HOKKAIDO UNIVERSITY

Title	Ring-opening alternating copolymerization of cyclic anhydrides and isobutylene oxide using organobase catalysts
Author(s)	Sugiyama, Moeno; Suzuki, Ryota; Ayakawa, Hiroto et al.
Citation	Polymer journal, 57(11), 1153-1163 https://doi.org/10.1038/s41428-025-01087-9
Issue Date	2025-11
Doc URL	https://hdl.handle.net/2115/98048
Rights	This version of the article has been accepted for publication, after peer review (when applicable) and is subject to Springer Nature's AM terms of use, but is not the Version of Record and does not reflect post-acceptance improvements, or any corrections. The Version of Record is available online at: http://dx.doi.org/10.1038/s41428-025-01087-9
Type	journal article
File Information	(Revised)10161_1_merged_1753231015.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Ring-opening Alternating Copolymerization of Cyclic Anhydrides and Isobutylene Oxide using Organobase Catalysts

Running head: A new method for crystalline polyester synthesis

Moeno Sugiyama,[1] Ryota Suzuki,[2] Hiroto Ayakawa,[1] Tianle Gao,[2] Feng Li,*[2] Takuya Yamamoto,[2] Takuya Isono,[2] Toshifumi Satoh*[2,3,4]

[1] Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, 060-8628, Japan

[2] Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

[3] List Sustainable Digital Transformation Catalyst Collaboration Research Platform, Institute for Chemical Reaction Design and Discovery, Hokkaido University, Sapporo, 001-0021 Japan

[4] Department of Chemical & Materials Engineering, National Central University, Taoyuan 320317, Taiwan

E-mail: feng.li@eng.hokudai.ac.jp, satoh@eng.hokudai.ac.jp

Abstract (up to 200 words)

Ring-opening alternating copolymerization (ROAC) of cyclic anhydrides and epoxides is a promising approach for the well-controlled synthesis of polyesters with versatile structures. ROAC typically yields amorphous polyesters owing to challenges in controlling the main-chain stereochemistry, whereas most applied polyesters are crystalline. Isobutylene oxide (IBO), a highly symmetric epoxide, can overcome this issue, thus facilitating the synthesis of crystalline polyesters via ROAC. However, low reactivity and potential side reactions remain major obstacles to achieving an IBO-based ROAC in a controlled manner. In this study, we successfully developed a well-controlled ROAC of cyclic anhydrides and IBO using environmentally benign organobase catalysts. Using *t*-BuP$_2$ as a catalyst, the ROAC of phthalic anhydride (PA) and IBO proceeds smoothly, yielding crystalline P(PA-*alt*-IBO) with narrow molecular weight distribution ($Đ \leq 1.1$). This method was extended to other cyclic anhydrides and initiators, enabling the synthesis of polyesters with diverse structures. Additionally, this ROAC system was applied to the synthesis of copolymers, including statistical copolymer of P(PA-*alt*-IBO) and P(PA-*alt*-butylene oxide), as well as block copolymer comprising P(PA-*alt*-IBO) and poly(trimethylene carbonate). This study not only expands the scope of epoxides in ROAC but also provides a straightforward and precise strategy for synthesizing crystalline polyesters and further macromolecular designs.

Keywords (2-7): crystalline polyesters, isobutylene oxide, ring-opening alternating copolymerization, organobase catalyst, self-switchable polymerization

Introduction

Polyesters are an important class of polymer materials, with the most representative example being polyethylene terephthalate (PET), which accounts for approximately 13% of total plastic usage worldwide [(1)]. With increasing awareness of the environmental issues caused by plastics, polyesters have been regarded as environmentally friendly alternatives to nondegradable polyolefins because of their hydrolyzable nature, which stems from the ester moieties in their main chains. Polyesters are primarily synthesized through two methods: polycondensation of diols and dicarboxylic acids and ring-opening polymerization (ROP) of cyclic esters. In addition, the ring-opening alternating copolymerization (ROAC) of cyclic anhydrides and cyclic ethers, particularly epoxides, has emerged as an attractive alternative. This method is favored because of its controllable polymerization behavior via a chain-growth polymerization mechanism and the versatility of the polyester structures achieved by varying the combinations of cyclic anhydrides and epoxides [(2) – (4)].

For practical applications, crystalline polyesters such as PET and polylactic acid (PLA) are far more widely used than their amorphous analogs. Crystalline polyesters are typically synthesized via polycondensation or ROP. By contrast, most polyesters obtained through ROAC are amorphous, primarily because of the use of racemic or meso-epoxide monomers in catalytic systems that lack or exhibit low stereoselectivity [(2)]. The limited successful examples of synthesizing crystalline polyesters via ROAC typically rely on the use of enantiopure epoxide monomers or sophisticated chiral catalysts to achieve stereoselective polymerization, thus realizing a high tacticity control level [(5) – (10)]. For example, Coates *et al.* used enantiopure propylene oxide (PO) in ROAC with succinic anhydride (SA). The obtained enantiopure P(SA-*alt*-PO) is not only crystalline but also forms a more thermally stable stereocomplex with the P(SA-*alt*-PO) made from the opposite enantiomer. [(7)] Lu *et al.* reported a highly enantioselective ROAC of racemic or meso-epoxides by an enantiopure chiral dinuclear Al(III) catalyst. [(5)]

While significant efforts are required to achieve tacticity control, the use of achiral and symmetric

monomers, which circumvent the issue of tacticity, offers a straightforward approach for synthesizing crystalline polymers. However, only a few examples of ROAC using symmetric epoxides such as ethylene oxide (EO) and isobutylene oxide (IBO) have been reported. EO is highly flammable and toxic and is difficult to handle [(11) – (13)]. IBO, which has a symmetric 1,1-dimethyl substitution, is an attractive monomer often used in cationic (co)polymerization [(14)]. To the best of our knowledge, only two successful examples of ROAC of IBO with cyclic anhydrides have been reported to date. Coates *et al.* achieved the ROAC of IBO with diglycolic anhydride (DGA) using a zinc complex catalyst [(6)], while Zhang *et al.* developed a heterogeneous zinc-cobalt complex for the ROAC of IBO with various cyclic anhydrides [(15)]. Both approaches rely on transition-metal complexes, which may lead to metal residues in the final product. Additionally, these polymerization methods resulted in relatively broad dispersities ($Đ$ = 1.5–1.7) and undefined chain-end functionalities, limiting their utility in block copolymer synthesis or other chain-end functionalization applications. Organocatalyzed ROAC of epoxides and cyclic anhydrides has been reported as an environmentally benign alternative to transition metal complex catalysts [(16), (17)]. Among them, commercially available organobase catalysts show high reactivity with a good level of control of polymerization [(18), (19)]. In this study, we demonstrate the use of organobase catalysts for the ROAC of IBO and cyclic anhydrides to synthesize crystalline polyesters. This environmentally friendly approach ensures superior polymerization control with low dispersity ($Đ \leq 1.1$). Moreover, it has been utilized in terpolymerization to synthesize statistical copolymers or block copolymers with different third monomers in one-pot and one-step (**Figure 1**).

(Figure 1)

Results and Discussion

Organobase-Catalyzed ROAC of Phthalic anhydride (PA) and Isobutylene oxide (IBO): Optimization of Polymerization Condition

The optimization began with the screening of organocatalysts, with a particular focus on organobase catalysts, based on our previous research experience with ROAC (**Scheme 1**) [(20) – (24)]. The ROAC of PA and IBO was selected as the model polymerizations for this study. Polymerization was conducted under bulk conditions at 80 ºC, using 1,4-benzenedimethanol (BDM) as a difunctional initiator with the ratio of $[PA]_0/[IBO]_0/[BDM]_0/[catatalyt] = 50/200/1/1$. Initially, phosphazene bases *t*-BuP_1, *t*-BuP_2, and *t*-BuP_4 were examined. When using *t*-BuP_1, the conversion of PA ($conv._{PA}$) reached 77.9% after 4 h (**Table 1**, **Figures S1** and **S3**, Run 1). The number-average molecular weight via size-exclusion chromatography ($M_{n,\,SEC}$ = 5,500) was relatively high, and the obtained polymer exhibited a very narrow dispersity ($Đ$ = 1.07). The molecular weight determined by nuclear magnetic resonance (NMR) ($M_{n,\,NMR}$ = 8,160) of the obtained polymer showed good agreement with the theoretical molecular weight ($M_{n,\,theo}$ = 8,720) calculated based on monomer conversion. When *t*-BuP_2 was used as the catalyst, the polymerization rate significantly increased, achieving a PA monomer conversion of 79.7% within 3 h (**Table 1**, Run 2). The turnover frequency (TOF) was 13.3 h^{-1}, approximately three times that obtained with *t*-BuP_1 (TOF = 4.39 h^{-1}) (**Figure S4**). The polymer dispersity ($Đ$ = 1.05) remained low, even with the increased polymerization rate (**Figure 2A**). Moreover, $M_{n,\,NMR}$ (10,700) and $M_{n,\,theo.}$ (8,920) were in relatively good agreement, indicating improved polymerization control (**Figure S2)**. Further increasing the basicity of the phosphazene base by using *t*-BuP_4, a similar polymerization rate (TOF = 13.6 h^{-1}) was observed as that using *t*-BuP_2. The polymer product was obtained with slightly broader dispersity with a small shoulder peak in the SEC trace ($Đ$ = 1.09) (run 3 in **Table 1** and **Figure S7**). The similar polymerization rates obtained with *t*-BuP_2 and *t*-BuP_4 suggest that beyond a certain basicity threshold, the organobase catalyst completely deprotonates the propagating chain end, generating naked anions [(18), (23)]. In addition to the phosphazene-type organobase catalysts, other basic organocatalysts were examined for ROAC (runs 4–5 in **Table 1**). Alkali metal carboxylates such as cesium pivalate (CsOPiv) are simple, efficient, and industrially relevant catalysts for the ROP of cyclic esters and the ROAC of

