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Polycondensation of methacrylates: Auto-tandem organocatalysis using N-heterocyclic carbene

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The first polycondensations of methacrylates have been realized by auto-tandem N-heterocyclic carbene (NHC) catalysis comprising transesterification and tail-to-tail dimerization. The single NHC catalyst promoted self-polycondensation of hydroxy-functionalized methacrylates and direct polycondensation of *n*-butyl methacrylate (*n*BMA) with diols to synthesize new unsaturated polyesters. The self-polycondensation efficiently produced polyesters in high yields. The short-time polymerization indicates that the transesterification and dimerization proceed simultaneously. The direct polycondensation can be used to readily produce a variety of polyesters by changing the diols under optimized conditions. Even in the presence of excess alcohols, the NHC efficiently catalyzes the dimerization through the umpolung of methacrylates combined with the activation of alcohols for transesterification.

Introduction

Tandem catalysis, which involves two or more catalytic cycles in a single reactor, allows the reduction of reaction time, cost, waste, and energy. A single catalyst can sometimes promote tandem catalysis without an additional reagent. Such auto-tandem catalysis^{1, 2} is operationally simple, and offers efficient catalyst utilization. Compared to widely developed auto-tandem catalysis in organic synthesis, there are only a few examples in polymer synthesis,³ such as synthesis of polyester through tandem cyclization/alternating copolymerization using a salen complex,⁴ tandem ring-opening/ring-closing metathesis polymerization using a Grubbs catalyst,^{5, 6} and tandem azide-alkyne cycloaddition/living radical polymerization using a Cu(I) catalyst.^{7, 8} These catalysts should be tolerant to various functional groups and efficiently promote multiple catalysis with high selectivity and activity. Due to these stringent requirements, polymerization via auto-tandem catalysis is a difficult process.

N-Heterocyclic carbene (NHC) as an organocatalyst has been extensively investigated for two decades and can promote various reactions.^{9–12} Auto-tandem catalysis using such a catalyst is a promising procedure for expanding the scope of reactions and polymerizations. However, there are a few examples of auto-tandem organocatalysis by NHC.^{13, 14} Ring-opening polymerization catalyzed by NHC is accepted as an effective procedure for producing living linear and cyclic polyesters.^{15–19} Propagation is extremely rapid under optimized

conditions,¹⁶ indicating that NHCs are highly active catalysts for transesterification^{20–22}. Polymerizations of various cyclic monomers are possible, and various NHC catalysts can be used. Among these, 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (TPT) or its methanol adduct (TPT-MeOH), which thermally generates active TPT, also catalyzed the controlled polymerization of lactide, leading to “on-demand” polymerization and the synthesis of star-shaped polymers.^{23–25} We and others have developed tail-to-tail dimerization of Michael acceptors through NHC-catalyzed umpolung.^{26–34} Compared with the ring-opening polymerization, effective catalysts are limited to TPT or TPT-MeOH, while the dimerization shows tolerance to various functional groups and accepts a wide range of substrates such as (meth)acrylates, (meth)acrylonitrile, (meth)acrylamides, vinyl pyridines and others. Additionally, this C-C bond forming reaction was applied to the polyaddition of dimethacrylates to produce unsaturated polyesters.^{35, 36} Given that the TPT-catalyzed dimerization and transesterification exhibit high selectivity and activity, combining these two reactions can fulfill the requirements for auto-tandem catalysis for polymer synthesis. Herein, we report the self-polycondensation of hydroxy-functionalized methacrylates and the direct polycondensation of *n*-butyl methacrylate (*n*BMA) with diols using auto-tandem organocatalysis comprising the transesterification and tail-to-tail dimerization catalyzed by TPT. Auto-tandem organocatalysis has recently been widely used in organic synthesis; however, to the best of our knowledge, no examples exist in polymer synthesis.^{1, 3} In this study, the first polycondensations of methacrylates were realized in the first auto-tandem organocatalytic polymerization reactions.

Experimental

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Materials

Ethylene glycol (**4**) (Wako Pure Chemical Industries, 99.5%), *N*-methyldiethanolamine (**5**) (Tokyo Chemical Industry, >99%), propylene glycol (**6**) (Kanto Chemical, >99%), and 1,4-butanediol (**9**) (Kishida chemical 98%) were stirred with Na at 100 °C for 2 h, distilled under reduced pressure three times, and stored in the presence of molecular sieves 3Å. 1,2-Dimethoxy ethane and *n*BMA (Kanto Chemical >98%) were distilled from CaH₂. 2-Hydroxyethyl methacrylate (**1**) (Kanto Chemical, >95%) and hydroxypropyl methacrylate (**3**) (a mixture of 2-hydroxypropyl methacrylate and 2-hydroxy-1-methylethyl methacrylate with molar ratio of 80:20, Tokyo Chemical Industry, >97%) were distilled under reduced pressure and stored in the presence of molecular sieves 3Å. Methacryloyl chloride (Iharanikkei Chemical industry), 1,4-cyclohexane diol (**7**) (Aldrich 99%), and 2-butyne-1,4-diol (**8**) (Nakarai >98%) were used as received.

