A General Polymerization Method Using Hydroalkoxylation and Hydrocarboxylation Reactions Catalyzed by Triflic Acid

Robert T. Mathers,*,† Carl LeBlond,‡ Krishnan Damodaran,§ Douglas I. Kushner,† and Valerie A. Schram†

Department of Chemistry, Pennsylvania State University, New Kensington, Pennsylvania 15068; Department of Chemistry, Indiana University of Pennsylvania, Indiana, Pennsylvania 15705; and Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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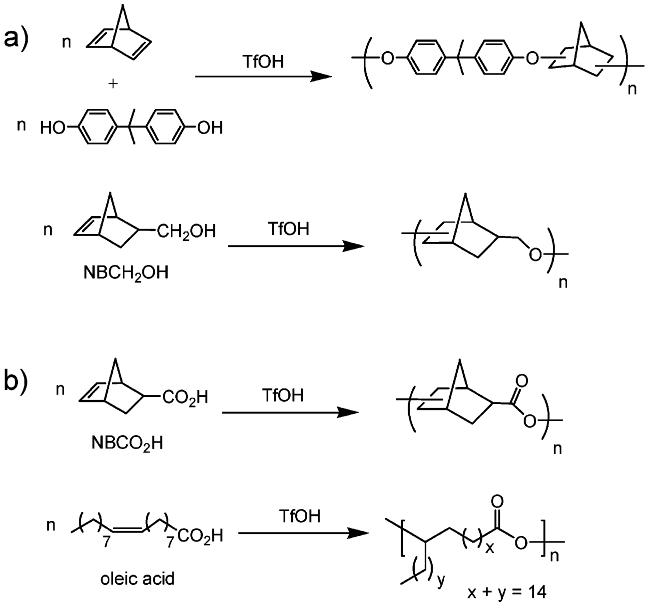
Polyesters and polyethers represent two very well-known classes of polymers. The wide-ranging capability of these polymers continues to expand and can be found in biomedical, optical, and nanotechnology applications.[1,2] Incorporation of bicyclic monomers benefits many of these applications by modifying the crystallinity and glass transition temperature.[3,4] Bicyclic monomers can also improve the refractive index and optical transparency of polymers. The ability to adjust these parameters can improve the physical properties of polymers and increase their performance.

The pursuit of polymerization methods that utilize green chemistry principles has become increasingly relevant.[5,6] An important aspect of green chemistry reduces the number of synthetic steps and uses catalytic processes to maximize the efficiency. Many polyester and polyether synthesis procedures involve the catalytic ring-opening of cyclic monomers.[7,8] A catalytic mechanism can offer several advantages over nucleophilic substitution reactions in terms of efficiency and maximizing the percentage of atoms in a monomer which become incorporated into the polymer.

This communication describes the first polymerization method using hydroalkoxylation and hydrocarboxylation reactions. Recently, these catalytic reactions were reported for the synthesis of cyclic ethers and esters.[9−12] Our strategy polymerizes alkenes with polar functionalities, such as alcohols and carboxylic acids. The combination of Bronsted acid catalysis with readily available monomers eliminates the need for metal catalysts and multiple synthetic steps. Utilizing nonmetal catalysts avoids removal of the metal for biomedical and electronic applications.[13,14]

Since alkenes, alcohols, and carboxylic acids are prevalent functional groups, many polymerization possibilities exist. As shown in Scheme 1, several initial prospects have been examined. Most of the polymerizations in Table 1 were conducted under neat conditions without stringent experimental conditions. The neat polymerization conditions were chosen to reduce the formation of cyclic oligomers and eliminate excess chemical waste. The polymerization of A−B monomers, such as 5-norbornene-2-carboxylic acid ($NBCO_2H$), 5-norbornene-2-methanol ($NBCH_2OH$), and oleic acid, was compared with the copolymerization of A_2 and B_2 monomers. Both methods produced monomodal polymers that were soluble in organic solvents, such as tetrahydrofuran and toluene. The reactivity of functional groups with norbornene alkenes in Table 1 decreased as follows: $-CO_2H$ > phenol > aliphatic −OH.