cyclic anhydrides and epoxides [20] – [22], [25]. When CsOPiv was used as the catalyst in the ROAC of PA and IBO, polymerization proceeded in a highly controlled manner but at a much slower rate than when using *t*-BuP$_2$ (run 4 vs. run 2 in **Table 1**). Tetramethylammonium acetate (TMAA) is an effective catalyst for ROAC of cyclic anhydrides and epoxides in our recent finding [26]. When applied to the ROAC of PA and IBO, TMAA exhibited catalytic performance between that of CsOPiv and *t*-BuP$_2$. However, the resulting polymer had a broader molecular weight distribution ($Đ$ = 1.24) with a bimodal SEC trace, presumably due to TMAA functioning as both a catalyst and a monofunctional initiator (run 5 in **Table 1** and **Figure S7**).

The ^{1}H NMR spectrum of the product obtained from run 2 (**Table 1**) confirms the presence of signals corresponding to the desired P(PA-*alt*-IBO) structure, with clear assignments for each proton of the repeating units and initiator (**Figures 2B** and **S6**). The structure of P(PA-*alt*-IBO) was also confirmed using ^{13}C NMR spectroscopy, in which only two peaks corresponding to carbonyl carbons were observed, indicating a regular head-to-tail connection (**Figure 3**) [15]. To further characterize the polymer, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy (MS) was performed on P(PA-*alt*-IBO). Although detailed structural features such as the initiator and chain ends could not be identified, the periodic peak spacing (220.4 Da) matched the sum of the molecular weights of PA and IBO (220.2 Da), supporting the formation of an alternating copolymer (**Figure S8**). Notably, Zhang *et al.* reported isobutyral (IBA) and cyclic acetal-isobutyleneisobutyral (IBIB) as byproducts of the ROAC of IBO and maleic anhydride (MA) using various catalysts, including phosphazene catalysts [15]. However, in the ROAC of IBO and PA using *t*-BuP$_2$ catalyst, no such byproducts were observed during the polymerization. Among the screened catalysts, *t*-BuP$_2$ exhibited excellent polymerization control and a high polymerization rate, making it an optimal organocatalyst. To gain further insights into the polymerization mechanism, kinetic studies were conducted using *t*-BuP$_2$ catalyst. The conversion of the PA monomer increased linearly with polymerization time (**Figure 4A, S3, S4**), indicating that the polymerization followed zero-order

kinetics with respect to the PA concentration. Considering that IBO was added in large excess (four times) compared with PA, these polymerization kinetics indicate that PA is not involved in the rate-determining step. Therefore, it leaves the only possibility to be the incorporation of PA was the fastest step in the polymerization, whereas the incorporation of IBO was the rate-determining step (**Figure 5**). This polymerization is consistent with previous reports on ROAC using cyclic anhydrides and other epoxides [18]. Regarding the regioselectivity of IBO, it is commonly known that the S_N2-type nucleophilic attack takes place at the less sterically hindered methylene carbon under neutral to basic conditions [27], [28]. The DFT calculation showed that the activation energy of ring-opening of IBO at the methylene carbon is 6.2 kcal/mol lower than that at the quaternary carbon (**Figure S31**). It further corroborated the regioselectivity and head-to-tail sequence. With the consumption of PA monomer, the $M_{n,NMR}$ increased linearly, while the dispersity ($Đ$) remained below 1.10, confirming a well-controlled polymerization process (**Figure 4B**).

To synthesize P(PA-*alt*-IBO) with different molecular weights, the monomer-to-initiator ratio, that is, the target degree of polymerization (DP), was adjusted to 100 and 150 in ROAC (runs 6 and 7 in **Table 1**). The obtained P(PA-*alt*-IBO)s had correspondingly higher molecular weights. The $M_{n,NMR}$ values were in reasonable agreement with $M_{n,theo.}$ The SEC traces of P(PA-*alt*-IBO) polymers with target DP values of 50, 100, and 150 showed narrow distribution ($Đ$ = 1.05–1.13), although a small shoulder peak was observed in the one having a target DP 150 (**Figure S10**). These results demonstrated that *t*-BuP_2 catalyzed ROAC of PA and IBO is well-controlled over a relatively broad range of molecular weights.

(Scheme 1)

(Table 1)

(Figure 2)

(Figure 3)

(Figure 4)

(Figure 5)

Initiator and Cyclic Anhydride Scope

After optimizing the catalytic conditions, various initiators and cyclic anhydrides were investigated to evaluate the versatility of the polymerization system (**Scheme 2**). First, alcohol initiators with different numbers of hydroxyl groups were examined. In addition to the bifunctional BDM described above, 3-phenyl-1-propanol (PPA) and trimethylolpropane (TMP) were also tested as mono- and trifunctional alcohol initiators, respectively (runs 1 and 2 in **Table 2**, **Figures S11–S14**). In both cases, the polymerization proceeded in a well-controlled manner, yielding polymers with very narrow dispersity indices ($Đ$ = 1.03–1.04) (**Figures S12 and S14**). The three-armed star-shaped P(PA-*alt*-IBO) was obtained using a TMP initiator. Based on the alternating polymerization mechanism, initiation should be feasible not only for alcohols but also for carboxylic acids. To confirm this, benzoic acid (BA) was used as the initiator (run 3 in **Table 2**, **Figures S15–S17**). Consequently, the polymerization proceeded at a rate comparable to that achieved using the PPA initiator, with 59.0% conversion of PA after 3 h. However, the resulting polymer showed a bimodal distribution in SEC with relatively broad dispersity ($Đ$ = 1.19). The $M_{n,SEC}$ of the lower-molecular-weight peak was approximately half that of the higher-molecular-weight peak (**Figure S16 and S17**). These peaks presumably correspond to P(PA-*alt*-IBO) originating from BA and water, respectively.

Following initiator screening, the monomer scope of the cyclic anhydride was investigated. Given the successful polymerization using PA, 5-norbornene-2,3-dicarboxylic anhydride (NA), which has a similar fused-ring structure, was first tested. When using NA, the NA conversion reached 65.0% after 7 h. Although the polymerization rate was slower than that of PA (run 4 in **Table 2**), it was well-controlled and gave the corresponding polymer P(NA-*alt*-IBO) with a narrow dispersity ($Đ$ = 1.09) (**Figures S18 and S19**). Monocyclic anhydrides, including diglycolic anhydride (DGA), glutaric anhydride (GA), and maleic anhydride (MA), were tested in ROAC with IBO (runs 5–7 in **Table 2**). When DGA was used, the polymerization proceeded smoothly, reaching nearly complete conversion after 5 h (run 5). The resulting P(DGA-*alt*-IBO) exhibited slightly broader dispersity compared to

those obtained using PA and NA ($Đ$ = 1.26) (**Figure S22**). The ^{1}H NMR spectrum of the obtained polymer matched the data previously reported by Coates *et al*., confirming the successful synthesis of P(DGA-*alt*-IBO) [6]. However, the regioselectivity was not well-controlled, and the underlying cause remains unclear (**Figure S20, S21**). In contrast to the moderate success achieved with DGA, the polymerization with GA was entirely different (Run 6). Although GA reached nearly full conversion after 10.5 h, the SEC analysis showed only peaks corresponding to low-molecular-weight compounds (M_n < 1 kDa) (**Figure S23**). The ^{1}H NMR spectrum of the obtained P(GA-*alt*-IBO) was relatively complicated with unidentified byproducts (**Figure S24**). The stark contrast between the results using DGA and GA may be attributed to the significantly higher reactivity of DGA toward alcohol nucleophiles compared to GA [29], thereby reducing undesired side reactions, for example, chain transfer. Finally, the ROAC of MA and IBO was examined (run 7); however, the expected P(MA-*alt*-IBO) was not observed by ^{1}H NMR. Instead, several isomerization byproducts were detected, which is consistent with the findings previously reported by Zhang *et al*. when using this specific cyclic anhydride monomer [15].