Instrumentation

NMR spectra were recorded on a Bruker Avance III HD spectrometer (400 MHz for ¹H, 100MHz for ¹³C) using TMS (0.0 ppm) for ¹H and CDCl₃ (77.1 ppm) for ¹³C as internal standards. Gel permeation chromatography (GPC) measurement was performed on a Shodex GPC-104 system equipped with two tandem LF-404 columns (Shodex) calibrated against standard polystyrenes and with a RI-74S (Shodex) detector using THF as eluent with a flow rate of 1.0 mL/min at 40 °C. ESI-MS was performed on a Waters Synapt G2 HDMS machine. TG-DTA measurements were performed on a DTG-60 (Shimadzu) apparatus with a heating rate of 10 °C/min under nitrogen atmosphere. Glass transition temperatures (*T*_gs) were taken as an onset of the transition for the average of second and third scans using a SSC/5200 SII DSC220C (Seiko) apparatus with a heating rate of 10 °C/min under nitrogen atmosphere.

General

All polymerizations were performed under a nitrogen atmosphere using a two-necked reaction flask equipped with a three-way stopcock; liquid materials were added via a syringe. When polymers were not purified by reprecipitation, the yields were calculated assuming that TPT was contaminated in the product.

Synthesis of 2-((2-hydroxyethyl)(methyl)amino)ethyl methacrylate (**2**)

To a solution of *N*-methyldiethanolamine (26.10 g, 219 mmol) and triethylamine (1.72 g, 17 mmol) in 22 mL of methylene chloride at 0 °C, was added dropwise a solution of methacryloyl chloride (4.39 g, 42 mmol) in 21 mL of methylene chloride. After stirring for 2 h at room temperature, the mixture was washed with aqueous NaHCO₃ and water, then dried over anhydrous MgSO₄. The radical inhibitor, 4-methoxyphenol (53 mg, 0.43 mmol) was added to the solution and concentrated under reduced pressure. Purification by silica gel column chromatography with acetone/hexane/triethyl amine (200:100:1) as an eluent and subsequent Kugelrohr distillation under reduced pressure yielded **2** (1.28 g, 6.4 mmol, 15% yield) as a colorless and viscous liquid.

¹H NMR (400 MHz, CDCl₃) δ: 6.12 (s, 1H), 5.58 (s, 1H), 4.26 (m, 2H), 3.58 (m, 2H), 2.77 (m, 2H), 2.62 (m, 2H), 2.34 (s, 3H), 1.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 167.1, 135.8, 125.4, 61.9, 58.5, 58.0, 55.4, 41.6, 18.0. HRMS (ESI) *m/z*: calculated for C₉H₁₈O₃N₁ [M+Na]⁺ 210.1106, found 210.1115. IR (NaCl): 3406, 2956, 2888, 2851, 2807, 1718, 1637, 1513, 1456, 1405, 1377, 1319, 1297, 1169, 1038, 945, 876, 816, 652 cm⁻¹.

Self-polycondensation

A mixture of **1** (0.137 g / 1.1 mmol), TPT-MeOH (6.7 mg, 0.020 mmol), and 4-methoxyphenol (0.1 mg, 0.8 μmol) in toluene (0.33 mL) was stirred at 120 °C for 6 h under a nitrogen atmosphere, and at 180 °C for 6 h under vacuum (0.3 mmHg). The mixture was dissolved in a small quantity of chloroform and reprecipitated in hexane to produce poly**1** (0.119 g) as a viscous solid in 86% yield.

poly **1**; ¹H NMR (400 MHz, CDCl₃) δ: 6.72 (1H), 5.94 (Z isomer), 4.38–4.29 (4H), 2.66–2.52 (2H), 2.36–2.29 (1H), 1.84 (3H), 1.18 (3H). ¹³C NMR (100 MHz, CDCl₃) δ: 175.4, 167.6, 139.5, 129.3, 62.44, 62.38, 38.9, 32.4, 16.9, 12.7. IR (ATR): 2972, 1732, 1709, 1651, 1456, 1377, 1253, 1219, 1165, 1088, 740 cm⁻¹.

