were obtained with poly(isobutyl vinyl ether) (PIBVE); see Table 2.

Synthesis of poly(propenyl ester)s (PPE)s

It has been reported that poly(propenyl acetate) may be prepared using a SnCl₄ catalyzed acetylation of poly(*tert*-butyl propenyl ether).^{28,29} However, this method requires large quantities of a metal catalyst (40 wt%) and results in low molecular weight polymeric products ($[\eta] = 0.05$). Building on our previous results, subsequent attention shifted toward the syn-

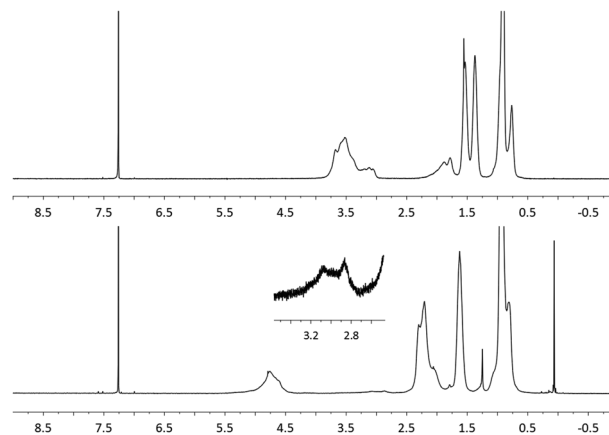


Fig. 3 ¹H NMR spectra of PBPE before (top) and after (bottom) oxidative modification (CDCl₃, 400 MHz).

thesis of poly(propenyl ester)s using the aforementioned post-polymerization oxidation methodology.

First, poly(butyl propenyl ether) (PBPE) was synthesized *via* the cationic polymerization of the corresponding monomer. Although PBPE is soluble in EtOAc, it often precipitates from solution in the presence of water. To circumvent this problem, butyl acetate was used in lieu of EtOAc as the solvent for subsequent experiments. The oxidation of PBPE using NaBrO₃/RuO₂·xH₂O at room temperature was found to be slower than that observed with PBVE (90% conversion after 72 h), presumably due to the differences in steric bulk. However, the rate of the oxidation reaction increased after raising the temperature of the corresponding reaction mixture to 60 °C. The polymeric product from the aforementioned reaction was isolated *via* precipitation and then analyzed by NMR spectroscopy as well as GPC. As shown in Fig. 3, diagnostic signals were recorded between 4.5–5.4 ppm and 1.9–2.4 ppm, and assigned to methine units in the main chain and methylene units α to ester groups in the side chains, respectively. Moreover, ¹H NMR signals that corresponded to the methylene and methine units positioned α to the ether repeat units (δ 3.0–3.7 ppm, CDCl₃) in the starting material were not observed, consistent with a high conversion to the corresponding poly(propenyl ester) product. Similar to the results described above, weak signals were observed near 3.0 ppm, which were assigned to a ketone by-product and calculated to be present in *ca.* 5 mol%. Analogous results were obtained when poly(ethyl propenyl ether) (PEPE)³⁰ or poly(ethyl isopropenyl ether) (PEIPE) was used as the starting material. Although GPC analysis indicated that chain cleavage occurred during the oxidation reaction (see Table 3), the molecular weights of the PPEs prepared as described above were relatively high when compared to those synthesized using other methodologies.

Modification of poly(tetrahydrofuran) (PTHF)

Aliphatic polyesters with high contents of γ -butyrolactone (γ -BL) repeat units are often difficult to prepare due to the low

Table 3 Oxidative modification of poly(propenyl ether)s

Starting material	Conversion (%)	Selectivity (%)	M_n (kDa)		M_n^a (kDa)	
			Pre-oxidation	D	Post-oxidation	D^a
PBPE ^b	99	94	30.1	2.6	21.8	2.3
PEPE ^c	99	95	35.2	2.5	10.9	2.1
PEIPE ^d	99	>99 ^e	8.9	1.4	7.2	1.6

^a Determined *via* GPC against polystyrene standards (THF, 35 °C).

