

# Oxa-Michael Addition Polymerization of Acrylates Catalyzed by N-Heterocyclic Carbenes

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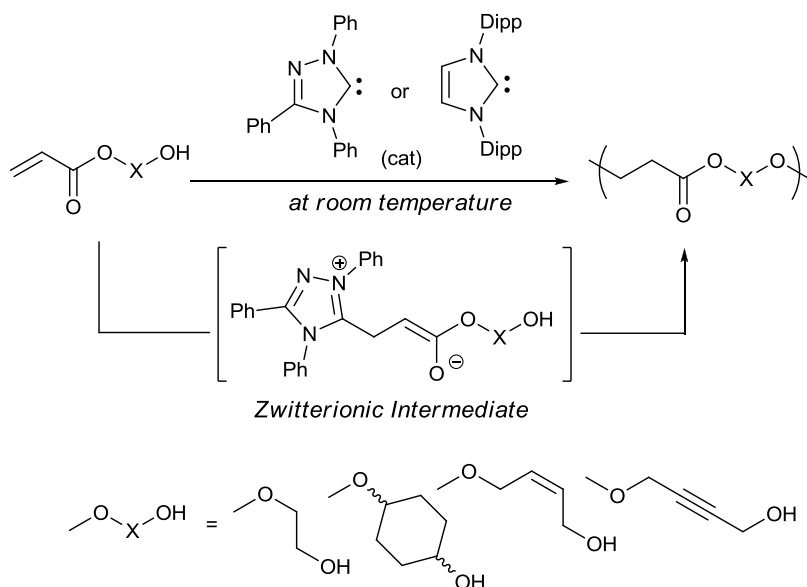
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N-Heterocyclic carbenes (NHCs) smoothly catalyze the oxa-Michael addition polymerization of hydroxyl functionalized acrylate monomers at room temperature via a zwitterionic intermediate.



## Abstract

N-Heterocyclic carbenes (NHCs) catalyze the oxa-Michael addition polymerization of hydroxyl functionalized acrylate monomers. This polymerization smoothly proceeded at room temperature to produce poly(ester-ether)s, which include new polymers having alicyclic, alkene, and alkyne groups in the main chain. The post polymerization modification of the alkene-functionalized polymer using thiol-ene “click” chemistry is demonstrated. The structure of poly(2-hydroxyethyl acrylate) was analyzed in detail by NMR and ESI-MS analyses and methanolysis, thus allowing estimation the frequency of the transesterification. The NHC catalyst was covalently linked to the C terminal of the polymer chain, indicating that the NHC acts as a Lewis base to generate the zwitterionic intermediate without directly activating the hydroxyl groups of the monomers.

## Introduction

Aza- or oxa-Michael addition polymerizations, or hydrogen transfer polymerizations, of NH or OH functionalized vinyl monomers are useful procedures to synthesize polyamide and poly(ether-ester)s. Saegusa et al. reported the first polymerization of hydroxyalkyl acrylates catalyzed by several bases, such as *t*-BuLi, NaH, and Ph<sub>3</sub>P, to produce polymers with molecular weights of 1000-2000.<sup>1</sup> Since then, such polymers have been used as inclusion complexes with amylose,<sup>2</sup> and the related hyperbranched polymers have been synthesized from AB<sub>2</sub> monomers.<sup>3</sup> Since these polymerizations<sup>4</sup> are usually carried out at high temperatures such as 80 °C, the resulting polymers may, in some cases, become insoluble gels probably through thermally-induced vinyl polymerization and transesterification. To selectively obtain poly(ester-ether)s, therefore, highly active catalytic systems need to be developed for the polymerizations at ambient temperatures. However, since the initial report, the polymerization catalyst, scope of monomers, and detailed polymer structure have not been well investigated. In particular, the selected catalysts are limited to conventional types developed by Saegusa et al.