(Scheme 2)

(Table 2)

Polymer material properties

After monomer scope screening, the material properties of the obtained polyesters were evaluated, with a focus on P(PA-*alt*-IBO). Thermogravimetric analysis (TGA) revealed that P(PA-*alt*-IBO) remains thermally stable up to temperatures around 200 °C, with a 5% weight loss temperature ($T_{d,5\%}$) of 208 °C (**Figure S25**). Differential scanning calorimetry (DSC) analysis on the solvent-cast sample showed that P(PA-*alt*-IBO) exhibits a relatively high glass transition temperature (T_g) of 56.4 °C and a melting point (T_m) of 118.0 °C (**Figure 6A**), suggesting its crystalline nature. These thermal properties were consistent with those previously reported by Zhang *et al* [15]. A comparison of T_g value between P(PA-*alt*-IBO) and its amorphous structural isomer, atactic P(PA-*alt*-BO) (BO = 1,2-butylene oxide), revealed that P(PA-*alt*-BO) has a lower T_g of 41.3 °C [30]. This difference is likely due to the higher flexibility of the ethyl side chain in P(PA-*alt*-BO) and reduced mainchain flexibility because of dimethyl substitution in P(PA-*alt*-IBO) (**Table S1**). The crystalline nature of P(PA-*alt*-IBO) was further investigated using wide-angle X-ray scattering (WAXS) and polarized optical microscopy (POM). The WAXS profile showed sharp scattering peaks, confirming the crystalline characteristics of P(PA-*alt*-IBO) with a peak pattern consistent with a previous report (**Figure 6B**) [15]. The crystallinity of P(PA-*alt*-IBO) is 42.4%. Under POM, the solvent-annealed P(PA-*alt*-IBO) sample exhibited clear Maltese cross patterns, indicating the formation of spherulites (**Figure 6C, D**).

(Figure 6)

Terpolymerization: synthesis of statistical and block copolymers

Copolymers synthesized from two or more monomers with different sequences, such as random or block, can exhibit drastically different material properties compared to those of homopolymers and polymer blends. Therefore, the incorporation of a third monomer into this newly developed cyclic anhydride/IBO ROAC polymerization system to evaluate its polymerization behavior is crucial for designing functional polymer materials. Moreover, the exceptional level of control, especially over dispersity, makes such an investigation possible in this organobase-catalyzed cyclic anhydride/IBO ROAC, compared to previously reported methods.

BO, a structural isomer of IBO, has been used in ROAC with cyclic anhydrides in various catalytic systems, including organocatalysts [30]. A comparison of the reactivities of BO and IBO in ROAC could provide valuable insights into the polymerization behavior of IBO. Therefore, the terpolymerization of BO, IBO, and PA was investigated (**Figure 7A**). Polymerization was performed at a ratio of $[PA]_0/[IBO]_0/[BO]_0/[BDM]_0/[t\text{-}BuP_2]$ = 50/100/100/1/1 at 80 °C in bulk. After 1.5 h, the monomer conversions of PA, BO, and IBO reached 76%, 22%, and 14%, respectively, indicating that BO exhibited a slightly higher reactivity than IBO in ROAC with PA (**Figure 7B**). Density functional theory (DFT) calculation of the ring-opening step of BO and IBO by benzoate anion was conducted. The activation energy of BO ring-opening is 1.5 kcal/mol lower than that of IBO, aligning well with the experimental results (**Figure S31**). The reactivity ratios, *r*(BO) and *r*(IBO), were determined to be 1.67 and 0.594, respectively, using the nonterminal model based on the reaction mechanism (**Figures 7C and S26**) [31]. Based on these polymerization kinetics, a statistical (nearly random) copolymer, P(PA-*alt*-BO)-*stat*-P(PA-*alt*-IBO), was obtained. The narrow dispersity ($Đ$ = 1.07) of the terpolymer exhibited good control in this terpolymerization (**Figure S27** and **S28**). However, in terms of material properties, P(PA-*alt*-BO)-*stat*-P(PA-*alt*-IBO) was obtained as a sticky liquid, in stark contrast to the solid states of both P(PA-*alt*-BO) (T_g = 41.3 °C) and P(PA-*alt*-IBO) (T_g = 56.4 °C, T_m = 118.0 °C). DSC analysis revealed a significantly low T_g (−10.3 °C) for this terpolymer, deviating

substantially from the expected linear trend between the T_g values of P(PA-*alt*-BO) and P(PA-*alt*-IBO) (**Figure S29** and **Table S1**). Although the reason for this intriguing deviation has not yet been clarified, it could be speculated that the nearly random incorporation of BO and IBO disrupts the polymer chain packing, thus weakening the intermolecular interactions and preventing the formation of possible locally rigid conformational structures that exist in either P(PA-*alt*-BO) or P(PA-*alt*-IBO) [(32)].

After terpolymerization of PA/IBO/BO, which resulted in a statistical copolymer with a nearly random sequence, the incorporation of PA/IBO ROAC in block copolymer synthesis was investigated. Self-switchable polymerization, a one-pot/one-step approach integrating different catalytic polymerization cycles such as the ROAC of cyclic anhydrides and epoxides with the ring-opening polymerization (ROP) of cyclic esters or cyclic carbonates, has gained significant attention [(33),(34)]. Herein, as a proof-of-concept, the terpolymerization of PA, IBO, and trimethylene carbonate (TMC) was investigated. Terpolymerization was conducted at a $[PA]_0/[IBO]_0/[TMC]_0/[t\text{-}BuP_2]/[BDM]_0$ = 40/200/80/1/1 in bulk (**Figure 8A**). The polymerization kinetics showed that the ROAC of PA and IBO proceeded first. Once PA was fully consumed, the ROP of TMC commenced at an even higher rate (**Figure 8B** and **S30**). SEC analysis showed a continuous shift toward the higher molecular weight region even after switching to the ROP of TMC (**Figure 8C**). Diffusion-ordered nuclear magnetic resonance (DOSY NMR) spectroscopy revealed a single diffusion coefficient corresponding to all polymer segments. This confirms the formation of the PTMC-*b*-P(PA-*alt*-IBO)-*b*-PTMC block copolymer (**Figure 8D**). The successful ROP of TMC from the chain end of P(PA-*alt*-IBO) suggested that the IBO-derived tertiary alkoxide initiated the ROP of TMC despite its steric hindrance.

(Figure 7)

(Figure 8)

Conclusion

In this study, we developed an organobase-catalyzed ring-opening alternating copolymerization (ROAC) of cyclic anhydrides and IBO in a well-controlled manner. The phosphazene base *t*-BuP_2 demonstrated superior catalytic activity and molecular weight controllability ($Đ \leq 1.1$), particularly in the ROAC of PA and IBO. The resulting P(PA-*alt*-IBO) exhibited crystallinity with the melting point of 118 °C, because of its symmetric molecular structure. Polyesters with various chemical compositions, chain-end structures, and topologies were obtained using different cyclic anhydrides and initiators. Furthermore, the ROAC of cyclic anhydrides and IBO was successfully integrated with other monomers, including butylene oxide and trimethylene carbonate, resulting in statistical and block copolymers, respectively, demonstrating the potential of this polymerization for the production of functional materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the Polymer Journal website.

Experimental procedure; polymerization kinetic plots; NMR spectra, MALDI-TOF spectra, SEC traces, and DSC and TGA curves of the synthesized polymers.

NOTES

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was financially supported by the Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Scientific Research(A) (24H00766), Grant-in-Aid for Early-Career Scientists (24K17719), Grant-in-Aid for JSPS Research Fellows, the Frontier Chemistry Center (Hokkaido University), the Photo-Excitonic Project (Hokkaido University), the List Sustainable Digital Transformation Catalyst Collaboration Research Platform (List-PF, Hokkaido University), the Project of Junior Scientist Promotion (Hokkaido University), and ENEOS TONENGENERAL Research/Development Encouragement & Scholarship Foundation. R.S. and T.G. gratefully acknowledges the JSPS Fellowship for Young Scientists. We would like to express our gratitude to Dr. Pingyu Jiang from the Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University for his help to the DFT calculation.

AUTHOR CONTRIBUTIONS

CRediT:

Moeno Sugiyama: Writing original draft, Methodology, Visualization, Data curation

Ryota Suzuki: Methodology, Data curation, Funding acquisition,

Hiroto Ayakawa: Methodology,

Tianle Gao: Data curation, Writing – review & editing, Funding acquisition

Feng Li: Supervision, Conceptualization, Methodology, Writing original draft, Writing – review & editing, Funding acquisition.

Takuya Yamamoto: Supervision

Takuya Isono: Supervision, Writing – review & editing

Toshifumi Satoh: Supervision, Conceptualization, Writing – review & editing, Funding acquisition.