poly **2**; ¹H NMR (400 MHz, CDCl₃) δ: 6.70 (1H), 5.91 (Z isomer), 4.24–4.16 (4H), 2.78–2.68 (4H), 2.63–2.51 (2H), 2.38–2.32 (4H), 1.84 (3H), 1.19 (3H). ¹³C NMR (100 MHz, CDCl₃) δ: 175.1, 167.3, 138.6, 129.0, 62.2, 61.9, 55.56, 55.55, 42.6, 38.4, 31.9, 16.4, 12.2. IR (ATR): 3423, 2953, 2798, 1729, 1708, 1650, 1456, 1379, 1349, 1255, 1219, 1171, 1136, 1089, 741, 696 cm⁻¹.

poly **3**; ¹H NMR (400 MHz, CDCl₃) δ: 6.70 (1H), 5.92 (Z isomer), 5.19 (1H), 4.20–3.95(2H), 2.58–2.51 (2H), 2.40–2.25 (1H), 1.83 (3H), 1.31–1.21 (3H), 1.18 (3H). ¹³C NMR (100 MHz, CDCl₃) δ: 175.3, 167.2, 139.5, 129.5, 68.6, 66.35, 66.39, 39.1, 32.5, 17.1, 16.9 16.8, 12.8. IR (ATR): 3520, 2979, 2939, 2879, 1708, 1650, 1595, 1498, 1455, 1379, 1254, 1175, 1138, 1075, 847, 741, 696 cm⁻¹.

Direct Polycondensation

A mixture of *n*BMA (0.487 g, 3.4 mmol), ethylene glycol (0.39 mL, 6.8 mmol), TPT-MeOH (50 mg, 0.15 mmol), and 4-methoxyphenol (0.3 mg, 2 μmol) was stirred at 160 °C for 6 h under nitrogen and for an additional 6 h under vacuum (300 mmHg), followed by heating at 180 °C for 6 h under vacuum conditions (0.3 mmHg) to give the polymer (0.280 g, 73% yield) as a viscous solid. For polymerizations of *n*BMA with **7** and **8**, diglyme (1.0 mL) was used as a reaction solvent.

Polymer obtained from *n*BMA with **7**; ¹H NMR (400 MHz, CDCl₃) δ: 6.69 (1H), 5.9 (Z isomer), 4.93–4.76 (1H), 3.76 (1H), 2.61–2.51 (2H), 2.33–2.30 (1H), 1.84 (3H), 1.46–1.35 (8H), 1.20 (3H). ¹³C NMR (100 MHz, CDCl₃) δ: 174.8, 166.8, 138.3, 129.2, 71.3, 64.1, 38.8, 31.7, 28.1, 27.2, 27.0, 18.9, 16.6. IR (ATR): 3415, 2957, 2936, 2872, 1730, 1709, 1651, 1596, 1498, 1456, 1359, 1257, 1069, 1019, 969, 935, 796, 742, 696 cm⁻¹.

Polymer obtained from *n*BMA with **8**; ¹H NMR (400 MHz, CDCl₃) δ: 6.77 (1H), 6.17 (Z isomer), 4.78–4.72 (4H), 2.68–2.50 (2H), 2.39–2.31 (1H), 1.87 (3H), 1.21 (3H). ¹³C NMR (100 MHz, CDCl₃) δ: 175.6, 168.9, 140.1, 128.6, 77.0, 64.4, 52.4, 38.9, 32.5, 19.1, 16.9. IR (ATR): 3431, 2960, 2934, 2874, 1713, 1650, 1596, 1496, 1455, 1376, 1258, 1219, 1138, 1090, 1027, 966, 802, 741, 694 cm⁻¹.

Polymer obtained from *n*BMA with **9**; ^1H NMR (400 MHz, CDCl_3) δ : 6.70 (1H), 5.90 (*Z* isomer), 4.18–4.07 (4H), 2.63–2.50 (2H), 2.35–2.29 (2H), 1.84 (3H), 1.77–1.59 (4H), 1.19 (3H). ^{13}C NMR (100 MHz, CDCl_3) δ : 176.0, 168.2, 139.0, 129.7, 64.7, 62.4, 39.2, 32.9, 29.5, 25.4, 19.3, 17.3. IR (ATR): 3446, 2957, 2874, 1708, 1650, 1596, 1499, 1458, 1389, 2352, 1257, 1221, 1175, 1139, 1068, 1043, 943, 802, 741, 695 cm^{-1} .