^b [Repeat unit]₀ = 0.2 M, BuOAc/H₂O (1 : 1 v/v), 4 equiv. NaIO₄ with respect to the polymer repeat unit, 60 °C, 16 h. ^c [Repeat unit]₀ = 0.4 M, BuOAc/H₂O (1 : 1 v/v), 2 equiv. NaBrO₃ with respect to the polymer repeat unit, 60 °C, 16 h. ^d [Repeat unit]₀ = 0.5 M, EtOAc/H₂O (1 : 1 v/v), 3 equiv. NaIO₄ with respect to the polymer repeat unit, r.t., 18 h. ^e Ketone formation was not observed *via* ¹H NMR spectroscopy.

polymerizability of the respective monomer.^{31,32} Indeed, the homopolymerization γ -BL typically requires high pressures. When γ -BL is copolymerized with other cyclic esters or ethers, the yield and molecular weight of the respective copolymer often decreases sharply with increasing feed ratio of γ -BL; the upper limit appears to be approximately 50%.³³

Using 1 wt% of RuO₂·xH₂O as the catalyst and 1.1 equiv. of NaBrO₃ with respect to the repeat unit of the polymeric starting material, relatively low and high molecular weight samples of poly(tetrahydrofuran) (PTHF) were independently oxidized to their corresponding poly(butyric ester)s. As shown in Table 4, GPC analyses of the products revealed that a significant reduction in molecular weight as well as the D had occurred over the course of the corresponding oxidation reactions. The use of buffered solutions or lower reaction temperatures did not significantly suppress the bond cleavage. Nonetheless, assuming that PTHF was randomly oxidized, three types of monomeric units are possible: (1) γ -BL, (2) 1,4-butanediol (BD) and/or (3) succinic acid (SA). All three types of units were identified in the aforementioned polymeric products *via* ¹H NMR spectroscopy (see Fig. 4) and calculated to be present in a ratio of 54 : 27 : 19 (BL : BD : SA) for low molecular weight product and 54 : 23 : 23 for the product of relatively high molecular weight. The compositions of the modified polymers were further confirmed upon saponification and subsequent spectroscopic analyses of the product mixtures (see the ESI† for additional details).³⁴

Table 4 Comparison of poly(tetrahydrofuran) and its oxidized derivative

Polymer	M_n^a (kDa)		M_n (kDa)		γ -BL% ^b (mol%)
	Pre-oxidation	D^a	Post-oxidation	D	
LMW-PTHF	3.2	2.3	1.2	1.7	54
HMW-PTHF	146.3	2.0	14.5	1.7	54

^a Determined *via* GPC against polystyrene standards (THF, 35 °C).

^b The composition of the modified PTHF was determined by ¹H NMR spectroscopy using formula: γ -BL% = $2I_{2.4 \text{ ppm}} / (2I_{2.4 \text{ ppm}} + I_{1.7 \text{ ppm}} + I_{2.6 \text{ ppm}}) \times 100\%$.

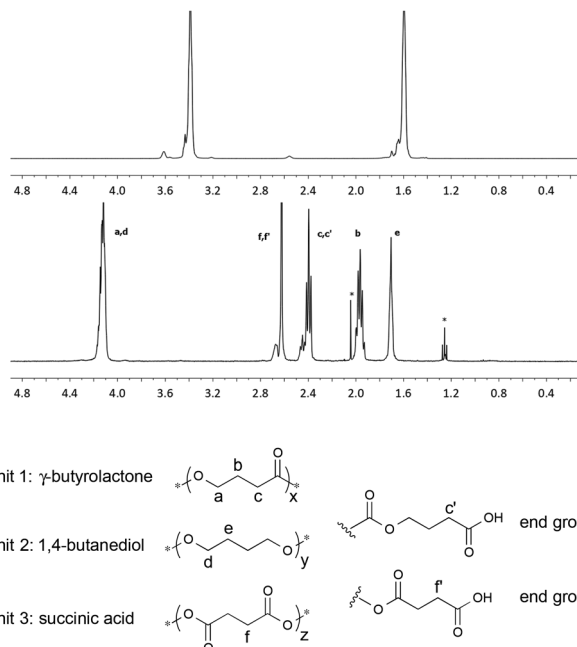


Fig. 4 ¹H NMR spectra (CDCl₃, 400 MHz) of PTHF (top) (Table 4, entry 1), an oxidized derivative of PTHF (middle) (Table 4, entry 1), and the corresponding structural analysis (bottom).

