Post-polymerization modification of unsaturated polyesters by Michael addition of N-heterocyclic carbenes

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Abstract

The post-polymerization modification of unsaturated polyesters, three polymaleates and a polyfumarate, was performed by the Michael addition of N-heterocyclic carbenes (NHCs) to produce thermally stable unsaturated polyesters. The model reactions of NHCs, 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (TPT) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp), with dibutyl fumarate and dibutyl maleate selectively proceeded to give the corresponding Michael adducts, whereas 1,3-di-*tert*-butylimidazol-2-ylidene (ItBu) exclusively catalyzed the isomerization of dibutyl maleate. Based on these results, reactions of the unsaturated polyesters with TPT and IDipp were investigated. The polyesters bearing NHCs as side chains were obtained in good to high yields. The number of NHC-incorporated units can be controlled by the amount of added NHCs, and the obtained polyesters showed better solubility in common organic solvents. It is noteworthy that the glass transition temperatures (T_gs) were widely tunable and increased linearly with increasing NHC content because of the stiff and bulky structure. In addition, reactions of the unsaturated polyesters with TPT in the presence of water allowed Michael addition and transfer hydrogenation to occur simultaneously. Radical cross-linking of the NHC-incorporated unsaturated polyesters with styrene produced thermally stable and fully miscible polyester resins.

Keywords

Introduction

Unsaturated polyester resins[1,2] are important raw materials for fiber-reinforced plastics. They are generally synthesized by the polycondensation of maleic anhydride and diols to produce unsaturated polyesters, followed by radical cross-linking with vinyl monomers, such as styrene. Recent advances in the synthetic procedures for unsaturated polyesters, i.e., polycondensation catalyzed by Lewis acids[3] or Brønsted acids[4] and metal-catalyzed ring-opening copolymerization of maleic anhydride and epoxides,[5-7] would lead to further applications thereof. Post-polymerization modification,[8-13] in general, facilitates the synthesis of a variety of polymers from a single polymeric precursor by changing the reactants and their incorporation ratios to advance the understanding of structure-property relationships. However, except for radical cross-linking, there are only a few examples of the post-polymerization modification of unsaturated polyesters derived from maleic anhydride. Specifically, selective reaction of the highly reactive double bonds of unsaturated polyesters has allowed for the preparation of micelles,[14, 15] reversible cross-linked materials,[16] water-soluble polyesters,[17] and double-network gels.[18] To control the glass transition temperature (T_g) of unsaturated polyesters, phthalic anhydride is generally used as a comonomer, in which the aromatic group introduced in the polyester main chain reduces the mobility of the polymer chain to result in an increase in T_g. However, the effects of the phthalic unit are not large; poly(butylene phthalate) shows a higher T_g than poly(butylene maleate) by only 30 °C.[4]

N-Heterocyclic carbenes (NHCs)[19] are neutral Lewis bases and are extensively used as organocatalysts.[20] NHCs undergo Michael addition[21-23] to catalyze cyclization,[24-26] tail-to-tail dimerization,[27-33] and polyaddition[34, 35] through deoxy-Breslow intermediates. In contrast, the intermediates generated from TPT with fumarates and maleates are quite stable and isolable, such that no further Michael addition occurs.[36] In the field of polymer chemistry, various organocatalytic polymerizations by NHC have been studied for more than a decade,[37-39] whereas much less attention has been paid to the use of NHCs as the structural component of polymeric materials.[40-43] In fact, there is only

one report on post-polymerization modification; NHC-incorporated polystyrenes were synthesized by the NHC-azide coupling reaction.[44] Our attention was directed towards such NHC modification for unsaturated polyesters, as the bulky aromatic groups can be introduced as polymer side chains.

Herein, we examined the Michael addition of NHCs to butyl fumarate and maleate and applied them to the post-polymerization modification of unsaturated polyesters to effectively increase and tune their T_g. Transfer hydrogenation in the presence of NHCs and water, developed by us,[45] was also employed for post-polymerization.