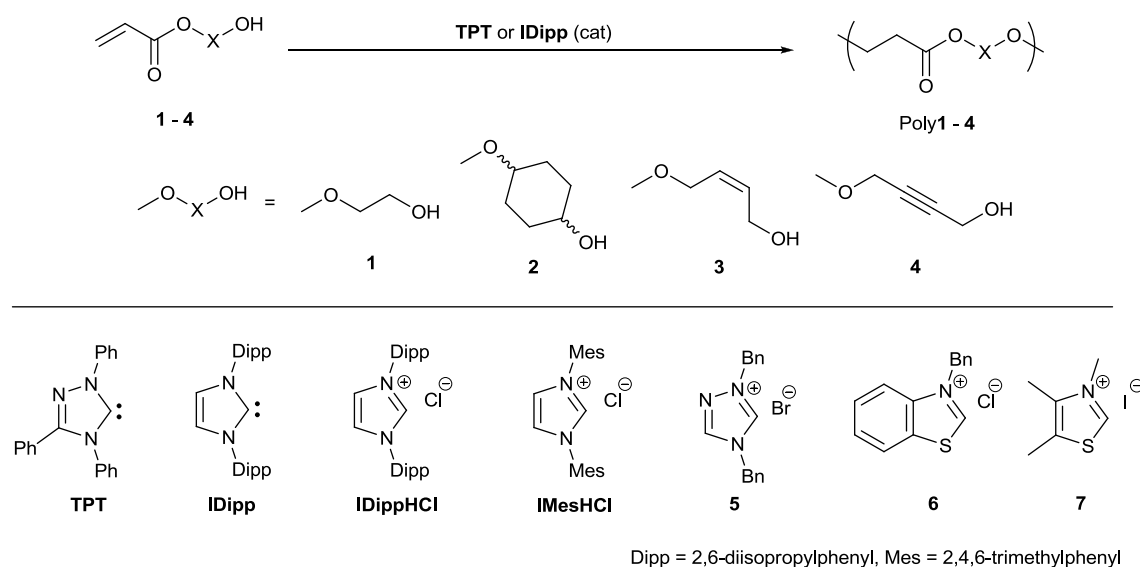
N-Heterocyclic carbenes<sup>5</sup> (NHCs) are interesting classes of Lewis bases and have been widely used as both ligands of metal complexes and organocatalysts. In view of the fact that a number of new reactions has been developed using NHC catalysts for more than a decade,<sup>6</sup> the discovery of new polymerization systems based on such organocatalysis is highly expected. Indeed, it was previously reported that they successfully catalyzed a variety of polymerizations,<sup>7</sup> including ring-opening,<sup>8</sup> vinyl,<sup>9</sup> and step-growth polymerizations,<sup>10</sup> the latter of which includes transesterification<sup>10a, 10b</sup> and dehydration polycondensations,<sup>10c</sup> benzoin polyaddition,<sup>10d</sup> and polyaddition for polyurethanes.<sup>10e-10g</sup> and epoxy/anhydride resins.<sup>10h</sup> We and others have been investigating the nucleophilic reactions of NHC toward Michael acceptors, such as acrylates and methacrylates, and already developed the catalytic tail-to-tail dimerizations,<sup>11</sup> cyclizations,<sup>12</sup> polymerizations,<sup>13</sup> and other transformations.<sup>14</sup> In addition to these reactions, NHCs have also been reported to catalyze various Michael additions.<sup>15</sup> Scheidt et al.

demonstrated the NHC-catalyzed oxa-Michael addition of  $\alpha,\beta$ -unsaturated ketones, and proposed a mechanism involving the direct activation of alcohols by NHC.<sup>15a</sup> Subsequently, we reported the NHC-catalyzed tandem oxa-Michael addition and dimerization of methacrolein, in which NHC first adds to the substrate followed by deprotonation of the alcohol.<sup>15b</sup> These previous reports indicated that NHCs are effective catalysts for the selective O-C bond forming reactions. We have thus extended this organocatalysis to the field of polymerization chemistry. We now report the oxa-Michael addition polymerization of hydroxyl functionalized acrylates catalyzed by NHCs. The polymer structure was revealed by NMR and ESI-MS analyses, leading us to propose a Lewis base mechanism.

## Results and Discussion

We initially carried out the polymerization of 2-hydroxyethyl acrylate (**1**) by the isolated NHC catalysts, TPT and IDipp, or the NHC precursors, IDippHCl, IMesHCl, **4**, **5**, and **6**, at room temperature (Table 1). Although the precursors with *i*-Pr<sub>2</sub>EtN were ineffective (entries 5-9), TPT and IDipp were active for the polymerization under both the bulk and THF solution conditions to produce the corresponding poly(ester ether) with  $M_n$ s of more than 1000 in moderate yields (entries 1-3). We then used TPT as the catalyst for further survey, as it can be readily isolated from its MeOH adduct. The polymerizations by TPT at 60 and -20 °C produced no product (entries 10 and 11). Since Scheidt et al. reported the Lewis acid additive, LiCl, more efficiently promoted the NHC-catalyzed oxa-Michael addition, we attempted to use such cooperative systems for the polymerization. However, the combination of TPT with Sc(OTf)<sub>3</sub>, Ti(O*i*Pr)<sub>4</sub>, Mg(OTf)<sub>2</sub>, and LiCl, which have been previously used as Lewis acids in cooperative NHC catalyses, were detrimental for the polymerization (entries 12-15). The 20 mol% catalyst loading did not enhance the yield and the molecular weight of the polymer (entry 16). The polymerization proceeded even at a low catalyst loading (2 mol%), though the yield and the molecular weight were low (entry 17).

Table 1. Oxa-Michael addition polymerization of acrylates catalyzed by NHCs for 24 h.