REFERENCES

(1) Yang R, Xu G, Tao W, Wang Q, Tang Y. Recycled Polymer: Green Roads for Polyester Plastics. Green Carbon. 2024;2:1–11.
(2) Longo JM, Sanford MJ, Coates GW. Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides with Discrete Metal Complexes: Structure-Property Relationships. Chem Rev. 2016;116:15167–97.
(3) Pappuru S, Chakraborty D. Progress in Metal-Free Cooperative Catalysis for the Ring-Opening Copolymerization of Cyclic Anhydrides and Epoxides. Eur Polym J. 2019;121:109276.
(4) Ryzhakov D, Printz G, Jacques B, Messaoudi S, Dumas F, Dagorne S, Le Bideau F. Organo-Catalyzed/Initiated Ring Opening Co-Polymerization of Cyclic Anhydrides and Epoxides: An Emerging Story. Polym Chem. 2021;12:2932–46.
(5) Li J, Liu Y, Ren WM, Lu XB. Enantioselective Terpolymerization of Racemic and Meso-Epoxides with Anhydrides for Preparation of Chiral Polyesters. PNAS 2020;117:15429–36.
(6) Jeske R C, DiCiccio AM, Coates GW, Alternating Copolymerization of Epoxides and Cyclic Anhydrides: An Improved Route to Aliphatic Polyesters. J Am Chem Soc. 2007;129:11330–1.
(7) Longo JM, Diciccio AM, Coates GW. Poly(Propylene Succinate): A New Polymer Stereocomplex. J Am Chem Soc. 2014;136:15897–900.
(8) Li J, Liu Y, Ren WM, Lu XB. Asymmetric Alternating Copolymerization of Meso-Epoxides and Cyclic Anhydrides: Efficient Access to Enantiopure Polyesters. J Am Chem Soc. 2016;138:11493–6.
(9) Wan ZQ, Longo JM, Liang LX, Chen HY, Hou GJ, Yang S, Zhang WP, Coates GW, Lu XB. Comprehensive Understanding of Polyester Stereocomplexation. J Am Chem Soc. 2019;141:14780–7.
(10) Li J, Ren BH, Chen SY, He GH, Liu Y, Ren WM, Zhou H, Lu XB. Development of Highly Enantioselective Catalysts for Asymmetric Copolymerization of Meso-Epoxides and Cyclic Anhydrides: Subtle Modification Resulting in Superior Enantioselectivity. ACS Catal. 2019;9:1915–22.
(11) Maeda Y, Nakayama A, Kawasaki N, Hayashi K, Aiba S, Yamamoto N. Ring-Opening Copolymerization of Succinic Anhydride with Ethylene Oxide Initiated by Magnesium Diethoxide. Polymer. 1997;38:4719-25.
(12) Wan Z, Ren W, Yang S, Li M, Gu G, Lu X. Reversible Transformation between Amorphous and Crystalline States of Unsaturated Polyesters by Cis – Trans Isomerization. Angew Chem Int Et. 2019;131:17800–4.
(13) O'Kelley L, Swanson B, Bishop-Royse JC. Integrative Literature Review: Ethylene Oxide Exposure Signs and Symptoms. Public Health Nurs. 2023;40:790–809.
(14) Hotta D, Kanazawa A, Aoshima S. Generation of "Living" Species Using Perfluoroalkylsulfonic Acids in Concurrent Cationic Vinyl-Addition and Ring-Opening Copolymerization via Crossover Reactions. Macromolecules. 2018;51:7983–92.
(15) Hu L, Zhang X, Cao X, Chen D, Sun Y, Zhang C, Zhang, X. Alternating Copolymerization of Isobutylene Oxide and Cyclic Anhydrides: A New Route to Semicrystalline Polyesters. Macromolecules. 2021;54:6182–90.
(16) Ryzhakov D, Printz G, Jacques B, Messaoudi S, Dumas F, Dagorne S, Bideau F. Organo-catalyzed/initiated ring opening co-polymerization of cyclic anhydrides and epoxides: an emerging story. Polym. Chem. 2021;12:2932-46.
(17) Zhang X, Zhang C, Zhang X. Organocatalyzed Ring-Opening Copolymerization of Cyclic Anhydride and Cyclic Ether (Acetal). In: Li Z, editor. Organocatalysts in Polymer Chemistry: Synthesis and Applications. Wiley-VCH GmbH; 2025. p. 79-113.
(18) Li H, Zhao J, Zhang G. Self-Buffering Organocatalysis Tailoring Alternating Polyester. ACS Macro Lett. 2017;6:1094–8.
(19) Li H, Luo H, Zhao J, Zhang G. Well-Defined and Structurally Diverse Aromatic Alternating Polyesters Synthesized by Simple Phosphazene Catalysis. Macromolecules. 2018;51:2247–57.
(20) Li F, Suzuki R, Gao T, Xia X, Isono T, Satoh T. Alkali Metal Carboxylates: Simple, Efficient, and Industrial

Relevant Catalysts for Controlled Polymer Synthesis. Bull Chem Soc Jpn. 2023;96:1003–18.
(21) Xia X, Suzuki R, Takojima K, Jiang DH, Isono T, Satoh T. Smart Access to Sequentially and Architecturally Controlled Block Polymers via a Simple Catalytic Polymerization System. ACS Catal. 2021;11:5999–6009.
(22) Gao T, Li F, Suzuki R, Li H, Yamamoto T, Xia X, Isono T, Satoh T. One-Step Synthesis of Poly(Amide Ester)-Based Block Copolymers with Defined Phase Separation Behavior. Macromolecules. 2023;56:8333–43.
(23) Ota I, Suzuki R, Mizukami Y, Xia X, Tajima K, Yamamoto T, Li F, Isono T, Satoh T. Organobase-Catalyzed Ring-Opening Copolymerization of Cyclic Anhydrides and Oxetanes: Establishment and Application in Block Copolymer Synthesis. Macromolecules. 2024;57:3741–50.
(24) Suzuki R, Gao T, Sumi A, Yamamoto T, Tajima K, Li F, Isono T, Satoh T. Synthesis of Amino-Functionalized Polyester via Ring-Opening Alternating Copolymerization of Glycidylamines with Cyclic Anhydrides. Polym. Chem. 2024;15:3349–58.
(25) Saito T, Aizawa Y, Yamamoto T, Tajima K, Isono T, Satoh T. Alkali Metal Carboxylate as an Efficient and Simple Catalyst for Ring-Opening Polymerization of Cyclic Esters. Macromolecules. 2018;51:689–96.
(26) Suzuki R, Takagi S, Matsuda M, Yamamoto T, Tajima K, Li F, Isono T, Satoh T. Synthesis of Polycarbonates and Polyesters via Tetraalkylammonium Salt-Catalyzed Ring-Opening Polymerization. Chem Lett. 2025;54:upae242.
(27) Qiang S, Hu R-B, Yeung Y-Y. Zwitterion-Catalyzed Ring-Opening of Epoxides with Carboxylic Acids. Asian J. Org. Chem. 2023;12:e202200673;
(28) Sujansky SJ, Hoteling GA, Bandar JS. A strategy for the controllable generation of organic superbases from benchtop-stable salts. Chem. Sci. 2024;15:10018–26.
(29) Xia X, Gao T, Li F, Suzuki R, Isono T, Satoh T. Sequential Polymerization from Complex Monomer Mixtures: Access to Multiblock Copolymers with Adjustable Sequence, Topology, and Gradient Strength. Macromolecules 2023;56:92–103.
(30) Zhang J, Wang L, Liu S, Li Z. Phosphazene/Lewis Acids as Highly Efficient Cooperative Catalyst for Synthesis of High-Molecular-Weight Polyesters by Ring-Opening Alternating Copolymerization of Epoxide and Anhydride. J Polym Sci. 2020;58:803–10.
(31) Beckingham BS, Sanoja GE, Lynd NA. Simple and Accurate Determination of Reactivity Ratios Using a Nonterminal Model of Chain Copolymerization. Macromolecules. 2015;48:6922–30.
(32) Huang CC, Du MX, Zhang BQ, Liu CY. Glass Transition Temperatures of Copolymers: Molecular Origins of Deviation from the Linear Relation. Macromolecules. 2022;55:3189–200.
(33) Hu C, Pang X, Chen X. Self-Switchable Polymerization: A Smart Approach to Sequence-Controlled Degradable Copolymers. Macromolecules. 2022;55:1879–93.
(34) Deacy AC, Gregory GL, Sulley GS, Chen TTD, Williams CK. Sequence Control from Mixtures: Switchable Polymerization Catalysis and Future Materials Applications. Journal of the American Chemical Society. 2021;143:10021–40.

Figure legends

Figure 1. (A) Organocatalyzed ROAC of cyclic anhydrides and IBO and (B) the obtained crystalline polyester with polarized optical microscopy (POM) image; (C) application of the ROAC of IBO in one-pot/one-step terpolymerization.

Figure 2. (A) SEC trace of P(PA-*alt*-IBO) catalyzed by *t*-BuP$_2$ (run 2 in Table 1) (eluent, THF; flow rate, 1.0 mL min^{-1}; polystyrene standard); (B) ^{1}H NMR spectrum of P(PA-*alt*-IBO) in $CDCl_3$ (400 MHz) (run 2 in Table 1).

Figure 3. ^{13}C NMR spectrum of P(PA-*alt*-IBO) in $CDCl_3$ (100 MHz) and the expanded spectrum (run 2 in Table 1) (165.0~168.0 ppm).

Figure 4. (A) Kinetic plots for the polymerization of PA and IBO obtained from run 2 in Table 1**.** Each plot shows conv.$_{PA}$ (■) and $Đ$ (■). (B) Dependence of $M_{n,NMR}$ (■) and $Đ$ (■) on PA monomer conversion.