Conclusion

We have demonstrated that the Ru-catalyzed C–H oxidation of poly(vinyl ether)s may be utilized to access poly(vinyl ester)s in high yield and selectivity. In addition, the methodology provided access to high molecular weight poly(propenyl ester)s which, to the best of our knowledge, are the first examples of their kind. We have also shown that polyesters with a relatively high content of γ -butyrolactone may be synthesized *via* the oxidation of poly(tetrahydrofuran). A limitation to the method described is inadvertent C–O cleavage/oxidation, although this side reaction may be minimized through judicious selection of the solvent. By finely controlling the quantities of oxidants and/or the reaction conditions employed, it should now be possible to synthesize a broad range of poly(vinyl ester)s and poly(propenyl ester)s as well as their ketone containing copolymers, effectively overcoming many of the limitations associated with existing (co)polymerization methodologies.

Experimental

Instrumentation

¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury 400, Varian Inova 500 or Varian DirectDrive 600 spectrometer and internally referenced to the residual solvent (CDCl₃: ¹H, δ = 7.26; ¹³C, δ = 77.2, D₂O: ¹H, δ = 4.80). IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with iD3 ATR accessory (Ge). Intrinsic viscosity ($[\eta]$) was measured using an Ubbelohde type visc-

ometer in benzene at 30 °C. Gel permeation chromatography (GPC) was performed in THF on a Viscotek 2001 GPC max system using a set of two columns (Viscotek MBHMW-3078 and Viscotek MBMMW-3078) thermostatted to 35 °C and operated at a flow rate of 1.0 mL min⁻¹. The GPC system was outfitted with an RI detector (Viscotek 3580) and a light scattering/viscometer dual detector (Viscotek 270), and calibration was carried out using narrow polystyrene standards purchased from Scientific Polymer Products. Trace metal analyses were performed on an Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS). Prior to each analysis, samples (~5 mg) were digested with a mixture of 0.5 mL of HNO₃ (15.8 N) and 0.1 mL of 30% H₂O₂ overnight, and then diluted to a total volume of 30 mL with deionized water followed by centrifugation.

Materials

Ethyl propenyl ether (98%, *cis/trans* = 2 : 1) as well as all other vinyl ethers were purchased from commercial sources, washed with aqueous KOH and distilled twice from CaH₂ before polymerization. Butyl propenyl ether (*cis/trans* = 3 : 2) was prepared *via* the Ru-catalyzed isomerization of butyl allyl ether by following a procedure reported in the literature.³⁵ Poly(ethyl vinyl ether) and poly(methyl vinyl ether) were purchased from Sigma Aldrich; poly(tetrahydrofuran) was purchased from Scientific Polymer Products. All oxidizing agents and Ru catalysts were purchased from commercial sources and used as received. All solvents used for polymerization were dried and degassed using a Vacuum Atmospheres Company solvent purification system and stored over molecular sieves in a nitrogen-filled glove box.

Cationic polymerization of butyl propenyl ether and ethyl propenyl ether

The polymerization reaction was performed under an atmosphere of dry nitrogen by adding 0.5–1 mol% BF₃·Et₂O to a mixture of the butyl propenyl ether and toluene (1 : 10 v/v) in a Schlenk flask at –78 °C. After stirring the mixture at –78 °C for 4 h, the reaction was quenched with cold methanol containing 5% (v/v) of aqueous ammonium hydroxide. The resulting mixture was then warmed to ambient temperature and poured into excess methanol. The precipitated solids were collected by filtration, washed with methanol and then dried under high vacuum to afford poly(butyl propenyl ether) as a white solid (1.32 g, 83% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.97–2.94 (m, 3H), 2.29–1.67 (m, 1H), 1.66–1.24 (m, 4H), 1.18–0.66 (m, 6H). *M*_n = 30.1 kDa, *D* = 2.6. Using a similar procedure, poly(ethyl propenyl ether) was obtained as a white solid (2.24 g, 96% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.91–2.97 (m, 3H), 2.26–1.62 (m, 1H), 1.23–1.06 (s, 3H), 1.06–0.67 (m, 3H). *M*_n = 35.2 kDa, *D* = 2.5.