Results and Discussion

We first examined the Michael addition of NHCs to dibutyl maleate (**1a**) and fumarate (**1b**) in THF and CH$_2$Cl$_2$. The reaction of TPT or IDipp with **1a** proceeds at room temperature in both solvents to give the corresponding adduct **2**-TPT or **2**-IDipp in moderate to high yields (Entries 1-4 in Table 1). For the reaction of TPT, CH$_2$Cl$_2$ was a better solvent, whereas use of THF led to a higher yield in the reaction of IDipp. The reaction with 0.5 equivalents of IDipp in THF under reflux gave a product that was quantitatively based on the amount of IDipp (Entry 5). Reactions of **1b** with NHCs were examined only in CH$_2$Cl$_2$ (Entries 6-9), as the unsaturated polyester with the *trans* diastereomer used in this study showed poor solubility in THF. The reactions of both NHCs gave products in moderate to high yields. Quantitative formation was also observed with 0.5 equivalents of TPT under reflux (Entry 7). Although a trace amount of a dimeric product (NHC + two substrate molecules) was detected in the ESI-MS spectra of the reaction mixtures, all of the reactions proceed selectively without forming any byproducts. In contrast to TPT and IDipp, the reaction of ItBu did not give the corresponding adduct at all. In this case, the selective isomerization of **1a** to **1b** occurred with 0.2 equivalents of ItBu at room temperature (Entry 10). The solvent effect on the isomerization was examined using THF, DMF, and toluene with 0.02 equivalents of ItBu (Entries 11-13). The catalytic turnover was greater than 20 in THF and toluene. As shown in Scheme 1, the Michael addition of ItBu to **1a** gave the zwitterionic intermediate (**3**), but the subsequent proton transfer to produce **2-ItBu** did not occur because of electronic effects or steric hindrance of the *tert*-butyl group. Instead, electron transfer in **3** resulted in isomerization to give the more stable *trans* diastereomer **1b**.

In general, a model reaction for post-polymerization modification requires high yield and high selectivity. Thus, we envisioned that the Michael addition of TPT and IDipp could be applied for the post-polymerization modification of polymaleates (**P1**, **3**, and **4**) and a polyfumarate (**P2**). Based on the above results of the reactions of **1a** with TPT, reactions of **P1** with 0.2, 0.5, or 1.0 equivalents of TPT

were carried out in CH_2Cl_2 at room temperature (Entries 1-3 in Table 2). The corresponding polymer, **P1-TPT**, was obtained in moderate to good yields. The polymer structure was confirmed by comparing the ^1H NMR spectrum of each reaction with that of **2-TPT**. The characteristic signal of the α-methylene group was observed at 2.89 ppm in the resulting spectra. The composition ratio (x) of the TPT-introduced unit was estimated by the ^1H NMR integral ratio between the unreacted vinylene group and the α-methylene group. More than half of the feed TPT was incorporated. The reaction of an equivalent of TPT under reflux reached a composition ratio of 0.76 (Entry 4). It is interesting to note that the glass transition temperature (T_g) increases with increasing values of x. The T_g increased from −30 °C (**P1**) to −6 °C, even with the low composition ratio of 0.11 (Entry 1), and reached 100 °C with 0.76 (Entry 4). The reaction of IDipp with **P1** similarly proceeded in THF (Entries 5-7). The reaction with an equivalent of IDipp under reflux gave the polymer with the highest composition ratio of 0.92 and the highest T_g of 111 °C. This thermal stability can be explained by the fact that the segmental mobility of polymer chains is significantly reduced by the stiff and bulky structure of the NHCs. As shown in Figure 1, the T_g increases almost linearly with increasing composition ratio, and TPT and IDipp have a similar effect on the values of T_g. Importantly, the T_g is tunable within a temperature range as wide as 140 °C. The DSC endothermic peaks corresponding to the T_gs are single and not broad, suggesting that the NHCs were randomly incorporated. Polyester **P2**, the *trans* analogue of **P1**, similarly undergoes post-polymerization modification in CH_2Cl_2 under reflux (Entries 8 and 9). The reaction with 0.50 equivalents of TPT produced **P2-TPT** in 82% yield with a high TPT incorporation of 0.44 and a high T_g of 80 °C. The melting points (T_ms) of **P1** and **P2** were observed at 28 °C and 138 °C, respectively, whereas all DSC profiles of the resulting polymers bearing NHCs did not show any T_m, indicating that they are amorphous. The reactions of **P3** and **P4** with TPT also proceeded to give the corresponding **P3-TPT** and **P4-TPT** products with high NHC incorporation (Entries 10-13). The T_gs increased with increasing composition

ratio, but their values were not as high as those of **P1-TPT**, **P1-IDipp**, and **P2-TPT**, suggesting that the rate at which T_g increases is somehow dependent on the structure of the polymer main chain.