Figure 5. Polymerization mechanism (rate-determining step and regio-selectivity).

Figure 6. (A) First heating DSC curve of P(PA-*alt*-IBO), at the heating rate of 10 °C min^{-1} under nitrogen atmosphere. (B) WAXS profile of P(PA-*alt*-IBO) (λ = 1.50 Å). (C), (D) POM image of P(PA-*alt*-IBO). (Note: the samples tested in this figure are prepared by solvent-casting using THF)

Figure 7. (A) Terpolymerization of PA, IBO, and BO; (B) plots of monomer conversion versus time monitored by the ^{1}H NMR spectrum. (C) the selectivity step of the terpolymerization that determines the reactivity ratio.

Figure 8. (A) Synthesis of block polyesters from the mixture of PA, IBO, and TMC; (B) plots of conv. of monomer PA and TMC versus time. Polymerization of PA, IBO, and TMC was performed at 80 °C using *t*-BuP$_2$ as the catalyst. (C) SEC trace of P(PA-*alt*-IBO)-*b*-PTMC (eluent, THF; flow rate, 1.0 mL min^{-1}; polystyrene standard) and (D) DOSY spectrum in $CDCl_3$ (600 MHz).

Scheme 1. ROAC of PA and IBO using various organocatalysts

Scheme 2. ROAC of cyclic anhydrides and IBO using various initiators.

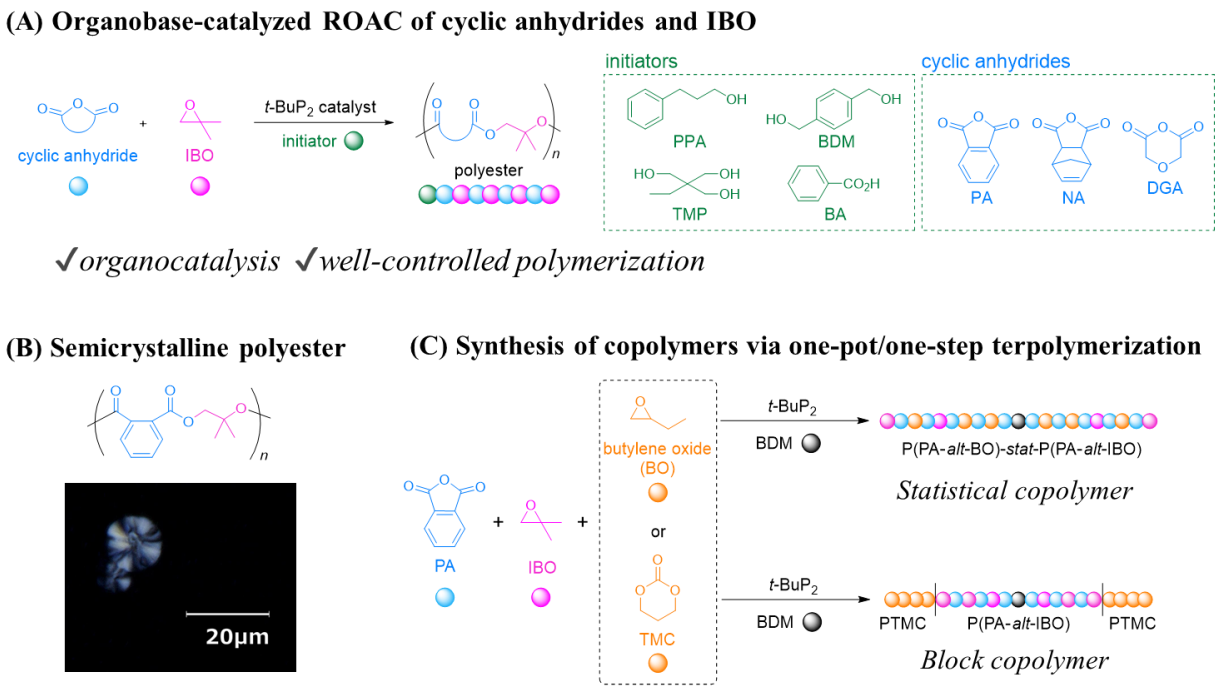

(A) Organobase-catalyzed ROAC of cyclic anhydrides and IBO
cyclic anhydride
IBO
t-BuP2 catalyst
initiator
polyester
initiators
PPA
BDM
TMP
BA
cyclic anhydrides
PA
NA
DGA
✓organocatalysis ✓well-controlled polymerization
(B) Semicrystalline polyester
20μm
(C) Synthesis of copolymers via one-pot/one-step terpolymerization
PA
IBO
butylene oxide (BO)
or
TMC
t-BuP2
BDM
P(PA-alt-BO)-stat-P(PA-alt-IBO)
Statistical copolymer
PTMC
P(PA-alt-IBO)
Block copolymer

Figure 1.

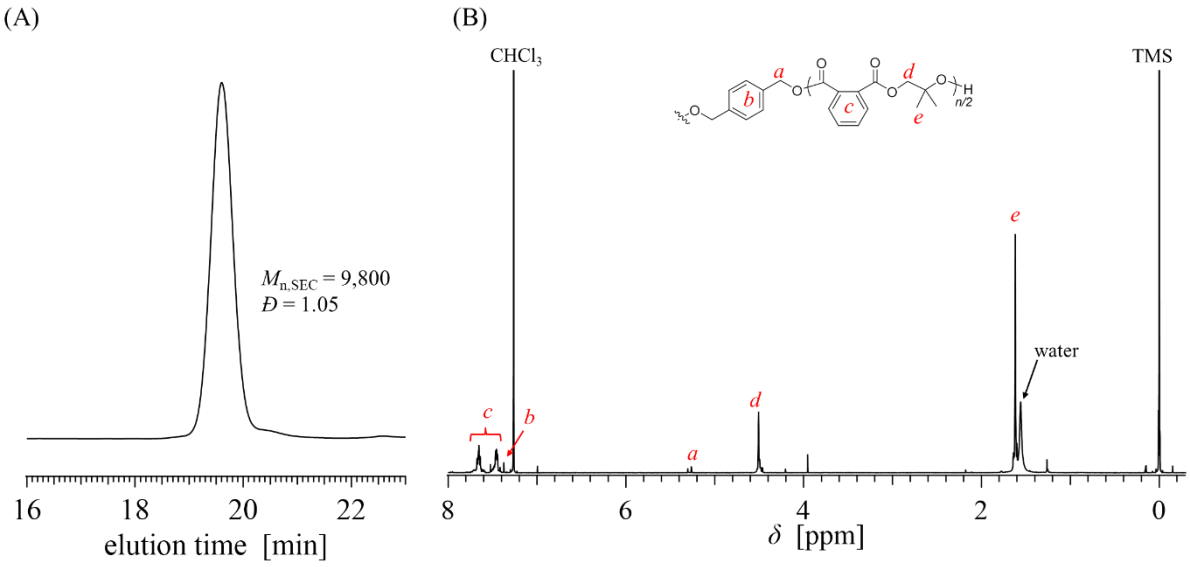

(A)
$M_{n,SEC}$ = 9,800
$Đ$ = 1.05
16
18
20
22
elution time [min]
(B)
$CHCl_3$
TMS
a
b
c
d
e
n/2
water
8
6
4
2
0
δ [ppm]

Figure 2.

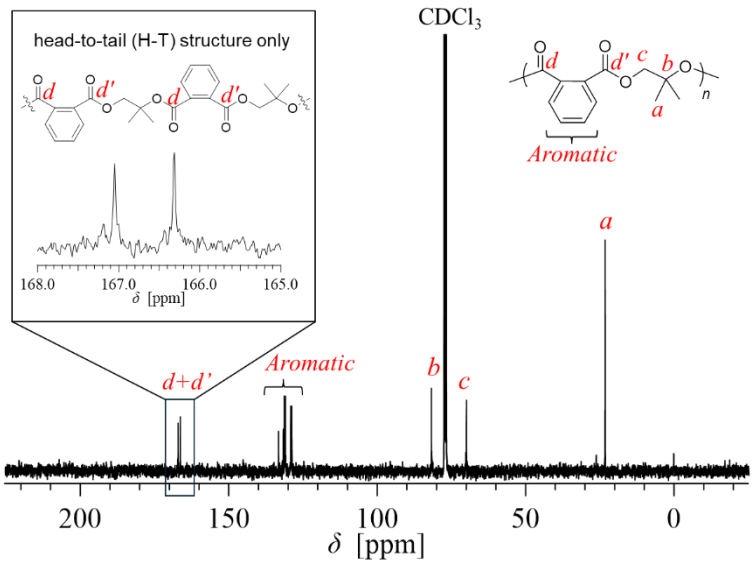

head-to-tail (H-T) structure only
d
d'
d
d'
168.0
167.0
166.0
165.0
δ [ppm]
CDCl3
d
d'
c
b
a
n
Aromatic
a
d+d'
Aromatic
b
c
200
150
100
50
0
δ [ppm]

Figure 3.