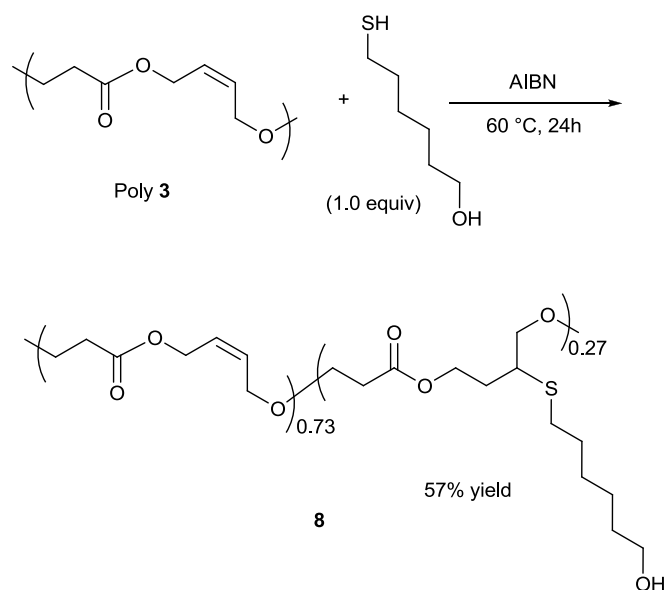


entry	monomer	catalyst		additive <sup>1)</sup>	temp	solvent <sup>2)</sup>	yield <sup>3)</sup> %	$M_n^{4)}$	$M_w/M_n^{4)}$
		type	mol%						
1	1	TPT	10	-	rt	-	56	1500	1.7
2	1	TPT	10	-	rt	THF	38	1200	1.6
3	1	Dipp	10	-	rt	-	64	1800	1.6
4	1	Dipp	10	-	rt	THF	32	540	1.3
5	1	IDippHCl	10	<i>i</i> -Pr <sub>2</sub> EtN	rt	-	0	-	-
6	1	IMesHCl	10	<i>i</i> -Pr <sub>2</sub> EtN	rt	-	0	-	-
7	1	<b>5</b>	10	<i>i</i> -Pr <sub>2</sub> EtN	rt	-	0	-	-
8	1	<b>6</b>	10	<i>i</i> -Pr <sub>2</sub> EtN	rt	-	0	-	-
9	1	<b>7</b>	10	<i>i</i> -Pr <sub>2</sub> EtN	rt	-	0	-	-
10	1	TPT	10	-	-20	-	0	-	-
11	1	TPT	10	-	60	-	0	-	-
12	1	TPT	10	Sc(OTf) <sub>3</sub>	rt	THF	0	-	-
13	1	TPT	10	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	rt	THF	0	-	-
14	1	TPT	10	Mg(OTf) <sub>2</sub>	rt	THF	0	-	-
15	1	TPT	10	LiCl	rt	THF	0	-	-
16	1	TPT	20	-	rt	-	48	1300	2.0
17	1	TPT	2	-	rt	-	trace	750	1.3
18	2	TPT	10	-	rt	-	21	910	1.2
19	3	TPT	10	-	rt	-	59	1900	1.9

20	4	TPT	10	-	rt	-	81	2400	3.8
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- 1) 10 mol%
- 2) entry 2: 0.91 mmol of **1**, 0.1 mL of THF; entry 4: 1.3 mmol of **1**, 0.4 mL of THF; entries 12-15: 1.1 mmol of **1**, 0.4 mL of THF
- 3) Since the NHC catalysts were connected to the chain end of the polymers, the yields were calculated by the weight percentage as follows: polymer/(monomer + NHC)×100.
- 4) Determined by the GPC using THF as the eluent relative to polystyrene standards.

We then applied the optimal conditions (entry 1) for the polymerization of other monomers, 4-hydroxycyclohexyl (**2**), (*Z*)-4-hydroxybut-2-enyl (**3**), and 4-hydroxybut-2-ynyl (**4**) acrylates, the polymerizations of which have not been previously investigated using other catalysts. Although monomer **2** has a bulky and secondary hydroxyl group, the polymerization proceeded to give a new polymer with the alicyclic structure in the main chain (entry 18). Monomers **3** and **4** also underwent the polymerization to produce new unsaturated polymers without side reactions on the alkene and alkyne functional groups (entries 19 and 20). For these polymers, the corresponding repeating monomer units were observed in the ESI-MS spectra. The polymerization of **4** shows a somewhat higher activity, producing a polymer with the  $M_n$  of 2400 and  $M_w/M_n$  of 3.8 in 81% yield. The relatively sharp signals due to the four kinds of methylene protons were observed in the  $^1\text{H}$  NMR spectrum of the poly**4**, indicating that the polymerization proceeded without transesterification in this case. We then demonstrated the post-polymerization modification of Poly**3**. The thiol-ene “click” reaction of poly**3** with 6-mercapto-1-hexanol produced a polymer bearing the polyhydroxy groups in the side chain without any gelation, the structure of which was determined by  $^1\text{H}$  and COSY NMR spectrometries.



Scheme 1. Post-polymerization modification of poly**3** using the thiol-ene “click” reaction.