The obtained NHC-incorporated polymers show good solubility in various organic solvents, such as CHCl$_3$, CH$_2$Cl$_2$, 1,4-DOX, THF, MeCN, DMF, and DMSO (Table 3). Interestingly, all resulting polymers are more soluble than the substrate polymers, **P1**-**P4**. Specifically, **P2** is only soluble in CHCl$_3$ and CH$_2$Cl$_2$ (Entry 5), whereas **P2-TPT**, with a composition ratio of only 0.16, is soluble in all the above solvents (Entry 6). In addition, **P2-TPT**, with a composition ratio of 0.44, was partially soluble in toluene, acetone, and MeOH, showing that the solubility increased with an increasing composition ratio (Entry 7). The addition of NHC renders the crystalline portion of **P2** amorphous, and **P2-TPT**s are readily miscible in these solvents. The obtained polymers showed good solubility, but they could not be filtered through a 0.45 μm pore size filter. Thus, GPC measurement could not be performed. We suggest that a trace amount of TPT would react with two equivalents of maleate unit, resulting in cross-linking with quite low density.

We previously reported that the combination of TPT and water promotes the transfer hydrogenation of fumarates, maleates, and imines.[45] Given that dibutyl fumarate and maleate selectively undergo hydrogenation at 150 °C through the intermediate **2-TPT**, we envisioned that the reaction under more ambient conditions may lead to simultaneous Michael addition and hydrogenation to produce a polyester (**P-TPT-H**) with TPT-incorporated (x) and hydrogenated (y) units. The reactions of **P1** with 0.2 or 0.5 equivalents of TPT and water in THF under reflux produce a polyester (**P1-TPT-H**) with a composition of x = 14, y = 3 or x = 36, y = 9, respectively (Entries 1 and 2 in Table 4). Since a stoichiometric amount of TPT is required for both Michael addition and transfer hydrogenation, the total values of x and y indicate that TPT works efficiently. Reaction at 120 °C using sealed vials under microwave irradiation increased the content of the hydrogenated unit (Entries 3 and 4). The reaction of **P2**, which is insoluble in THF, was attempted in 1,2-dichloroethane under the same conditions, but

hydrogenation did not occur. In contrast, **P3** and **P4** underwent this post-polymerization modification in THF. Except for Entry 6, the composition ratios of the hydrogenated unit were comparable to those of the TPT-incorporated unit. Compared with the saturated analogues of **P1** and **P3**, the T_gs of which are reported to be -45 °C[46] and -10 °C,[47] respectively, the obtained polyesters showed high thermal stability.

The obtained polyesters still have reactive vinylene groups, leading us to demonstrate radical cross-linking with styrene. **P1** and **P1-TPT** (x = 0.28, T_g = 44 °C) are miscible with styrene, and the mixtures (**P1-TPT**/styrene weight ratio of 2:3) were heated in the presence of AIBN at 60 °C for 20 h to produce the cross-linked resins quantitatively. The resin derived from **P1** showed two T_gs at 16 and 85 °C, corresponding to the polyester and polystyrene. In contrast, the resin derived from **P1-TPT** and styrene showed a single T_g at 87 °C, suggesting that polystyrene is miscible with **P1-TPT** probably because of π-π interactions among the phenyl groups. The cross-linking of **P1-TPT** with styrene increased not only the T_g but also the decomposition temperature, as the 10% weight loss temperature measured by TGA increased from 280 °C to 365 °C.

Conclusion

We have demonstrated a post-polymerization modification method for unsaturated polyesters to increase the thermal stability, solubility, and miscibility. The values of T_g linearly increased with an increasing amount of NHC-incorporated units and can be controlled in a range as wide as 140 °C. The use of stiff and bulky NHCs as a structural component of the polymer side chain resulted in the effective reduction of the mobility of the polymer chain. This Michael addition is suitable for post-polymerization modification, as it proceeds chemoselectively without any catalyst at ambient temperature. Transfer hydrogenation promoted by TPT and water was also applied to the post-polymerization modification. By using NHCs as stoichiometric reagents and promoters for transfer hydrogenation, the unsaturated polyesters can be converted into various structures. This work successfully demonstrates that, in addition

to the developed coordination and organocatalytic chemistries, NHCs work as rigid structural modifiers in materials chemistry.