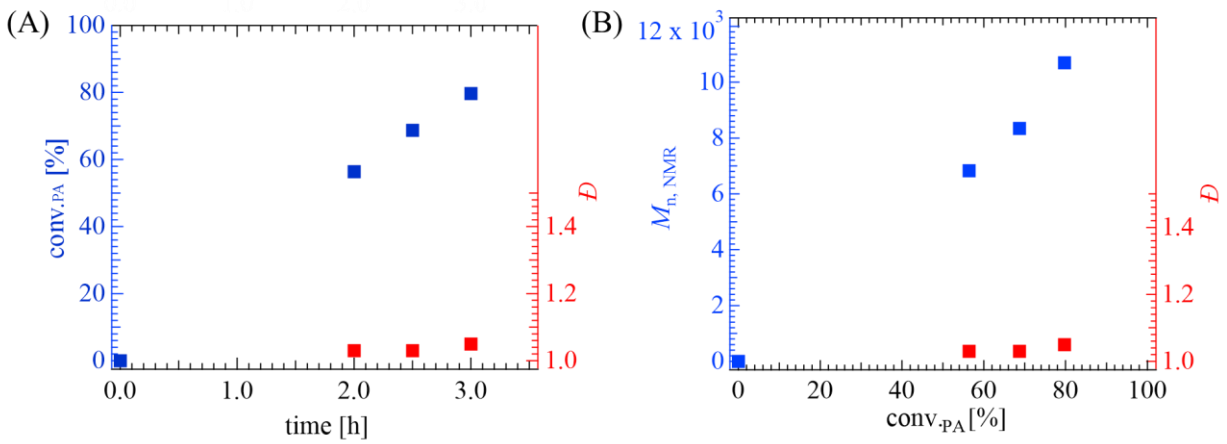

(A)
100
80
60
40
20
0
conv.PA [%]
1.4
1.2
1.0
Đ
0.0
1.0
2.0
3.0
time [h]
(B)
12 x 10^3
10
8
6
4
2
0
Mn, NMR
1.4
1.2
1.0
Đ
0
20
40
60
80
100
conv.PA [%]

Figure 4.

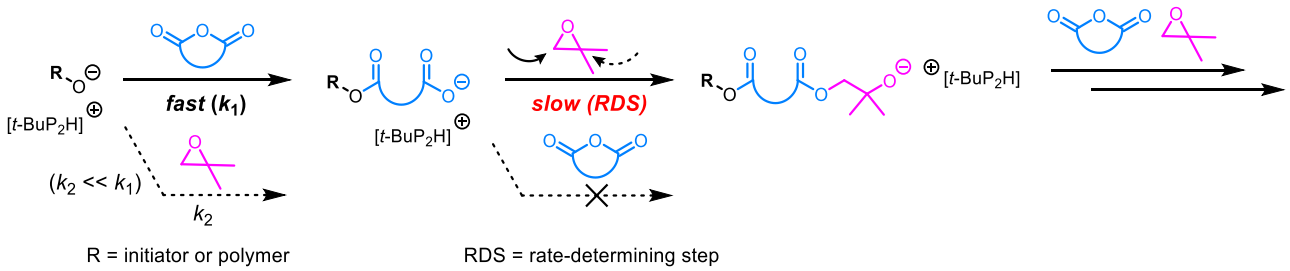

fast (k_1)
slow (RDS)
[t-BuP2H]
(k_2 << k_1)
k_2
R = initiator or polymer
RDS = rate-determining step

Figure 5.

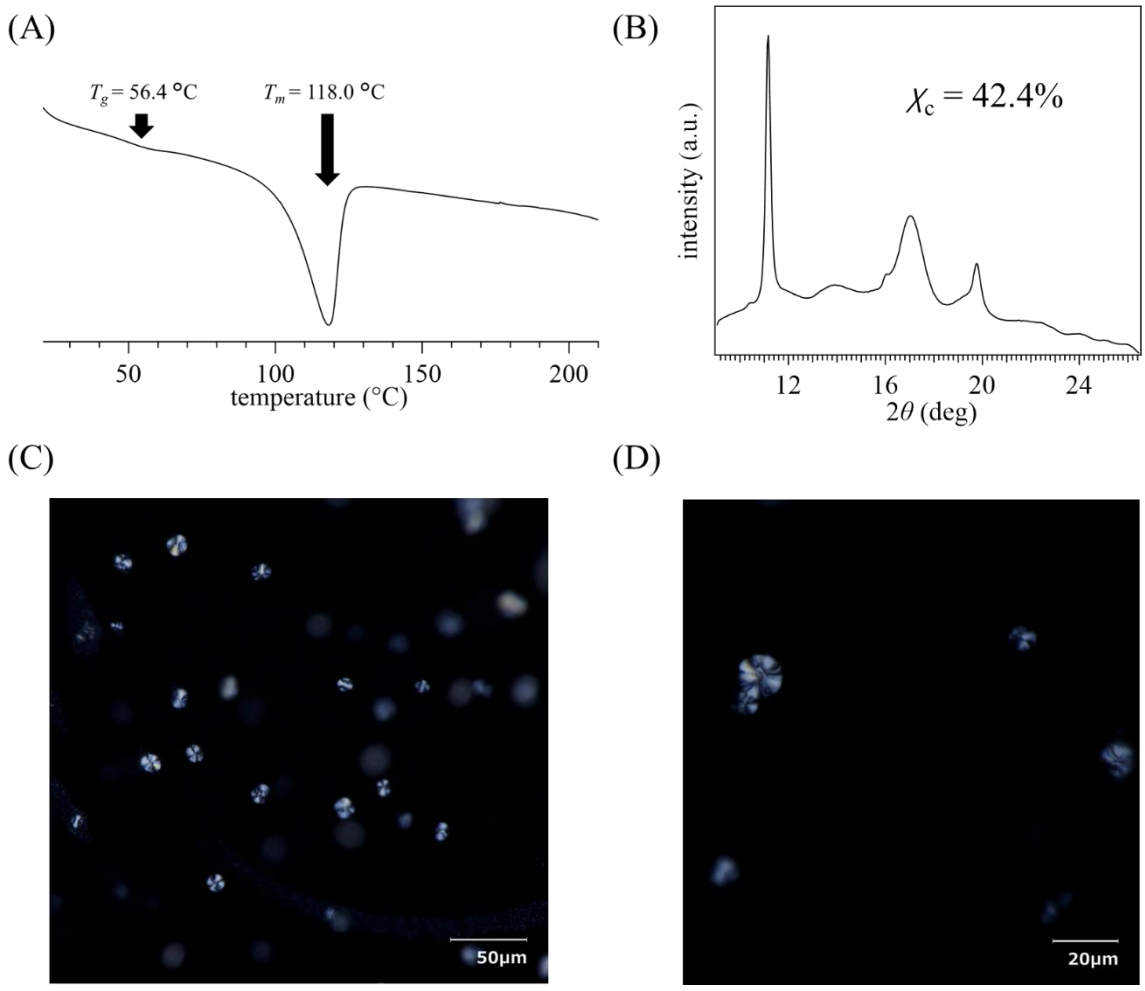

(A)
T_g = 56.4 °C
T_m = 118.0 °C
50
100
150
200
temperature (°C)
(B)
χ_c = 42.4%
intensity (a.u.)
12
16
20
24
2θ (deg)
(C)
50μm
(D)
20μm

Figure 6.