Scheme 1. Polymerizations Using (a) Hydroalkoxylation and (b) Hydrocarboxylation Reactions Catalyzed with Triflic Acid (TfOH) (1−2 mol %)



The hydroalkoxylation and hydrocarboxylation reactions were catalyzed by trifluoromethanesulfonic or triflic acid (TfOH). TfOH is a Bronsted acid that exhibits good thermal stability and does not act as a sulfonating agent.[15] Compared to TfOH, polymerizations with H_2SO_4 gave very low conversions and did not result in the formation of polymer. Although this seems surprising, the Hammett acidity value for TfOH ($H_0 = -14.2$) is much stronger than many acids, including H_2SO_4 ($H_0 = -11.9$), HNO_3 ($H_0 = -6.3$), and HF ($H_0 = -11$).[16−18] In fact, using 1−2 mol % TfOH is often optimal, and larger catalyst loadings can adversely affect functional groups or cause decomposition of olefins.[9] To determine whether the polymerization was acid catalyzed, entry 1 was modified by adding 2,6-di-*tert*-butylpyridine (DTBP, 2 mol %). DTBP is a bulky base that scavenges acidic protons.[19] After 24 h at 70 °C, no polymer was detected by gel permeation chromatography (GPC). Additionally, hydroalkoxylation reactions in entry 1 were not observed when TfOH was substituted with sodium triflate (NaOTf). On the basis of these control experiments and the ability of TfOH to promote electrophilic addition to 1,1-diphenylethylene[20] and isobutylene,[21] ether and ester formation probably begins with a protonation step.[22]

The conversion, weight-average (M_w) molecular weight and intrinsic viscosity ($[\eta]$) data increased with increasing time (0.5−48 h) and temperature (25−70 °C). The conversions were based on the polymer and monomer peak areas as measured by GPC using a differential refractometer. Although several M_w values in Table 1 were low, the results agree with the expectations for a step-growth polymerization. The weight-average degree of polymerization (X_w) resulting from step-growth kinetics can be calculated on the basis of conversion (p) using a well-known equation: $X_w = (1 + p)/(1 - p)$.[23] For example, a calculated value of X_w for entry 8 corresponds to an M_w value of 2630 g/mol. This value agrees

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* To whom correspondence should be addressed. E-mail: rtm11@psu.edu.
† Pennsylvania State University.
‡ Indiana University of Pennsylvania.
§ University of Pittsburgh.

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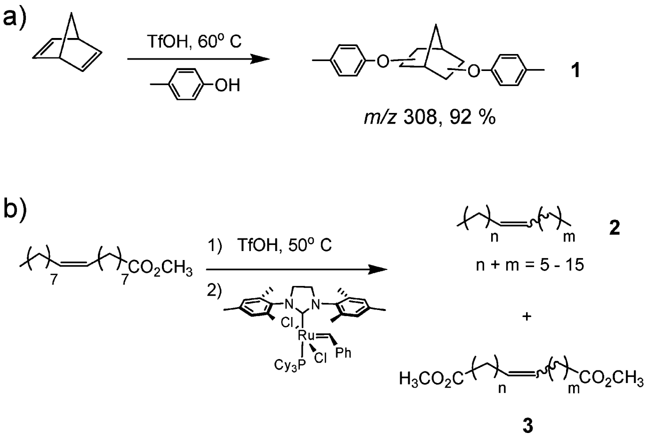
Table 1. Polymerization Data for the Hydroalkoxylation and Hydrocarboxylation Reactions[a]