Transesterification may potentially occur during the oxa-Michael addition polymerization, but the detailed chemical structure of the produced polymers has not been previously revealed. We have thus analyzed Poly**1** by IR, ESI-MS, MS/MS and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , COSY, HMQC, DEPT135) spectroscopies. In the IR spectrum, no stretching vibration due to the hydroxyl group is observed, and all aliphatic  $^{13}\text{C}$  signals of the obtained polymer correspond to the methylene groups, indicating that there is no vinyl addition sequence. The  $^1\text{H}$  NMR spectrum showed resonances of the polymer repeating unit **9** at 2.62, 3.76, and 4.22 ppm, and the corresponding  $^{13}\text{C}$  resonances were observed at 34.8, 66.4, and 63.5 ppm. The relatively small resonances at 3.60 and 4.30 ppm in the  $^1\text{H}$  NMR spectrum and 62.2 and 72.1 ppm in the  $^{13}\text{C}$  NMR are derived from units **10** and **11** (Figure 1).<sup>16</sup> Unit **10** is formed by transesterification between the terminal alcohols, accompanied by elimination of the ethylene glycol. The oxa-Michael addition of ethylene glycol with the terminal vinyl group produces unit **11**. The integral ratio of the  $^{13}\text{C}$  resonances at C-3, 5, and 6 indicated the ratio of **9** : **10** : **11** = 69 : 24 : 7. This ratio was verified by a methanolysis experiment. Poly**1** (entry 1) was treated with MeONa, and the amount of the ethylene glycol

generated only from unit **10** was measured. Consequently, the content of **10** was calculated to be 17%, which agrees with the value determined from the NMR integral ratio.

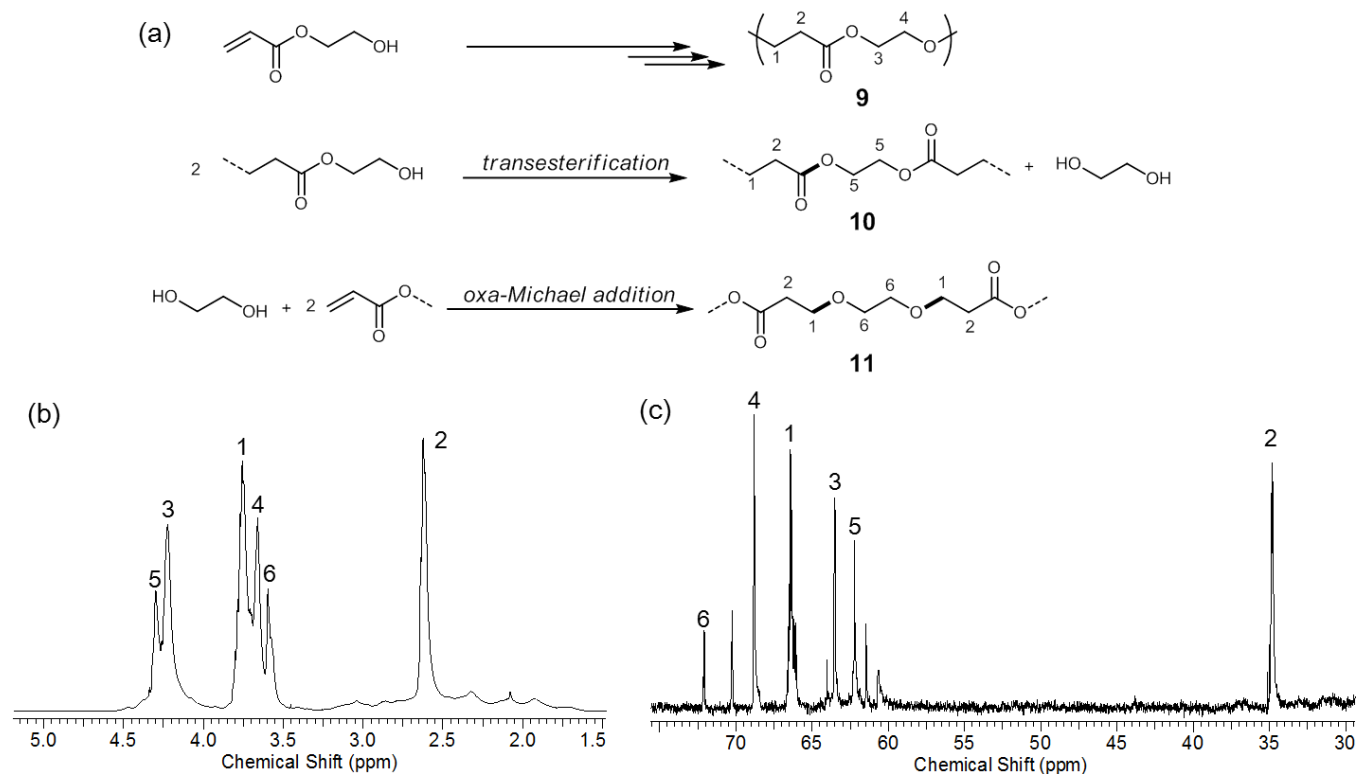


Figure 1. (a) The structure, (b)  $^1\text{H}$ , and (c)  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ ) of poly **1**.