Cationic polymerization of ethyl isopropenyl ether

The polymerization reaction was performed under an atmosphere of dry nitrogen and initiated by adding 0.5 mL of a solution of iodine ([I₂]₀ = 0.05 M in Et₂O) to a mixture of 3 mL of

monomer and 30 mL of toluene in a Schlenk flask at –78 °C.³⁶ After stirring the mixture at –78 °C for 4 h, the reaction was quenched with cold methanol containing 5% (v/v) of aqueous ammonium hydroxide. The resulting mixture was then warmed to ambient temperature and poured into excess methanol. The precipitated solids were collected by filtration, washed with methanol and then dried under high vacuum to afford the desired polymer as a white solid (0.84 g, 37% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.58–3.17 (s, 2H), 2.05–1.64 (m, 2H), 1.53–1.21 (m, 3H), 1.22–0.99 (m, 3H). *M*_n = 8.9 kDa, *D* = 1.4.

Cationic polymerization of butyl vinyl ether

Using a modified procedure,³⁷ 3 mL of BVE was dissolved in 30 mL of hexane in a Schlenk flask at 0 °C. The resulting mixture was charged with 0.05 mL of a HCl solution (1 M in Et₂O) and then stirred for 15 min. The polymerization was initiated by adding 0.020 mL of a ZnCl₂ solution (1.0 M in Et₂O) to the mixture, and then stirred for 5 h at 0 °C. The polymerization was quenched using 1 mL of cold methanol containing 5% (v/v) of aqueous ammonium hydroxide. After the resulting mixture was washed with 10% aqueous sodium thiosulfate followed by water, it was evaporated under reduced pressure, which afforded the desired product as a colorless semisolid (2.0 g, 87% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.73–3.23 (m, 3H), 1.92–1.26 (m, 6H), 0.97–0.82 (t, 3H). *M*_n = 21.9 kDa, *D* = 1.3.

Cationic polymerization of isobutyl vinyl ether

Using a modified procedure,³⁸ 1 mL of IBVE was dissolved in 10 mL of toluene in a Schlenk flask at 0 °C for 10 min. The mixture was then charged with 0.1 mL of an initiator (IBVE-CF₃COOH adduct) solution which was freshly prepared by mixing 0.2 mL of IBVE and 0.1 mL of CF₃COOH in 3 mL CCl₄ at 0 °C for 15 min. The polymerization was initiated by adding 0.05 mL of a ZnCl₂ solution (1.0 M in Et₂O) to the aforementioned mixture and stirred for 12 h at 0 °C. The polymerization was quenched with 1 mL of cold methanol containing 5% (v/v) of aqueous ammonium hydroxide. The quenched mixture was washed with 10% of aqueous sodium thiosulfate followed by water and then evaporated under reduced pressure to afford the desired product as a pale yellow semisolid (0.66 g, 86% yield). ¹H NMR (400 MHz, CDCl₃): δ 3.70–2.98 (m, 3H), 1.95–1.23 (m, 3H), 1.08–0.68 (d, 6H). *M*_n = 10.4 kDa, *D* = 1.4.

Cationic ring opening polymerization of tetrahydrofuran (THF)

In a dry box, 1 mL of BF₃·Et₂O was added to 10 mL of dry THF and the mixture was stirred at ambient temperature for 48 h. After pouring the resulting viscous solution into 200 mL of deionized water, the precipitated solids were collected and purified twice by dissolution/precipitation with THF/water. The final product was obtained as a white solid (0.8 g). ¹H NMR (400 MHz, CDCl₃): δ 3.50–3.38 (s, 4H), 1.70–1.50 (s, 4H) *M*_n = 146.3 kDa, *D* = 2.0.

General post-polymerization oxidation procedure

In a reaction vessel, 0.1 mmol of a poly(vinyl ether) was dissolved in 1 mL of EtOAc and then mixed with 1 mL of an aqueous solution containing an oxidant (0.4 M). Afterward, mixture was charged with 1 mg $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ or $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, and then stirred at room temperature for 16 h. Upon settling, two layers were observed: the bottom layer was removed with a pipette and the faintly yellow colored top layer was diluted with 4 mL EtOAc and then quickly charged with 2 mL of freshly prepared 10% aqueous sodium hydrosulfite. The resulting mixture was then stirred and the bottom layer was removed. The organic layer was washed with brine, dried with anhydrous sodium sulfate and then evaporated to dryness to afford corresponding poly(vinyl ester). Larger scale reactions (>1 mmol polymer) were successfully performed at concentrations up to 0.4 M with catalyst loadings as low as 1 wt%.

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