Two-step one-pot polymerization

A mixture of *n*BMA (0.430 g, 3.0 mmol), TPT-MeOH (49 mg, 0.15 mmol), and 4-methoxyphenol (0.3 mg, 2 μmol) was stirred at 120 $^\circ\text{C}$ for 2 h under a nitrogen atmosphere. Ethylene glycol (0.34 mL, 6.0 mmol) was subsequently added, and the mixture was stirred at 160 $^\circ\text{C}$ for 6 h under a nitrogen atmosphere and at 180 $^\circ\text{C}$ for 6 h under vacuum (0.3 mmHg) to give the polymer (0.288 g, 83% yield) as a viscous solid.

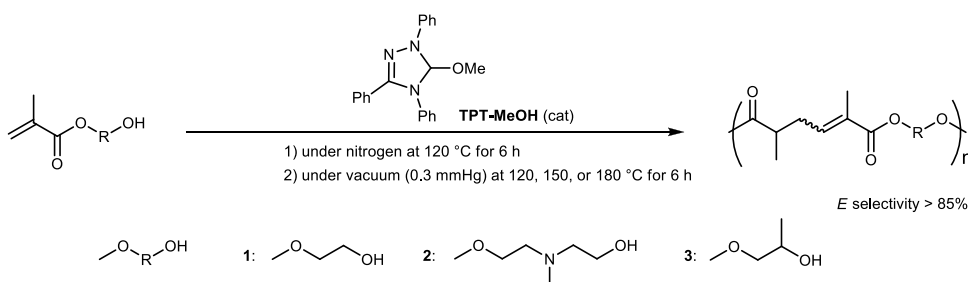
Transesterification polymerization

A mixture of *n*BMA dimer (0.427 g, 1.50 mmol), ethylene glycol (0.34 mL, 6.0 mmol), TPT-MeOH (49 mg/0.15 mmol), and 4-methoxyphenol (0.3 mg, 2 μmol) was stirred at 160 $^\circ\text{C}$ for 6 h under a nitrogen atmosphere and for an additional 6 h under vacuum (300 mmHg), followed by heating at 180 $^\circ\text{C}$ for 6 h under vacuum (0.3 mmHg) to give the polymer (0.267 g) in 77% yield.

Results and discussion

We initially investigated the self-polycondensation of **1**. When polymerization of **1** with 5 mol% TPT-MeOH was performed at 80 $^\circ\text{C}$ for 6 h, the conversion of **1** reached 61%. Increasing the reaction temperature to 120 $^\circ\text{C}$ resulted in complete consumption of **1** even with 2 mol% of TPT-MeOH (entry 1, Table 1). The ^1H NMR spectrum of the resulting mixture exhibited signals corresponding to vinylidene (6.7 (*E*-isomer), 5.9 (*Z*-isomer) ppm), diastereotopic methylene (2.3, 2.5 ppm), and methyl (1.2, 1.8 ppm) protons, which are characteristic of the tail-to-tail dimer, indicating that the hydroxy group of the monomer did not impede dimerization. GPC analysis revealed oligomer formation ($M_n = 500$), indicating that transesterification also occurred. To promote transesterification equilibrium, after the polymerization at 120 $^\circ\text{C}$ for 6 h under nitrogen, this was continued for an additional 6 h under vacuum (0.3 mmHg) (entries 2–7). Increasing the vacuum temperature from 120 $^\circ\text{C}$ to 150 $^\circ\text{C}$ and 180 $^\circ\text{C}$ increased the M_n of poly**1** from 1300 to 3300 with unimodal GPC curves. Even when the amount of TPT-MeOH

Table 1. Self-polycondensation of **1–3**^a



entry	monomer	TPT-MeOH	temp. ($^\circ\text{C}$)	yield ^c	M_n^d	M_w/M_n^d	<i>E/Z</i>
	type	mol%	under vacuum	%			
1	1	2	-	-	500	1.7	-
2	1	2	120	93	1300	2.1	95:5
3	1	2	150	63	3000	2.3	90:10
4	1	2	180	86 (28) ^e	3300(10,700) ^e	2.0(1.3) ^e	88:12
5	1	10	180	78	1700	3.0	91:9
6	1	5	180	85 (>99) ^f	2700(1700) ^f	2.4(3.1) ^f	89:11
7	1	1	180	75	3200	1.9	91:9
8	2	10	180	36	1600	2.6	86:14
9	2	2	180	65	2900	1.7	90:10
10	3	10	180	90	1800	2.2	89:11
11	3	2	180	55	2600	1.6	90:10
12 ^b	1, 3	2	180	71	2700	2.3	83:17

^a Polymerizations were performed under nitrogen at 120 $^\circ\text{C}$ for 6 h followed by under vacuum (0.3 mmHg) for 6 h in the presence of 4-methoxyphenol (0.1 mol% for **1** and **3**, 5.0 mol% for **2**). Conv. = 100 % measured by ^1H NMR. ^b Copolymerization of **1** (1.0 equiv) with **3** (1.0 equiv) in the presence of TPT-MeOH (0.04 equiv).