The ESI-MS spectrum also indicated the transesterification. Three series of peaks corresponding to the repeating unit of **1** were observed in the range of less than  $m/z$  of 1500 (Figure 2(a)). Although a series of low-intensity peaks could not be assigned, the two most intensive peaks corresponded to the polymer structure of **A** and **B**, respectively. Series **B** indicated the polymer obtained through the transesterification of series **A**. Since NHC can react with both electron-deficient olefins and alcohols, there are two possible structures with NHC bonded at the C or O terminal. The ESI-MS/MS fragments of the species detected at  $m/z = 530$  showed signals of  $m/z = 486$ ,  $442$ , and  $324$ , and the corresponding structures are depicted in Figure 2(b). It is clear that this fragmentation takes place from the O terminal. We thus determined that the polymer is functionalized with the NHC moiety at the C terminal.



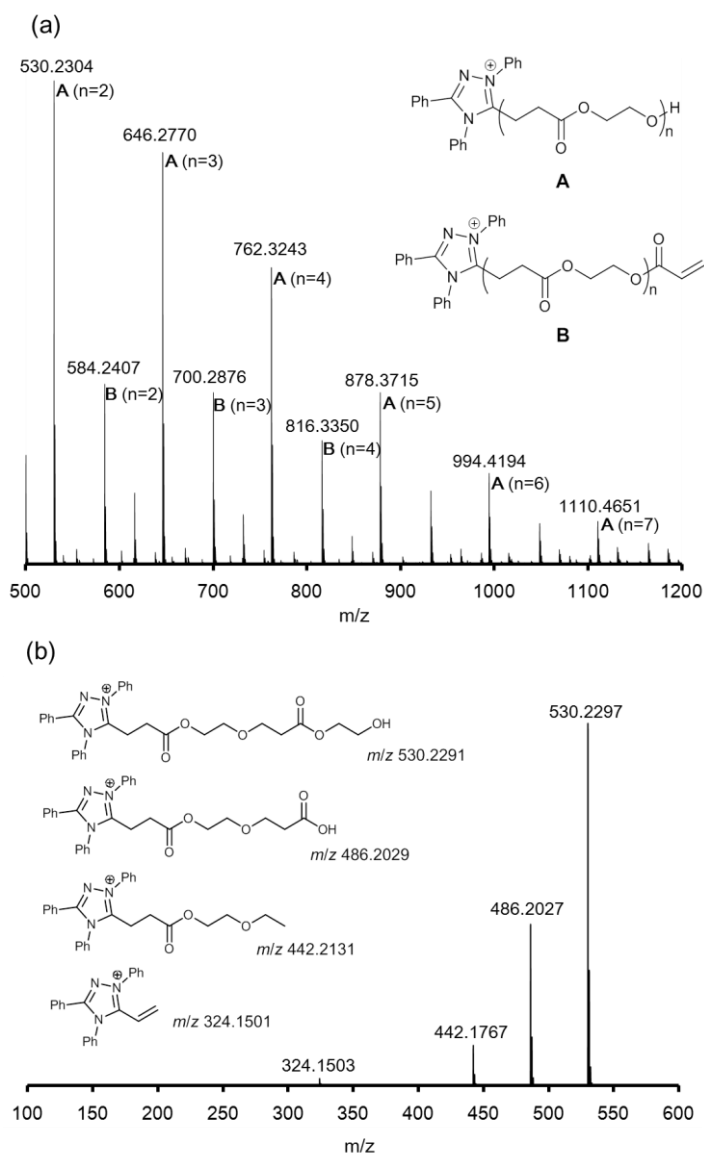


Figure 2 (a) ESI-MS spectrum of poly1, and (b) ESI-MS/MS spectrum of  $m/z = 530$ .

The NHC catalyst can act as a Brønsted or Lewis base. In the present polymerization, the terminal structure elucidated by ESI-MS spectrometry led us to propose a Lewis base mechanism (Figure 3).<sup>18</sup> NHC first reacts with **1** to generate the zwitterionic intermediate (**I**) followed by proton transfer. The resulting alkoxide (**II**) undergoes oxa-Michael addition to form the O-C bond and to generate an enolate (**III**). The subsequent proton transfer produces the poly(ether-ester) and generates the active alkoxide (**II**)

again. It should be noted that this catalytic cycle affords the polymer with the NHC at its C-terminal. The alkoxide **II** often attacks the ester carbonyls in the main chain or monomer **1** resulting in the transesterification. It has been reported that the NHC-catalyzed oxa-Michael addition of less reactive  $\beta$ -substituted Michael acceptors involves the direct activation of the alcohol by NHC.<sup>15a</sup> In contrast, we now postulate that NHC attacks the  $\beta$ -carbons of the acrylates even in the presence of hydroxy groups due to their higher electrophilicity. We and others previously reported the umpolung reactions of methacrylates and acrylates for the tail-to-tail dimerization, in which the zwitterions generated from NHC and the substrates undergo proton transfer to generate quite stable deoxy-Breslow intermediates<sup>17</sup> at relatively high temperatures such as 80 °C.<sup>11</sup> In the present polymerization, however, such an intermediate may not be formed from **I** and **II** at room temperature, thereby resulting in the selective O-C bond forming reaction of **II** with vinyl groups.