Experimental

All reactions were performed under nitrogen atmosphere. TPT,[36] IDipp,[48] and ItBu[48, 49] were synthesized according to previous reports. Anhydrous THF and CH_2Cl_2 were used as received. Other solvents, **1a**, **1b**, 1,4-butanediol, diethylene glycol, and styrene were distilled from CaH_2 before use. AIBN was recrystallized from methanol. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD (400 MHz for ^{1}H, 100 MHz for ^{13}C) NMR spectrometer. Chemical shifts were referenced to an internal TMS standard (0.0 ppm for ^{1}H) or $CDCl_3$ resonance (77.1 ppm for ^{13}C). DSC measurement was performed using a SSC/5200 SII DSC220C (Seiko) with a heating rate of 10 °C/min. The T_gs were taken as the onset of the transition for the average of the second and third scans. Gel permeation chromatography (GPC) using THF as the eluent was performed on a Shodex GPC-104 system equipped with two tandem LF-404 columns (Shodex) and a Shimadzu SPD-20A UV detector with a flow rate of 1.0 mL/min at 40 °C. GPC using $CHCl_3$ as the eluent was performed with a TSKgel MultiporeH$_{XL}$ column and UV-1570 detector (JASCO) with a flow rate of 1.0 mL/min at 20 °C. The columns were calibrated with polystyrene standards. Electrospray ionization mass spectrometry (ESI-MS) was measured in methanol solution using 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 JASCO FT/IR-460 Plus spectrometer. Microwave-assisted reactions were performed using a Biotage Initiator microwave reactor, the temperature of which was measured by a surface sensor.

*Typical Procedure for the Michael addition of NHCs with **1a** or **1b***

To a two-necked flask equipped with three-way stopcock, TPT (0.20 mmol, 59.5 mg), CH_2Cl_2 (1.0 mL), and **1a** (0.20 mmol, 45.7 mg) were added in this order. After the mixture was stirred for 2 h at room temperature, CS_2 (0.1 mL) was added to quench the active NHC. After evaporation of the solvent, the crude product was subjected to ^{1}H NMR spectrometry. The ^{1}H NMR yield was measured by the

integral ratio between the alkenyl group of maleate and the methylene protons (CCH_2C=O, 2.90 ppm for **2-TPT**, 2.88 ppm for **2-IDipp**) of the products.

2-TPT; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.81 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H), 1.19 (m, 4H), 1.31 (m, 2H), 1.54 (m, 2H), 2.90 (s, 2H), 3.47 (t, J = 6.6 Hz, 2H), 3.97 (t, J = 6.9 Hz, 2H), 7.22-7.77 (m, 15H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.8, 13.9, 19.2, 30.8, 31.2, 33.5, 61.9, 62.3, 64.3, 119.0, 122.8, 125.4, 127.3, 127.4, 127.9, 128.5, 128.7, 129.2, 129.4, 129.7, 130.6, 135.8, 140.8, 150.4, 155.7, 167.4, 174.2. HRMS (ESI) m/z: calcd for C$_{32}$H$_{35}$N$_3$O$_4$ [M+H]$^+$ 526.27058, found 526.2706. IR (ATR): 2959, 1724, 1642, 1594, 1524, 1494, 1455, 1407, 1284, 1260, 1167, 1092, 1025,966, 917, 801, 758, 731, 692 cm^{-1}.