entry	monomer(s)[b]	catalyst[c]	[monomer]/ [catalyst]	solvent	temp (°C)	time (h)	conv (%)	M_w (g/mol)[d]	M_w/M_n[d]	[η] (dL/g)[e]
1	BPA/NBD	TfOH	100	1,4-dioxane	70	0.5	48	1800	1.2	0.038
2	BPA/NBD	TfOH	50	1,4-dioxane	60	2	82	3600	1.6	0.068
3	BPA/NBD	H_2SO_4	50	1,4-dioxane	70	2	<3	*f*	*f*	
4	$NBCO_2H$	TfOH	50	neat	25	24	92	3600	1.2	0.059
5	$NBCO_2H$	TfOH	100	neat	70	0.5	97	9100	1.4	0.102
6	$NBCO_2H$	H_2SO_4	50	neat	70	0.5	8	*f*	*f*	0.024
7	$NBCH_2OH$	TfOH	100	neat	70	4	47	800	1.2	0.019
8	$NBCH_2OH$	TfOH	100	neat	70	24	91	3000	1.8	0.034
9	oleic acid	TfOH	50	neat	25	24	10	*f*	*f*	0.026
10	oleic acid	TfOH	50	neat	70	24	40	1400	1.2	0.031
11	oleic acid	TfOH	50	neat	70	48	68	2600	1.3	0.040

[a] Polymerization conditions: monomer (1−2 mmol), catalyst (1−2 mol %), and solvent (0.2 mL). [b] BPA = bisphenol A; NBD = norbornadiene; $NBCO_2H$ = 5-norbornene-2-carboxylic acid; $NBCH_2OH$ = 5-norbornene-2-methanol. [c] TfOH = triflic acid. [d] Weight-average (M_w) molecular weights and molecular weight distributions (M_w/M_n) were calculated by light scattering in tetrahydrofuran (THF). [e] Intrinsic viscosity ([η]) was measured in THF at 35 °C using a gel-permeation chromatography system with a viscometer detector. [f] Below instrument detection level.

Scheme 2. Model Reactions of (a) Norbornadiene (NBD) with *p*-Cresol and (b) Methyl Oleate in the Presence of Grubbs Catalyst



reasonably well with the M_w value of 3000 g/mol measured by GPC.

FTIR spectroscopy identified the formation of ether and ester functional groups for the polymers in Table 1. During the copolymerization of bisphenol A (BPA) and norbornadiene (NBD) and the polymerization of $NBCH_2OH$, new ether absorbances were detected at 1047 and 1079 cm^{-1}, respectively. These polymerizations and the model reaction in Scheme 2a were accompanied by a substantial decrease in alkene and alcohol absorbances. After the polymerization of $NBCO_2H$, the carboxylic acid absorbance at 1705 cm^{-1} was replaced with an ester absorbance at 1728 cm^{-1}.[24] Oleic acid polymerizations with TfOH gave an ester absorbance at 1734 cm^{-1}. FTIR analysis of the reaction of norbornene and benzoic acid in the presence of TfOH also resulted in an ester absorbance at 1712 cm^{-1}, but no oligomerization or polymer was detected by GPC. This control experiment indicates that the addition of the carboxylic acid to the alkene is faster than the cationic polymerization of norbornene.

^1H and ^{13}C NMR analysis detected ether and ester resonances resulting from the polymerizations in Scheme 1. In Figure 1, a decrease in the alkene resonances (δ 5.8−6.4 ppm) suggests the carboxylic acid reacts with an alkene to generate an ester (δ 4.6 ppm). After the polymerization, the alkene end groups were detected by ^1H NMR. A comparison of M_n values from NMR end-group analysis (M_n = 7000 g/mol) and GPC (M_n = 6500 g/mol) may indicate a small fraction of cyclic oligomers. Characterization of the polyesters by ^{13}C NMR detected several carbonyl resonances (δ 165−175 ppm). On the basis of ^{13}C NMR calculations, the microstructure for entry 4 and 5 contains *exo/exo*, *exo/endo*, *endo/exo*, and *endo/endo* monomer sequences.[25] For the polyether polymerizations, several ether resonances were detected by ^1H NMR (δ 4.1−4.7 ppm).