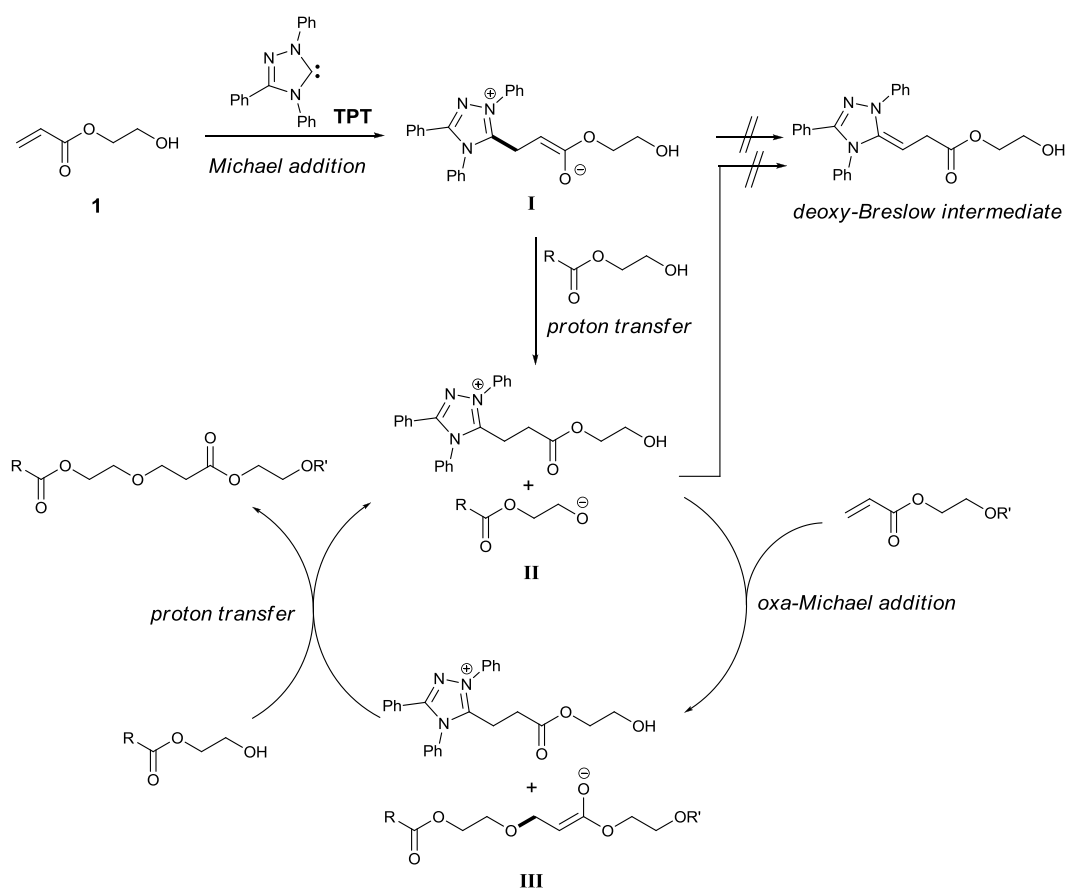


Figure 3. The proposed polymerization mechanism.

## Conclusions

We have described the first example of the Michael addition polymerization catalyzed by NHC. While the polymerizations by conventional catalysts were usually carried out at high temperatures, the NHC-catalyzed polymerizations smoothly proceeded at room temperature to give poly(ester-ether)s with alicyclic, alkene, and alkyne groups in the main chain. The frequency of the transesterification in the polymerization of **1** was revealed by an NMR analysis and methanolysis. The ESI-MS and tandem MS/MS measurements support the fact that the polymer is functionalized with NHC at the C terminal. We thus propose an alcohol activation mechanism in which NHC acts as a Lewis base to generate the zwitterionic intermediate. This efficient O-C bond forming polymerization can provide new opportunities for the synthesis of various polyethers, which have been paid less attention, compared to polyamides, polyesters, and polycarbonates.

## Experimental Section

### Material

Monomer **1** (2-hydroxyethyl acrylate, Nakalai Tesque, Inc.) was dried with CaCl<sub>2</sub>, and then distilled under reduced pressure. TPT<sup>19</sup>, IDipp<sup>20</sup>, IDippHCl<sup>21</sup>, IMesHCl<sup>20</sup>, **5**<sup>21</sup>, **6**<sup>22</sup>, and **7**<sup>23</sup> were synthesized according to the previous reports. *i*-Pr<sub>2</sub>EtN (Wako Pure Chemical Industries, Ltd. >97%) was distilled from CaH<sub>2</sub>. Acryloyl chloride (Tokyo Chem. Industry Co. Ltd., >95%), 1,4-cyclohexanediol (cis- and trans- mixture) (Sigma Aldrich 99%), *cis*-2-butene-1,4-diol (Acros Organics), 2-butyne-1,4-diol (Nakalai Tesque, Inc.), THF (tetrahydrofuran, Kanto Chemical, Co. Inc., dehydrated, stabilizer free), Sc(OTf)<sub>3</sub> (Apollo Scientific Ltd. 99%), Ti(O<sup>*i*</sup>Pr)<sub>4</sub> (Kishida Chem. Co. Ltd., 99%), Mg(OTf)<sub>2</sub> (Tokyo

Chem. Industry Co. Ltd., >98%), LiCl (Nakalai Tesque, Inc., 98%), and 6-mercapto-1-hexanol (Tokyo Chem. Industry Co. Ltd., >98%) were used as received.

