Macromolecules

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Polyaddition of Discrete Oligo(butylene succinate)s with Divinyl Ethers for Periodic and Selectively Cleavable Main-Chain Acetal Linkages

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Cite This: *Macromolecules* 2025, 58, 2599−2608

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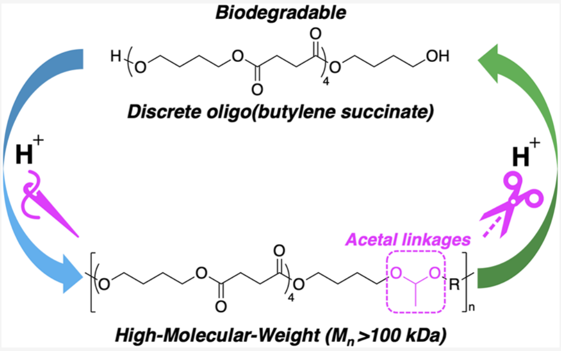
ABSTRACT: Poly(butylene succinate) (PBS) is a promising biodegradable and sustainable thermoplastic, but its poor degradability in marine environments is a cause for concern. In this study, we aimed to mitigate this issue by developing novel PBS derivatives with labile acetal linkages periodically distributed along the polymer backbone. An efficient protection−deprotection synthesis yielded monodisperse dihydroxy oligo(butylene succinate)s (OBS) with precisely controlled molecular weights, which were consequently employed as the telechelic macromonomers to be polymerized with divinyl ethers in a step-growth fashion. The obtained poly(OBS-acetal)s had high-molecular-weight (M_n > 100,000 Da) and showed PBS-like semicrystalline properties due to the presence of well-defined crystallizable OBS segments joined together by labile spacers. Selective cleavage of the backbone acetal linkages under acidic conditions enabled rapid depolymerization into simpler oligomers with better degradability. Therefore, this general strategy could be utilized to improve the degradability of the polymers while retaining their physical properties.



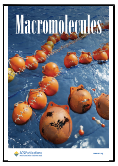
■ INTRODUCTION

The accumulation of commercial plastic waste that cannot be degraded by nature over a long period of time has caused severe land and water pollution. To address this issue, the development of novel materials that possess robustness for everyday use while being easily recyclable and biodegradable under appropriate conditions has been an important focus of polymer research. Polyesters are among the most explored class of sustainable polymers because of the wide availability of renewable monomers, tunable properties, better degradability, and recyclability.[1] Polybutylene succinate (PBS) is an important biodegradable polyester with ever-growing applications such as packaging films, fishing nets, biomedical products, and agricultural materials.[2−5] Due to recent developments in the renewable production of succinic acid and 1,4-butanediol, combined with its excellent thermal and mechanical properties, PBS is being considered as a good sustainable thermoplastic.[6−8] Although PBS demonstrates good biodegradability in composting conditions, its marine biodegradability is poor and inconsistent, which has been attributed to the lack of a wide variety of suitable marine microbial organisms that can assimilate the polymer.[9−13]

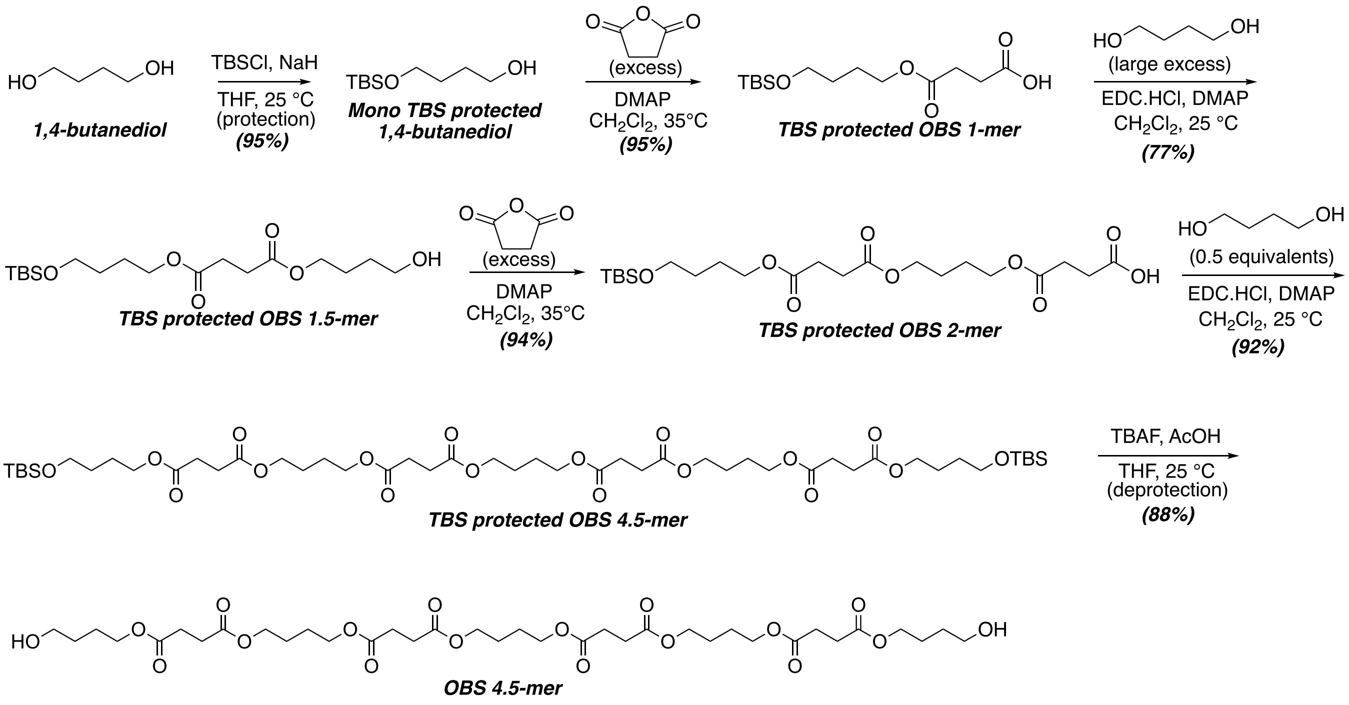
The degradability and degradation rate of biodegradable polyesters in the environment are also dependent on their molecular weight, an important factor that influences physical properties such as tensile strength, thermal characteristics, crystallinity, wettability, etc.[14−16] Detailed investigations revealed that unlike the polymers with high molecular weight, their oligomers with short enough chain length could undergo degradation at a faster rate.[17−20] We studied the toxicity of oligocaprolactones (OCLs) with defined chain ends and found that, in addition to the molecular weight, the chain-end structures and additives also play an important role in the toxicity toward *Daphnia magna*.[21,22]