2-IDipp; ^{1}H NMR (400 MHz, CDCl$_3$) δ: 0.72 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H), 1.00-1.41 (m, 32H), 2.88 (s, 2H), 2.97 (m, 4H), 3.41 (t, J = 6.6 Hz, 2H), 3.61 (t, J = 6.9 Hz, 2H), 6.52 (s, 2H), 7.17 -7.37 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 13.8, 13.9, 19.1, 22.7, 25.5, 28.8, 30.7, 31.5, 34.5, 61.2, 63.3, 119.5, 123.9, 124.3, 129.1, 135.1, 146.1, 156.0, 166.6, 172.8. HRMS (ESI) m/z: calcd for C$_{39}$H$_{56}$N$_2$O$_4$ [M+H]$^+$ 617.4318, found 617.4318. IR (ATR): 2960, 2870, 1740, 1658, 1518, 1456, 1414, 1384, 1362, 1259, 1231, 1200, 1156,1113, 1060, 1034, 931, 802, 731 cm^{-1}.

Synthesis of Unsaturated Polyesters

P1 and **P4** were prepared from maleic anhydride and 1,4-butanediol or diethylene glycol using 0.5 mol% Sc(OTf)$_3$ according to a previous report[4]. **P1**: cis selective, M_n = 6,800, M_w/M_n= 1.5 (GPC using THF as the eluent), M_n = 3,900, M_w/M_n = 5.0 (GPC using CHCl$_3$ as the eluent), T_g = −30 °C, T_m = 27 °C. P4: M_n = 4,000, M_w/M_n = 1.5, (GPC using THF as the eluent), T_g = − 13 °C. **P2** was prepared by the isomerization of **P1** catalyzed by NHEt$_2$ according to previous reports[4, 18]. **P2**: *trans* selective, M_n = 3,300, M_w/M_n = 3.7 (GPC using CHCl$_3$ as the eluent), T_g = 16 °C. **P3** was prepared from maleic anhydride and ethylene glycol using 0.5 mol% *p*-toluenesulfonic acid according to a previous report.[50] **P3**: *cis/trans* = 89/11, M_n = 2500, M_w/M_n = 1.3 (GPC using THF as the eluent), T_g = −5 °C.

Post-polymerization Modification by the Michael Addition of NHC

TPT (71 mg, 0.24 mmol) was added to a solution of **P1** (201 mg, 1.18 mmol (monomer unit)) in CH_2Cl_2 (5.9 mL). The mixture was stirred for 2 h at room temperature, and then CS_2 (0.1 mL) was added. After the evaporation of volatiles, the crude mixture was dissolved in a small amount of $CHCl_3$, followed by precipitation into a mixture of Et_2O and MeOH (16/1) to give **P1-TPT** (180 mg, 66%). The other polymers, **P1-IDipp**, **P2-TPT**, **P3-TPT**, and **P4-TPT**, were synthesized in the same way. For ^1H and ^{13}C NMR spectra, see the Supplementary Information.

Post-polymerization Modification by the Michael Addition of NHC and Transfer Hydrogenation

P1 (156 mg), distilled water (1.38 mmol, 24.8 mg), TPT (0.46 mmol, 137 mg), and THF (5.0 mL) were added to a vial for microwave experiment. The vial was sealed and stirred at 120 °C for 2 h. CS_2 (0.1 mL) was added to the mixture and the volatiles were evaporated. The crude product was dissolved in a small amount of $CHCl_3$, and precipitated into Et_2O/MeOH (16:1) to give the product (169 mg) in 82% yield. The other polymers, **P1-TPT-H**, **P3-TPT-H**, and **P4-TPT-H** were synthesized in the same way.

Cross-linking of **P1-TPT** *with Styrene*

P1-TPT (118 mg), styrene (176 mg, 1.69 mmol), and AIBN (14.7 mg, 0.0895 mmol) were added to a test tube. After three freeze-pump-thaw cycles, the mixture was stirred at 60 °C for 20 h. The evaporation of styrene gave quantitative amounts of the resin (294 mg).

Acknowledgements

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Titles and legends to figures

Table 1. Reactions of NHCs with dibutyl fumarate or maleate: Michael addition or isomerization.

Scheme 1. Isomerization of **1a** catalyzed by ItBu.

Table 2. Post-polymerization modification of unsaturated polyesters by the Michael addition of TPT and IDipp.

Figure 1. Relationship between the composition ratio (x) and the T_g of **P1-TPT** (filled circles) and **P1-IDipp** (filled squares).

Table 3. Solubility of the obtained polymers.

Table 4. Post-polymerization modification of the unsaturated polyesters by simultaneous Michael addition of TPT and transfer hydrogenation.