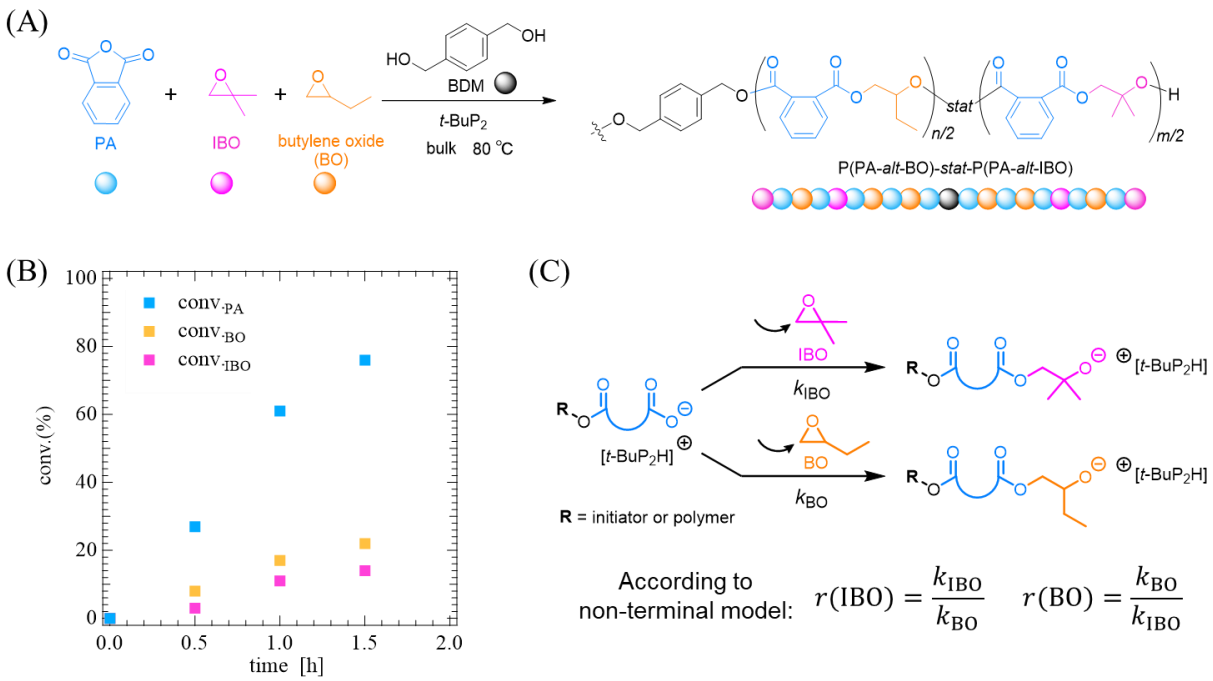

(A)
PA
IBO
butylene oxide
(BO)
HO
OH
BDM
t-BuP2
bulk 80 °C
stat
n/2
m/2
H
P(PA-alt-BO)-stat-P(PA-alt-IBO)
(B)
conv.-PA
conv.-BO
conv.-IBO
conv.(%)
time [h]
(C)
IBO
kIBO
BO
kBO
[t-BuP2H]
R = initiator or polymer
According to
non-terminal model:
r(IBO) = kIBO/kBO
r(BO) = kBO/kIBO

Figure 7.

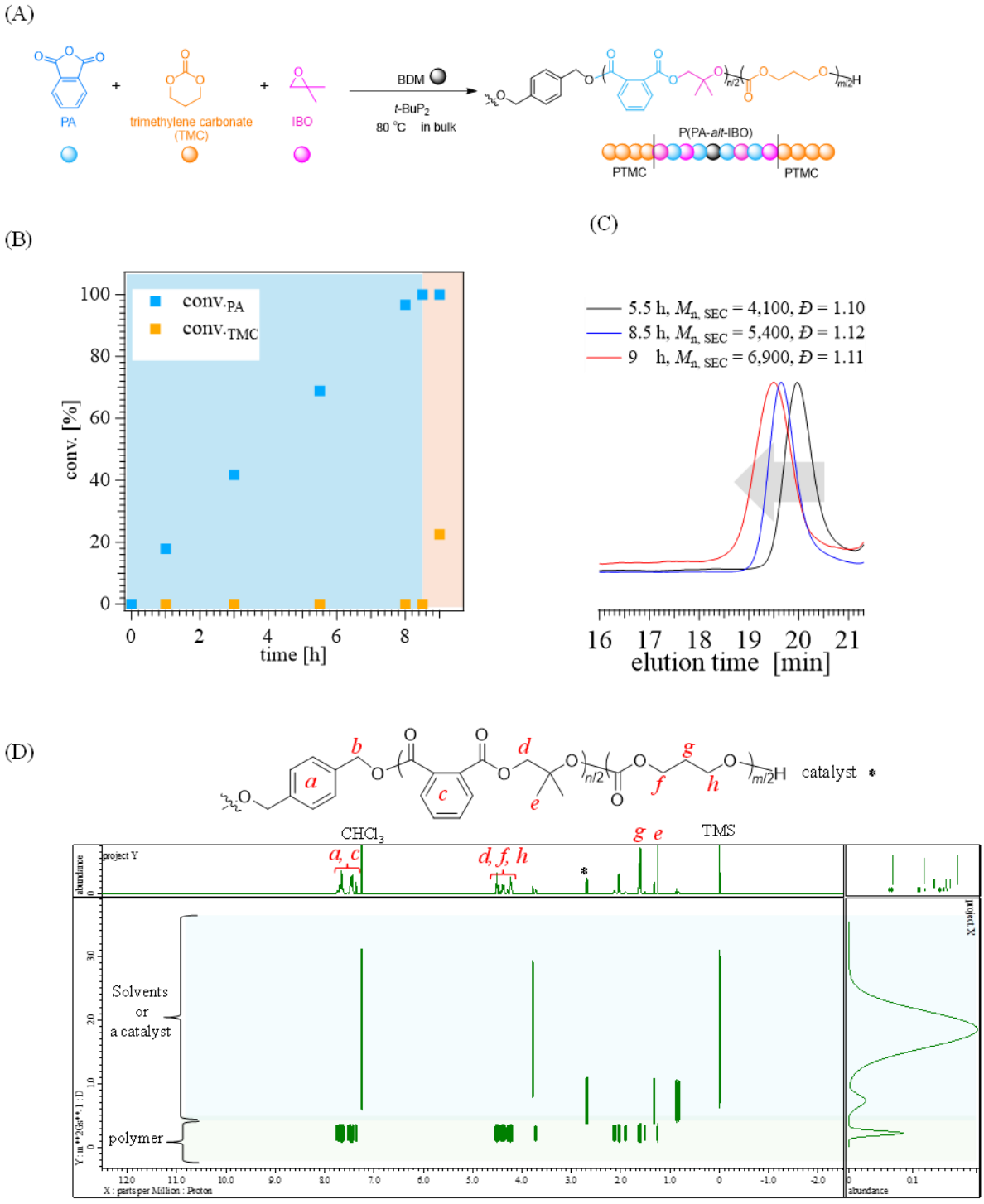
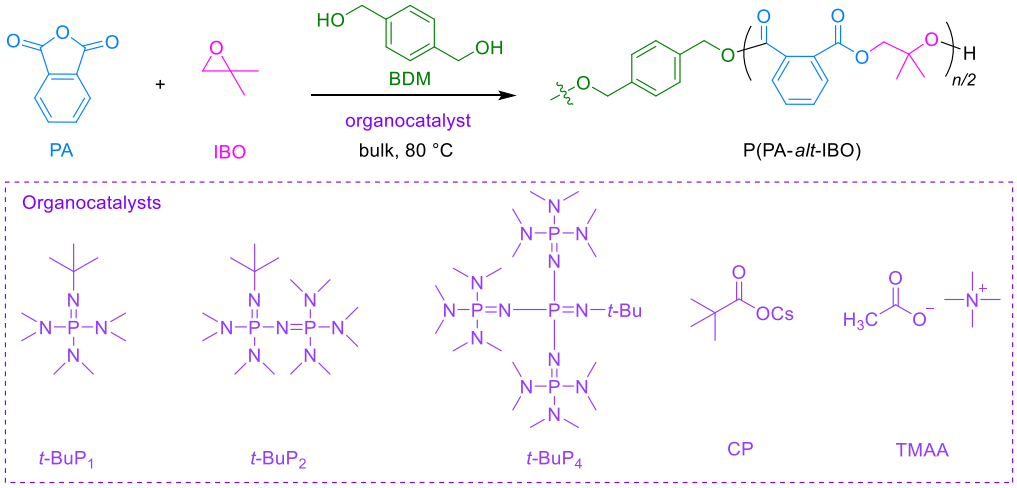

(A)
PA
trimethylene carbonate (TMC)
IBO
BDM
t-BuP2
80 °C in bulk
P(PA-alt-IBO)
PTMC
PTMC
(B)
conv.PA
conv.TMC
conv. [%]
time [h]
(C)
5.5 h, Mn, SEC = 4,100, Đ = 1.10
8.5 h, Mn, SEC = 5,400, Đ = 1.12
9 h, Mn, SEC = 6,900, Đ = 1.11
elution time [min]
(D)
catalyst
CHCl3
a, c
d, f, h
g e
TMS
Solvents or a catalyst
polymer
X : parts per Million : Proton

Figure 8.

Scheme 1.


PA
IBO
BDM
organocatalyst
bulk, 80 °C
P(PA-alt-IBO)
Organocatalysts
t-BuP1
t-BuP2
t-BuP4
CP
TMAA

Scheme 2.