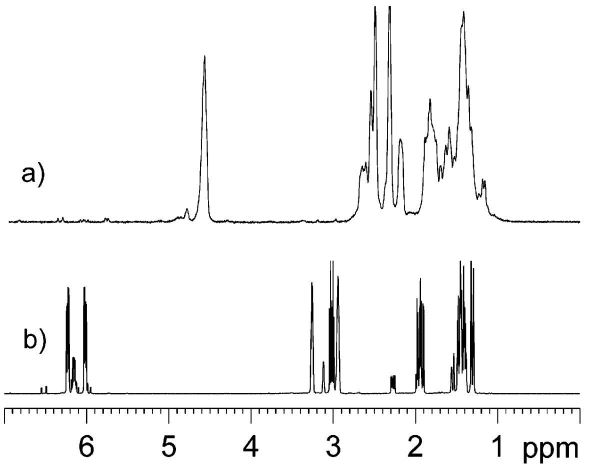


Figure 1. ^1H NMR spectra (300 MHz, $CDCl_3$) for (a) the product resulting from the polymerization of 5-norbornene-2-carboxylic acid ($NBCO_2H$) with triflic acid (1 mol %) after 0.5 h at 70 °C and (b) $NBCO_2H$.

The polyether synthesis was optimized and characterized with model reactions to examine the possibility of electrophilic aromatic substitution (EAS) or cationic polymerizations. The possibility of EAS products was confirmed by reacting a protected phenol and an alkene with catalytic amounts of TfOH. In the case of anisole and 1-hexene, alkylation was detected by GC/MS (>90%). Although NBD is known to cationically polymerize with Lewis acids,[26] the reaction depicted in Scheme 2a did not result in formation of polymer as detected by GPC. GC/MS analysis of **1** (*m/z* 308) detected the addition of two phenols to NBD. On the basis of this model reaction, the amount of EAS and cationic polymerization products appears to be <10%. Depending on the order of addition of the NBD and BPA to TfOH, the copolymerization of aromatic monomers with NBD could be more prone to undesirable reactions than aliphatic monomers, such as $NBCO_2H$. These side reactions are less likely than hydroalkoxylation reactions under concentrated phenol conditions (~4−5 M), low catalyst loadings (1−2 mol %), and reasonable temperatures (i.e., 50−60 °C) but may increase at high conversions. As a result, we choose to limit the polymerization time and conversion in entry 2.

A comparison of acyclic and cyclic alkenes was investigated in the context of alkene reactivity with carboxylic acids vs alkene migration and isomerization. In Table 1, the cyclic alkene in norbornene was compared with the acyclic *cis*-alkene in oleic acid. The polymerization activity for $NBCO_2H$ was much higher than oleic acid and resulted in higher conversions and M_w values. Consequently, strained cyclic alkenes appear more reactive than acyclic alkenes. The formation of cyclic oligomers during the polymerization of neat oleic acid may partially explain the lower M_w values. For entry 11, GPC detected a cyclic product (4%) at higher elution volume than oleic acid. To further understand the differences between $NBCO_2H$ and oleic acid, another control experiment was conducted. Using a methyl ester of oleic acid in Scheme 2b, alkene migration and isomerization were examined without the possibility of hydrocarboxylation reactions. After the reaction of TfOH with methyl oleate, FTIR spectroscopy detected the isomerization of *cis*-alkenes (723 cm^{-1}) to *trans*-alkenes (968 cm^{-1}). Since alkene isomerization could occur without migration, the experiment in Scheme 2b was designed so that metathesis reactions could estimate the amount of alkene migration using GC/MS. In the absence of alkene migration, the metathesis of methyl oleate would result in *cis* and *trans* isomers of two products ($n = 7$, $m = 7$). However, Scheme 2b resulted in a distribution of metathesis products ($n + m = 5-15$). The resulting distribution of **2** ranging from decene ($n + m = 6$) to nonadecene ($n + m = 15$) indicates that alkenes can migrate one to six carbon atoms. When the temperature for the reaction of TfOH and methyl oleate was increased from 25 to 50 °C, the amount of alkene migration also increased from 1% to 40%. Although the Grubbs catalyst can cause migration of terminal alkenes,[27] a control experiment with methyl oleate and the second generation Grubbs catalyst after 24 h at 50 °C only resulted in two products (~95% yield) corresponding to **2** ($n = 7$, $m = 7$) and **3** ($n = 7$, $m = 7$). In view of the fact that the ruthenium hydride responsible for isomerization[27] would probably favor terminal alkenes over disubstituted alkenes, the methodology in Scheme 2b was preferred over the reaction of methyl oleate with ethylene to produce terminal alkenes. Since Scheme 2b suggests a propensity for alkene migration under Bronsted acid conditions, polymerizations of oleic acid with TfOH are less controlled than $NBCO_2H$.