^c After reprecipitation into hexane. ^d GPC (THF). ^e After reprecipitation into Et_2O . ^f Crude.

was reduced to 1 mol%, a polyester with a M_n of 3200 and a M_w/M_n of 1.9 was obtained in 75% yield (entry 7). However, 10 mol% of TPT-MeOH gave a lower molecular weight polyester with a M_n of 1700 and a M_w/M_n of 3.0 (entry 5). The polymers were formed quantitatively and were obtained in good to high yields after reprecipitation into hexane. Using diethyl ether as a reprecipitation solvent gave a higher molecular weight fraction ($M_n = 10,700$, $M_w/M_n = 1.3$) in 28% yield (entry 4). ESI-MS analysis showed three series of signals with constant intervals due to the polymer repeating unit, indicating reasonable terminal structures with hydroxy and vinylidene groups and the TPT moiety (Figure S14). The main series of signals is corresponding to the polymer having vinylidene groups at both terminals. This polymer has same molecular weight as the cyclic polymer (Figure S14). The ^1H NMR spectrum showed very small signals due to the vinylidene groups, suggesting that the obtained polymer may contain both linear and cyclic structures, the latter of which is formed by the C-C coupling between terminal vinylidene groups of the linear polymer.

We then examined the self-polycondensation of other hydroxy-functionalized monomers, **2** and **3**. These were also completely consumed in the reaction with 2 mol% of TPT-MeOH at 120 °C under a nitrogen atmosphere for 6 h, and subsequent reactions at 180 °C for 6 h under vacuum (0.3 mmHg) yielded poly**2** and poly**3** (entries 8–11). The polymerizations of **2** and **3** present difficulties associated with the higher boiling point of the alcohol eliminated from **2** and with the larger steric hindrance of the secondary alcohol of **3**. However, polymerization using 2 mol% of TPT-MeOH produced poly**2** with a M_n of 2900 and a M_w/M_n of 1.7 in 65% yield (entry 9), and poly**3** with a M_n of 2600 and a M_w/M_n of 1.6 in 55% yield (entry 11). Copolymerization of **1** with an equimolar amount of **3** was performed under similar conditions to give a copolymer with equimolar compositions of **1** and **3**, a M_n of 2700 and a M_w/M_n of 2.3, and a unimodal GPC curve in 71% yield (entry 12). As with the polymerization of **1**, lower catalyst loadings produced higher molecular weight polyesters. This is probably because the equivalence between vinylidene and hydroxy groups was destroyed by the formation of a TPT adduct with a vinylidene polymer terminal. Previously, we noted that the 1:1 and 1:2 adducts of TPT and methyl methacrylate are sufficiently stable to be detected by ESI-MS measurement after complete dimerization.^{26, 28} Therefore, intermediates, II and IV, shown in Figure 1, in the dimerization cycle are believed to be resting states that exist in the reaction mixture even at high conversions. They can undergo transesterification, yielding polyesters containing the TPT moiety at the polymer terminal or in the main chain. At high TPT loadings, the number of inactive TPT terminals increases, resulting in polyesters with a decreased molecular weight. To investigate the polymerization mechanism, 2 mol% of TPT-MeOH was reacted with **1** in toluene for 15 min at 120 °C. The ^1H NMR spectrum indicated that the conversions of both the vinylidene and methylene ($-\text{CH}_2\text{OH}$) groups of **1** were 48%, suggesting that dimerization and transesterification proceeded simultaneously. The detailed polymerization mechanisms are given in Figure 1. During the dimerization, TPT nucleophilically attacks the β -

carbon of methacrylate to form zwitterionic intermediates I, followed by intermolecular proton transfer to generate deoxy-Breslow intermediate II. During this process, the β -carbon of methacrylate becomes nucleophilic. Intermediate II reacts with another methacrylate to give zwitterionic intermediate III. The subsequent proton transfer forms a 2:1 adduct of methacrylates and TPT (IV). Further proton transfer of IV and subsequent liberation of TPT produce C-C coupling product VIII. TPT also functions as a transesterification catalyst, as transesterification of the dimer of *n*BMA with ethylene glycol (**4**) did not occur in the absence of TPT-MeOH (entry 1, Table 3). There are two possible mechanisms for the transesterification; activation of the hydroxy group or the ester carbonyl group. We now propose the former mechanism, since TPT catalyzes the dimerization of methacrylates even at high temperatures with no nucleophilic attack of TPT on the ester carbonyl group. Thus, alkoxide VI is formed from TPT and methacrylate, followed by nucleophilic attack on another ester carbonyl group to generate VII. Dimethacrylate IX is then formed by diol elimination. The activation of the hydroxy group by the zwitterionic ester enolates, I and III, is also possible mechanism. The produced VIII and IX then undergo C-C coupling or transesterification with the monomer or VIII or IX, respectively, to generate X, XI, and XII. Specifically, the hydroxy-functionalized methacrylate, X, is formed via transesterification of VIII with monomer, IX with VIII, or C-C coupling of IX with the monomer. Diol XI is formed via C-C coupling of IX with two monomer molecules, or transesterification of VIII. Dimethacrylate XII is formed by the dimerization of IX. Further tandem reactions produce the target aliphatic polyester. Oxa-Michael addition catalyzed by TPT catalyst is a potential side reaction; however, the model reaction of *n*-butyl methacrylate (*n*BMA) and *n*-butanol in the presence of TPT catalyst under similar conditions did not occur. Thus, the formation of XIII and XIV can be excluded.