#### Instrumentation

Gel permeation chromatography (GPC) was performed on a Shodex GPC-104 system equipped with a Shodex RI-74S detector and two tandem LF-404 columns. In the case of Poly**2**, a JASCO RI-1531 detector and tandem KF-802 and KF-8025 columns were used. THF was used as the eluent with a flow rate of 1.0 mL/min at 40 °C (Shodex system) or 25 °C (JASCO system). All columns were calibrated with polystyrene standards. Nuclear magnetic resonance (NMR) spectra were obtained on an Avance III 400 MHz (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ ) spectrometer in  $\text{CDCl}_3$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts were referenced to tetramethylsilane (0.0 ppm) and  $\text{CDCl}_3$  resonance (77.1 ppm), respectively. Electrospray ionization mass spectrometry (ESI-MS) was performed for methanol solutions on a Waters Synapt G2 HDMS tandem quadrupole orthogonal acceleration time-of-flight instrument equipped with a Z-spray nanoelectrospray ionization source. Infrared spectra were obtained on a FT/IR-460 Plus spectrometer equipped with a ZnSe crystal ATR accessory.

#### Synthesis of **2** (4-hydroxycyclohexyl acrylate)

To the solution of 1,4-cyclohexanediol (cis- and trans- mixture) (3.50 g, 30.2 mmol) and triethylamine (2.8 mL, 20 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL), the solution of acryloyl chloride (1.6 mL, 20 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added slowly at 0 °C under nitrogen atmosphere. The mixture was stirred for 2 h at room temperature. The filtration and silica gel column chromatography using  $\text{CH}_2\text{Cl}_2/\text{EtOAc}$  (1:1, v/v,  $R_f = 0.42$ ) as the eluent gave the transparency liquid **2** (0.44 g, 2.58 mmol) in 13 % yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm) 1.40-2.03 (m, 9H), 3.74 (m, 1H), 4.82 (m, 0.5H), 4.94 (m, 0.5H), 5.82 (m, 1H), 6.06-6.16 (m, 1H), 6.38 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm) 27.4, 28.6, 30.6, 32.6, 68.0, 69.0,

70.0, 71.9, 128.9, 129.1, 130.49, 130.52, 165.7, 165.8. HRMS (ESI)  $m/z$ : calcd for  $C_9H_{14}NaO_3$   $[M+Na]^+$  193.0841, found 193.0848. IR (neat,  $cm^{-1}$ ): 3422, 2941, 2864, 1717, 1406, 1272, 1192, 1054, 967, 809.

#### Synthesis of **3** ((*Z*)-4-hydroxybut-2-enyl acrylate)

To the solution of *cis*-2-butene-1,4-diol (2.5 mL, 30 mmol) and triethylamine (2.8 mL, 20 mmol) in THF (10 mL), the solution of acryloyl chloride (1.6 mL, 20 mmol) in THF (10 mL) was added slowly at 0 °C under nitrogen atmosphere. The mixture was stirred for 2 h at 0 °C. The filtration and silica gel column chromatography using  $CH_2Cl_2/EtOAc$  (5:1, v/v,  $R_f = 0.38$ ) as the eluent gave the transparency liquid **3** (0.81 g, 5.7 mmol) in 29% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$ (ppm) 2.75 (brs, 1H), 4.27 (d, 2H,  $J = 6.4$  Hz), 4.76 (d, 2H,  $J = 6.8$  Hz), 5.65 (m, 1H), 5.86 (m, 2H), 6.12 (dd, 1H,  $J = 17.3, 10.3$  Hz), 6.42 (dd, 1H,  $J = 17.3, 1.3$  Hz).

$^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$ (ppm) 58.3, 60.3, 125.2, 128.2, 131.2, 133.6, 166.3. HRMS (ESI)  $m/z$ : calcd for  $C_7H_{10}NaO_3$   $[M+Na]^+$  165.0528, found 165.0529. IR (neat,  $cm^{-1}$ ): 3403, 3030, 2942, 2875, 1721, 1405, 1294, 1270, 1181, 1030, 981, 809.