The polymerization of oleic acid with metal triflates, such as scandium triflate [$Sc(OTf)_3$] and silver triflate (AgOTf), was undertaken to compare Lewis acids with TfOH. Initially, we were intrigued with the possibility of recycling metal triflates. However, our results and the observations of others[9] indicate that metal triflates may release protic acids. First, reacting neat oleic acid with $Sc(OTf)_3$ at 100 °C for 24 h resulted in hydrocarboxylation reactions, but these reactions did not occur in the presence of DTBP. Since the *tert*-butyl groups on DTBP prevent a reaction with BF_3,[19] the pyridine base should have limited interaction with larger Lewis acids and probably scavenges protic acids. Second, undertaking the reaction shown in Scheme 2b with $Sc(OTf)_3$ instead of TfOH resulted in similar amounts of alkene migration. Third, the light-sensitive AgOTf catalyzes hydrocarboxylation reactions but decomposes to give an observable silver film. Repeating entry 10 with AgOTf in an amber vial gave no detectable amounts of conversion.

A preliminary examination of the thermal properties was conducted by DSC. The T_g value for the product resulting from the polymerization of $NBCO_2H$ (entry 5, $T_g = 119$ °C) was higher than the polyether sample in entry 2 ($T_g = 33$ °C). Polyethers usually have more flexible polymer chains and lower T_g values than polyesters.[28] Initially, the polymerization of neat $NBCO_2H$ was a liquid, but after 0.5 h at 70 °C the reaction solidified. Because the polymerization temperature is below the T_g, the maximum M_w value for the polymerization of neat $NBCO_2H$ may be limited by diffusion of monomer and polymer. A further investigation is underway to determine the stability of ester linkages at polymerization temperatures above the T_g.

In summary, hydroalkoxylation and hydrocarboxylation reactions represent a new method for polymerizing monomers containing alkenes and polar functionalities, such as alcohols and carboxylic acids. This general method can incorporate bicyclic monomers and polymerize renewable resources, such as oleic acid. The molecular weight and conversion depend on the choice of alkene and polar functionality.

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Supporting Information Available: FTIR, GPC, ^1H NMR, and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Further investigation into the mechanism of this polymerization is forthcoming.

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(24) As measured by ^1H NMR, the commercially available $NBCO_2H$ is obtained as a mixture of *endo* (75 %) and *exo* (25 %) monomers. During the polymerization of $NBCO_2H$, the *endo*-$NBCO_2H$ can undergo an intramolecular reaction to produce a lactone (FTIR 1774 cm^{-1}). Precipitating the polymer into methanol allowed purification of the polymer and removal of the intramolecular products.

(25) In addition to the possible *exo* and *endo* sequences, the microstructure for the polymerization of 5-norbornene-2-carboxylic acid also contains 2,5- and 2,6-linkages. The estimated ratio of 2,5-*exo*/*exo* and 2,6-*exo*/*exo*:2,5-*endo*/*exo* and 2,5-*exo*/*endo*:2,6-*endo*/*exo* and 2,6-*exo*/*endo*:2,6-*endo*/*endo* and 2,5-*endo*/*endo* was 1.0:0.95:0.3:0.04. See Supporting Information for more details.

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