The three polyesters obtained were readily soluble in various organic solvents. Poly**1** is soluble in toluene, dichloromethane, chloroform, THF, ethyl acetate, acetonitrile, and DMF, but insoluble in water, DMSO, methanol, hexane, and acetone. Poly**2** and poly**3** are soluble in all the above solvents apart from water and hexane. The 10% weight loss temperatures (T_{10}) are 344 °C (poly**1**), 302 °C (poly**2**), and 280 °C (poly**3**), and the glass transition temperatures (T_g) are -23 °C (poly**1**), -43 °C (poly**2**), and -22 °C (poly**3**). Poly**2** showed a lower T_g due to its longer soft main chain.

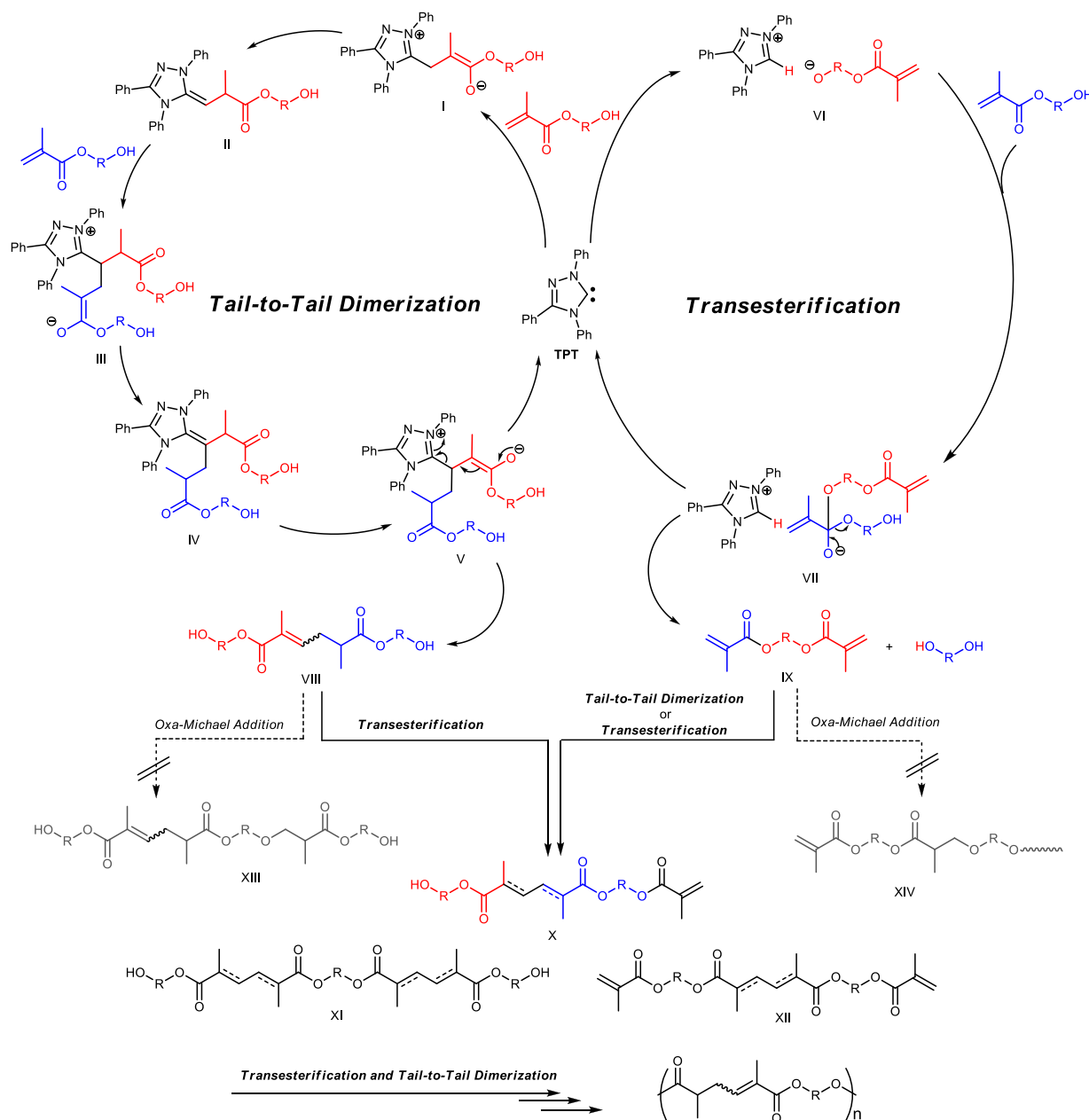


Figure 1. Proposed mechanism of the self-polycondensation of hydroxy-functionalized methacrylates.

This efficient tandem TPT catalysis involving dimerization and transesterification prompted us to develop a direct

synthesis of polyesters from *n*BMA with diols. When *n*BMA and ethylene glycol, **4**, were treated with 5 mol% of TPT-MeOH under a nitrogen atmosphere at 160 °C for 6 h, the conversions

of dimerization and transesterification reached >99% and 73%, respectively. Even in the presence of diol, the dimerization proceeded, but the molecular weight of the polyester was low ($M_n < 400$). To accelerate the transesterification, we performed an additional reaction at 180 °C under vacuum (0.3 mmHg) for 6 h (Condition A), varying the feed ratio of **4**/*n*BMA from 1.0 to 4.0 (entries 1–4, Table 2). The best result was obtained with 2.0 equiv. of **4**, giving a polyester with a M_n of 1800 and a M_w/M_n of 2.0 in 71% yield (entry 2). At 2 mol% of catalyst loading, a gel was formed even in the presence of 1 mol% of 4-methoxyphenol as a radical inhibitor, probably due to thermally-induced vinyl polymerization occurring as a side reaction. The ^1H NMR spectrum resembles that of poly**1** obtained by self-polycondensation (Table 1), indicating that the polymerization proceeded without side reactions; however peaks attributed to the butyl group were detected. Even increasing the polymerization time to 24 h under vacuum (0.3 mmHg) did not increase the molecular weight of the polyester, giving 84% conversion for the transesterification, estimated from the ^1H NMR integral ratio between butyl and methyl groups in the polymer main chain.