#### Synthesis of **4** (4-hydroxybut-2-ynyl acrylate)

To the solution of 2-butyne-1,4-diol (2.6 g, 30 mmol) and triethylamine (2.8 mL, 20 mmol) in THF (10 mL), the solution of acryloyl chloride (1.6 mL, 20 mmol) in THF (10 mL) was added slowly at -30 °C under nitrogen atmosphere. The mixture was stirred for 2 h at -30 °C. The filtration and silica gel column chromatography using  $CH_2Cl_2/EtOAc$  (5:1, v/v,  $R_f = 0.50$ ) as the eluent gave the transparency liquid **4** (1.20 g, 8.5 mmol) in 43% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$ (ppm) 3.41 (t, 1H,  $J = 5.8$  Hz), 4.31 (d, 2H,  $J = 5.8$  Hz), 4.81 (s, 2H), 5.91 (dd, 1H,  $J = 10.4, 1.1$  Hz), 6.16 (dd, 1H,  $J = 17.2, 10.4$  Hz), 6.47 (dd, 1H,  $J = 17.2, 1.1$  Hz).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$ (ppm) 50.5, 52.4, 79.0, 85.3, 127.5, 131.9, 165.5. HRMS (ESI)  $m/z$ : calcd for  $C_7H_8NaO_3$   $[M+Na]^+$  163.0371, found 163.0372. IR (neat,  $cm^{-1}$ ): 3437, 1723, 1407, 1266, 1172, 1137, 1016, 967, 808.

#### Polymerization of **1**

To a dried two-necked glass tube equipped with a three-way stopcock and containing TPT (27.1 mg, 0.091 mmol) and a magnetic stirrer, monomer **1** (106 mg, 0.91 mmol) was added at room temperature. After 24 h, the mixture was dissolved in small amount of CH<sub>2</sub>Cl<sub>2</sub> and the precipitation into Et<sub>2</sub>O gave Poly **1** (56 mg, 57%). The polymerizations of **2**, **3**, and **4** were performed by the similar procedure.

Poly **1**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 2.62 (s, 2.0H), 3.60 (s, 0.7H), 3.66 (s, 1.2H), 3.76 (s, 2.0H), 4.23 (s, 1.6H), 4.30 (s, 0.7H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 34.7, 34.8, 61.8, 62.1, 63.4, 66.3, 68.7, 70.2, 72.0, 129.4, 171.3. . HRMS (ESI) *m/z*: 530.2304, 584.2407, 646.2770, 700.2876, 762.3243. IR (neat, cm<sup>-1</sup>): 2951, 2879, 1729, 1593, 1491, 1386, 1252, 1174, 1117, 1068, 754, 696

Poly **2**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 1.42 (s, 2.9H), 1.71 (s, 3.7H), 1.96 (s, 3.4H), 2.49 (s, 1.6H), 3.71 (s, 1.0H), 4.75 (s, 1.0H), 7.20-7.71 (m, 3.2H). HRMS (ESI) *m/z*: 638.3244, 808.4187, 978.5143. IR (neat, cm<sup>-1</sup>): 2938, 2863, 1717, 1182, 1068, 969.

Poly **3**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 2.59 (s, 2H), 3.70 (m, 1.4H), 4.07 (m, 2.0H), 4.67 (m, 2.3H), 5.72 (m, 2.2H), 7.18-7.77 (m, 1.6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 35.0, 35.1, 58.3, 58.6, 60.2, 60.4, 65.5, 65.6, 66.6, 66.7, 126.6, 128.0, 129.5, 130.7, 171.2. HRMS (ESI) *m/z*: 582.2601, 724.3224, 866.3847, 1008.4470, 1150.5084, 1292.5706, 1434.6340. IR (neat, cm<sup>-1</sup>): 2871, 1730, 1593, 1375, 1173, 1097, 910, 727.

Poly **4**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 2.65 (m, 2.0H), 3.79 (m, 1.8H), 4.21 (m, 2.1H), 4.75 (m, 2.0H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ(ppm) 34.5, 52.2, 52.3, 58.4, 58.5, 64.95, 64.99, 65.04, 65.07, 80.4, 80.7, 82.2, 82.6, 170.5. HRMS (ESI) *m/z*: 438.1807, 578.2285, 718.2753, 858.3222, 998.3696, 1138.4156, 1278.4629, 1419.5145. IR (neat, cm<sup>-1</sup>): 2878, 1738, 1596, 1164, 1089, 908, 727.

Post-polymerization modification of Poly **3**.

Poly **3** (79 mg) was weighed into a dried two-necked glass tube containing a magnetic stirrer and equipped with a three-way stopcock. Azobisisobutyronitrile (3.4 mg, 0.021 mmol), THF (0.14 mL), and 6-mercapto-1-hexanol (88 mg, 0.65 mmol) were added at room temperature. After three freeze-thaw cycles, the mixture was stirred at 60 °C for 24 h. The mixture was then dissolved in small amount of CH<sub>2</sub>Cl<sub>2</sub> and the precipitation into Et<sub>2</sub>O gave poly **8** (58 mg, 27 % conv., 57 % yield). Poly **8**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ(ppm) 1.38 (s, 1.8H), 1.57 (m, 1.9H), 2.59 (s, 3.1H), 3.61 (s, 0.8H), 3.70 (s, 1.7H), 4.10(m, 2.5H), 4.66 (m, 2.3H), 5.74 (m, 2.0H).

## References and Notes

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