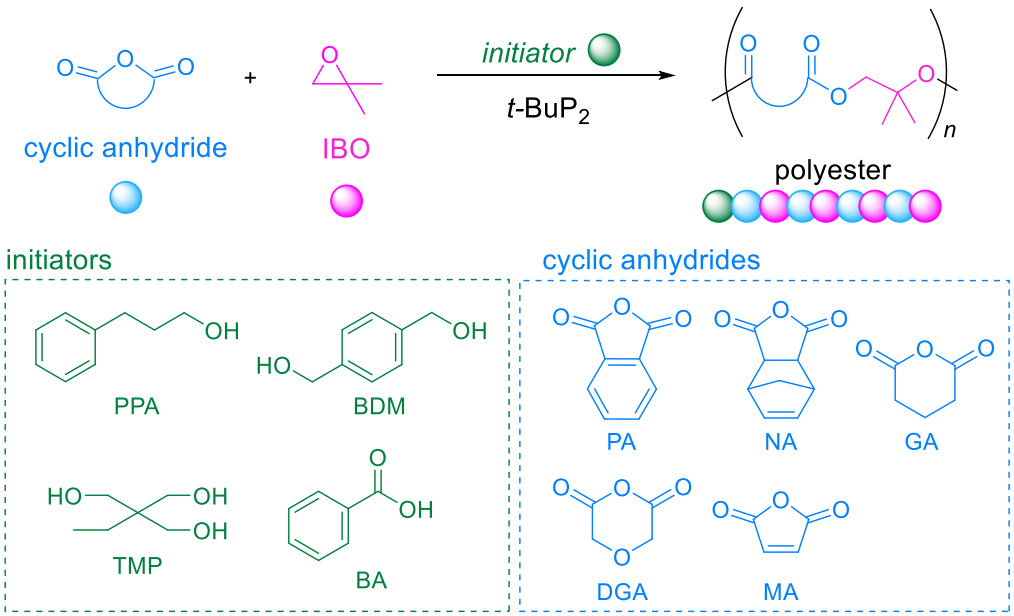

cyclic anhydride
IBO
initiator
t-BuP2
polyester
n
initiators
PPA
BDM
TMP
BA
cyclic anhydrides
PA
NA
GA
DGA
MA

Table 1. ROAC of PA and IBO using various organocatalysts [a]

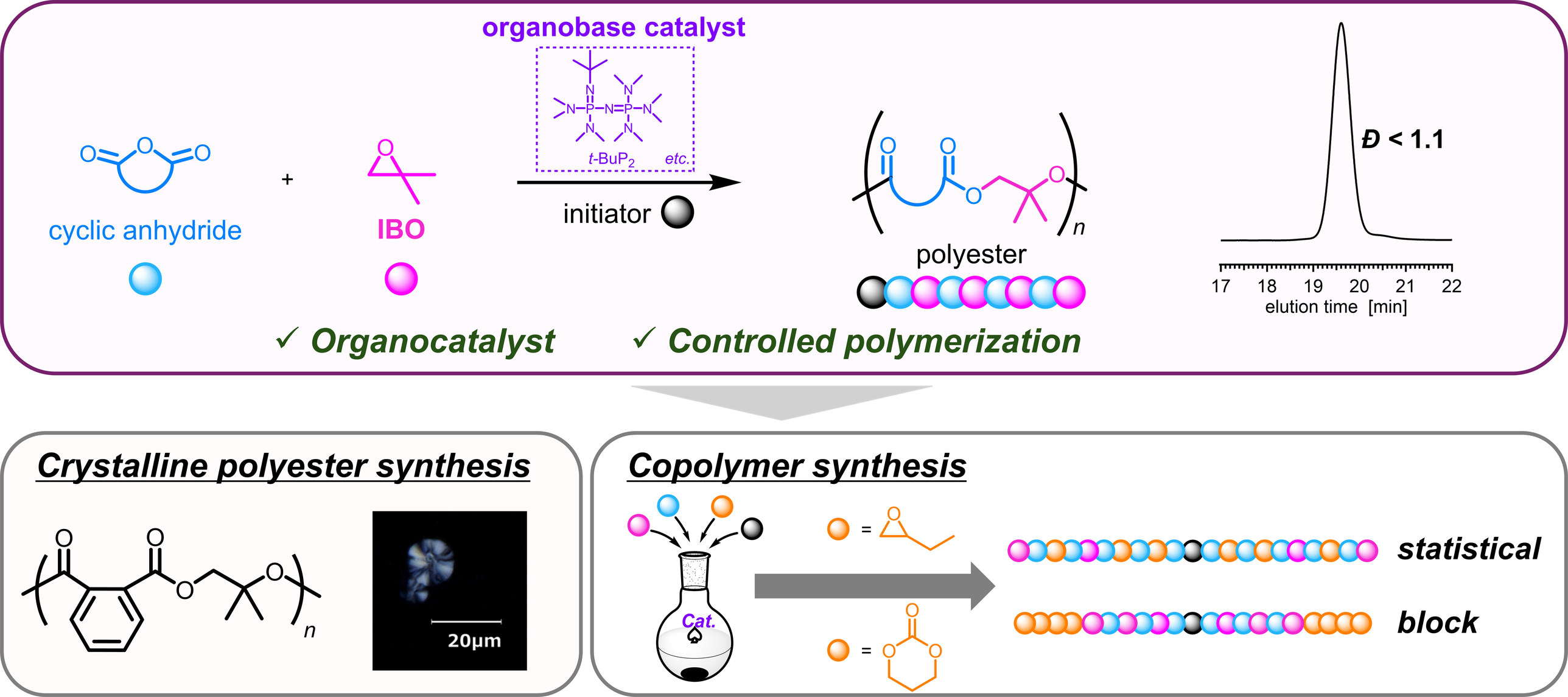
run	cat.	time (h)	conv.$_{PA}$ [b] (%)	$M_{n,theo.}$ [c]	$M_{n,NMR}$ [b]	$M_{n,SEC}$ [d]	$Đ$ [d]	TOF [e] (h^{-1})
1	*t*-BuP_1	4	77.9	8,720	8,160	5,500	1.07	9.74
2	*t*-BuP_2	3	79.7	8,920	10,700	9,800	1.05	13.3
3	*t*-BuP_4	2.75	75.0	8,400	9,260	6,400	1.09	13.6
4	CsOPiv	23.5	82.7	9,240	9,960	6,800	1.02	1.80
5	TMAA	7	76.4	8,550	9,740	6,800	1.24	5.46
6 [f]	*t*-BuP_2	8	74.3	16,500	19,900	14,500	1.08	n.d.
7 [g]	*t*-BuP_2	14	76.4	25,400	29,700	18,500	1.13	n.d.

[a] Polymerization conditions: atmosphere, Ar; temp., 80 °C; initiator, BDM, $[PA]_0/[IBO]_0/[ini.]_0/[cat.]$ = 50/200/1/1. [b] Determined by ^{1}H NMR spectroscopy in $CDCl_3$ (see **Figure S2** for details of calculation method). [c] Calculated from (M.W. of BDM) + $[PA]_0/[BDM]_0$×((M.W. of PA) + (M.W. of IBO))×conv.$_{PA}$ /100 [d] Determined by SEC in THF using a polystyrene standard, and the peak with the highest M. W. region was calculated. [e] Turnover Frequency (TOF) = ($[PA]_0$×conv.$_{PA}$/100)/([cat.]×time (h)) [f] $[PA]_0/[IBO]_0/[ini]_0/[cat.]$ = 100/400/1/1. [g] $[PA]_0/[IBO]_0/[ini]._0/[cat.]$ = 150/600/1/1.

Table 2. ROAC of IBO and various initiators and cyclic anhydrides

run	ini.	cyclic anhydride	time (h)	conv. [b] (%)	$M_{n,theo.}$ [c]	$M_{n,NMR}$ [b]	$M_{n,SEC}$ [d]	$Đ$ [d]
1	PPA	PA	3	73.2	8,320	7,000	6,300	1.04
2	TMP	PA	1.5	82.2	9,170	10,800	10,300	1.03
3	BA	PA	3	59.7	6,700	7,080	4,400	1.19
4	BDM	NA	7	65.0	7,820	5,000	4,600	1.09
5	BDM	DGA	5	≥ 99	9,500	8,040	5,400	1.26
6	BDM	GA	10.5	≥ 99	9,450	13,000	_ [e]	
7	BDM	MA	3	n.d.	n.d.	n.d.		

[a] Polymerization conditions: atmosphere, Ar; temp., 80 °C; catalyst, *t*-BuP$_2$; [cyclic anhydride]$_0$/[IBO]$_0$/[ini.]$_0$/[*t*-BuP$_2$] = 50/200/1/1. [b] Determined by ^{1}H NMR spectroscopy in $CDCl_3$ (see **Figure S2** for details of calculation method). [c] Calculated from (M.W. of ini.) + [cyclic anhydride]$_0$/[BDM]$_0$×((cyclic anhydride MW) + (IBO MW))×conv. /100 [d] Determined by SEC in THF using a polystyrene standard, and the peak with the highest M. W. region was calculated. [e] Polymers with M.W. > 1 kDa could not be identified


organobase catalyst
t-BuP2 etc.
cyclic anhydride
IBO
initiator
polyester
Đ < 1.1
17 18 19 20 21 22
elution time [min]
✓ Organocatalyst
✓ Controlled polymerization
Crystalline polyester synthesis
20μm
Copolymer synthesis
Cat.
statistical
block

Caption of the Graphical Abstract

A well-controlled ring-opening alternating copolymerization (ROAC) of cyclic anhydrides and isobutylene oxide (IBO) using organobase catalysts was developed. Using *t*-BuP_2 as a catalyst, the ROAC of phthalic anhydride (PA) and IBO proceeds smoothly, yielding crystalline P(PA-*alt*-IBO) with narrow molecular weight distribution ($Đ \leq 1.1$). This method was extended to other cyclic anhydrides and initiators. Additionally, this ROAC system was applied to the synthesis of copolymers, including statistical copolymer and block copolymer. This study provides a straightforward and precise strategy for synthesizing crystalline polyesters and further macromolecular designs.

(87 words)