We then slightly altered the vacuum pressure to selectively remove butanol from the reaction mixture. The reaction was performed by heating at 160 °C under 300 mmHg for 6 h and then at 180 °C under 0.3 mmHg for 6 h (Condition B). The resultant polymer had a slightly higher molecular weight ($M_n = 1900$, $M_w/M_n = 2.8$), and the conversion of the transesterification reached 97% (entry 5). Under the optimal conditions, polycondensations of *n*BMA with other diols, **5–9**, were performed. Since **7** and **8** are solid at room temperature, 1,2-dimethoxyethane was added as the solvent to homogenize the mixtures. Although polymerization with a bulky diol, **7**, gave an oligomer with M_n below 400, the other diols produced the corresponding polyesters with M_n values of 800–1900 and M_w/M_n values of around 2.0 in moderate to high yields. The ^1H NMR spectra confirmed that the polymers obtained from **5** and **6** had the same structures as poly**2** and poly**3** obtained by self-polycondensation. The ESI-MS spectrum of the polyester obtained from diol **9** (entry 10) showed the expected repeating unit with reasonable terminal structures containing hydroxy and vinylidene groups and the TPT moiety (Figure S15).

Table 2. Direct Polycondensation of *n*BMA with diols.^a

Condition A: 160 °C (under N₂), 6h; 180 °C (0.3 mmHg), 6h.
Condition B: 160 °C (under N₂), 6h; 160 °C (300 mmHg), 6h; 180 °C (0.3 mmHg), 6h.

entry	TPT-MeOH		diol		conditions	solvent		yield ^b %	M_n^c	M_w/M_n^c	E/Z
	mol%	type	equiv	type		mL					
1	5	4	1.0	A	-	-	67	1000	2.1	87:13	
2	5	4	2.0	A	-	-	71	1800	2.0	90:10	
3	2	4	2.0	A	-	-	- ^e	- ^e	- ^e	-	
4	5	4	4.0	A	-	-	53	900	2.4	93:7	
5	5	4	2.0	B	-	-	73	1900	2.8	83:17	
6	5	5	2.0	B	-	-	75	800	1.9	88:12	
7	5	6	2.0	B	-	-	78	1100	1.9	89:11	
8	5	7	2.0	B	DME ^d	1	77	<400	-	98:2	
9	5	8	2.0	B	DME ^d	1	45	800	2.2	97:3	
10	5	9	2.0	B	-	-	91	1200	2.0	91:9	

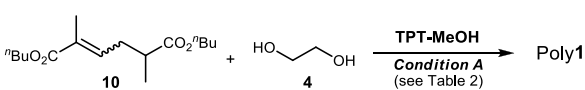
^a *n*BMA; 3.0 mmol, TPT-MeOH (5 mol%), 4-methoxyphenol 0.1 mol%. ^b crude. ^c GPC (THF). ^d 1,2-dimethoxy ethane. ^e gelation.

As well as self-polycondensation (Table 1) and the direct polycondensation (Table 2), we examined two other

procedures, i.e., transesterification polymerization (Table 3) and two-step one-pot polymerization (Table 4), to give

polymers with the same structure. When 5 mol% of TPT-MeOH was used under condition A (Table 2), the four types of polymerizations gave similar polymers with M_n values of 1800 to 2700 and M_w/M_n values of 1.9 to 2.4 (entry 2 in Table 3 and entry 1 in Table 4). Conversely, at 2.0 mol% of catalyst loading, a large difference was observed. As shown in Table 2, gelation occurred during the direct polycondensation, even though 10 mol% of the radical inhibitor, 4-methoxyphenol, was added. In the two-step one-pot polymerization (entry 2, Table 4), TPT may be partially deactivated during the dimerization, significantly decreasing its activity for transesterification, giving the oligomer ($M_n < 400$). The transesterification polycondensation gave poly1 with a M_n of 1500 and a M_w/M_n of 3.0 in 31% yield (entry 3 in Table 3), while the self-polycondensation produced poly1 with a M_n of 3300 and a M_w/M_n of 2.0 in 86% yield (entry 4 in Table 1). This result suggests that TPT is not a highly active catalyst for transesterification. Since the transesterification is an equilibrium reaction, transesterification polymerization was difficult to complete. For the self-polycondensation, the monomers were already esterified. Additionally, since the dimer of hydroxy-functionalized methacrylates generated in situ in the self-polycondensation has a higher boiling point than the *n*BMA dimer used in the transesterification polymerization, this is more suitable for polymerization at high temperatures under vacuum. The *n*BMA dimer tends to be removed from the polymerization mixture, giving lower yields. For these reasons, self-polycondensation is the most efficient procedure based on both the yield and molecular weight of the resulting polyesters.

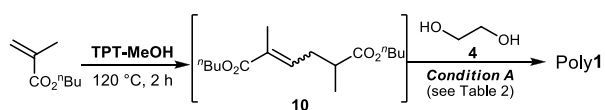
Table 3. Transesterification polymerization of *n*BMA dimer (**10**) with **4**.



entry	TPT-MeOH		M_n^c	M_w/M_n^c
	mol%	yield ^b		
1	0	0	-	-
2	5	77	2200	1.9
3	2	31	1500	3.0

^a *n*BMA dimer; 1.5 mmol. **4**; 6.0 mmol, 4-Methoxyphenol; 0.2 mol% relative to **10**. ^b Crude. ^c GPC (THF).

Table 4. Two-step one-pot synthesis of poly1 via tail-to-tail dimerization of *n*BMA followed by transesterification.



entry	TPT-MeOH		M_n^c	M_w/M_n^c
	mol%	yield ^b		
1	5	83	1300	1.9
2	2	38	<400	1.6

^a *n*BMA; 3.0 mmol, **4**; 6.0 mmol. 4-Methoxyphenol; 0.1 mol% relative to *n*BMA. ^b Crude. ^c GPC (THF).

Conclusions

We have shown that TPT effectively and simultaneously catalyzes tail-to-tail dimerization and transesterification of methacrylates to yield new unsaturated polyesters. This auto-tandem catalysis is the first polycondensation of methacrylates, and also the first tandem polymerization catalyzed by NHC. We studied four types of polymerization: self-polycondensation, direct polycondensation, transesterification polycondensation, and two-step one-pot polymerization. Among these, self-polycondensation is the best procedure for synthesizing higher molecular weight polymers in higher yields; only 1 mol% of TPT-MeOH catalyst produced a polymer with a M_n of 3200 and a M_w/M_n of 1.9 in 75% yield. Direct polycondensation readily gave polyesters with M_n values of 800 to 1900 in good yields under optimized temperature and pressure. Compared to the vinyl addition polymerization of methacrylates widely used in the chemical industry, this study demonstrates a conceptually different polymerization for synthesizing condensation polymers.

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