These observations highlight the importance of designing oligomers with discrete molecular weights to precisely study their degradability. Advances in precision synthesis and purification methodologies such as single-unit monomer insertions, iterative exponential growth strategy, automated flash chromatographic separation, etc., enabled multigram synthesis of oligomers with precise control over their chain lengths, sequence of repeating units, and chain-end functionalities.[23−29] Previously, we had synthesized molecularly defined telechelic monomers through iterative addition followed by

Received: December 20, 2024
Revised: January 28, 2025
Accepted: February 3, 2025
Published: February 17, 2025



Scheme 1. Synthesis of Monodisperse OBS 4.5-mer



step-growth polymerization to yield vinyl polymers with precise control over the repeat unit sequence, tacticity, and molecular weight.[30−32]

Consequently, we hypothesized that introducing labile chemical linkages periodically along the polymer backbone could result in controlled cleavage of the polymer main chain to form potentially more degradable and/or nontoxic oligomers under suitable stimulus. Several groups have reported similar approaches by incorporating disulfides, thioesters, thioacetals, orthoesters, etc., that are selectively labile to certain stimuli.[33−36] Acetal groups can also be suitable labile linkages because they readily degrade under mild acidic conditions ($\mathrm{pH} < 5.5$) while showing resistance to other chemical conditions.[37−40] Linear polymers with acetal linkages have been efficiently synthesized under mild conditions by acid-catalyzed polyaddition of diols with divinyl ethers.[41−44] Hashimoto and co-workers demonstrated the self-polyaddition of hydroxy vinyl ethers with an acid catalyst to synthesize high-molecular-weight polyacetals with a tunable main chain structure.[45] Additionally, efforts have been made by numerous groups to incorporate acetal linkages into polymer backbone of polyesters, polyamides, polyurethanes, polycarbonates, epoxy resins, and other materials to enhance their chemical degradability and recyclability while preserving the characteristic thermomechanical properties.[46−51] The degradation products obtained after hydrolysis of the acetal containing polymers were demonstrated as useful monomer precursors for open/closed loop recycling.

In this work, we report a general approach to synthesize PBS derivatives with periodically distributed acetal linkages along the polymer backbone that can selectively degrade in a mild acidic environment to generate more biodegradable oligo(butylene succinate)s. A novel and efficient protection−deprotection strategy was employed to synthesize monodisperse oligomers of butylene succinate with discrete molecular weights in the multigram scale. These well-defined OBS macromonomers with dihydroxy end groups were polymerized with various divinyl ethers using acid-catalyzed step growth polyaddition to obtain poly(OBS-acetal)s. The oligomers and the polymers were characterized using DSC, TGA, SAXS, and WAXS analyses to elucidate their thermal and crystalline properties.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Discrete Oligo(butylene succinate)s. Monodisperse and discrete oligomers of butylene succinate were synthesized by a protection−deprotection strategy. Succinic anhydride and 1,4-butanediol were added step-by-step to mono-TBS-protected 1,4-butanediol as shown in Scheme 1. After obtaining the OBS 2-mer with −OTBS and carboxylic acid end groups, esterification with 0.5 equiv of 1,4-butanediol resulted in the formation of di-TBS-protected OBS 4.5-mer. Finally, TBS deprotection was carried out using TBAF with acetic acid as a proton source to give monodisperse OBS 4.5-mer. OBS 6.5-mer was synthesized from OBS 4.5-mer by esterification with excess of TBS-protected OBS 1-mer followed by TBS deprotection (Scheme S1A). Similarly, the OBS 8.5-mer was synthesized by coupling OBS 4.5-mer and TBS-protected OBS 2-mer followed by TBS deprotection (Scheme S1B).

The obtained oligomers were characterized by ^{1}H NMR, ^{13}C NMR, SEC, and MALDI-TOF mass spectrum. The purity of the oligomers was verified by ^{1}H NMR studies, which revealed that the ratio of the methylene protons alpha to the hydroxy end groups to the succinate protons agreed with the calculated values for OBS 4.5-mer, OBS 6.5-mer, and OBS 8.5-mer (Figure 1A and Figure S1). The desired monodisperse nature of the oligomers was corroborated by the SEC analysis. As shown by the SEC curves in Figure 1B and Figure S2, final oligomers and their precursors indeed showed narrow monomodal peaks with $M_w/M_n \leq 1.05$. Oligo(butylene succinate)s at each synthesis step were also characterized by the MALDI-TOF mass spectrum to verify their purity as shown in Figure 1C. The molecular weights obtained from sharp monomodal peaks in MALDI-TOF

https://doi.org/10.1021/acs.macromol.4c03178
Macromolecules 2025, 58, 2599−2608

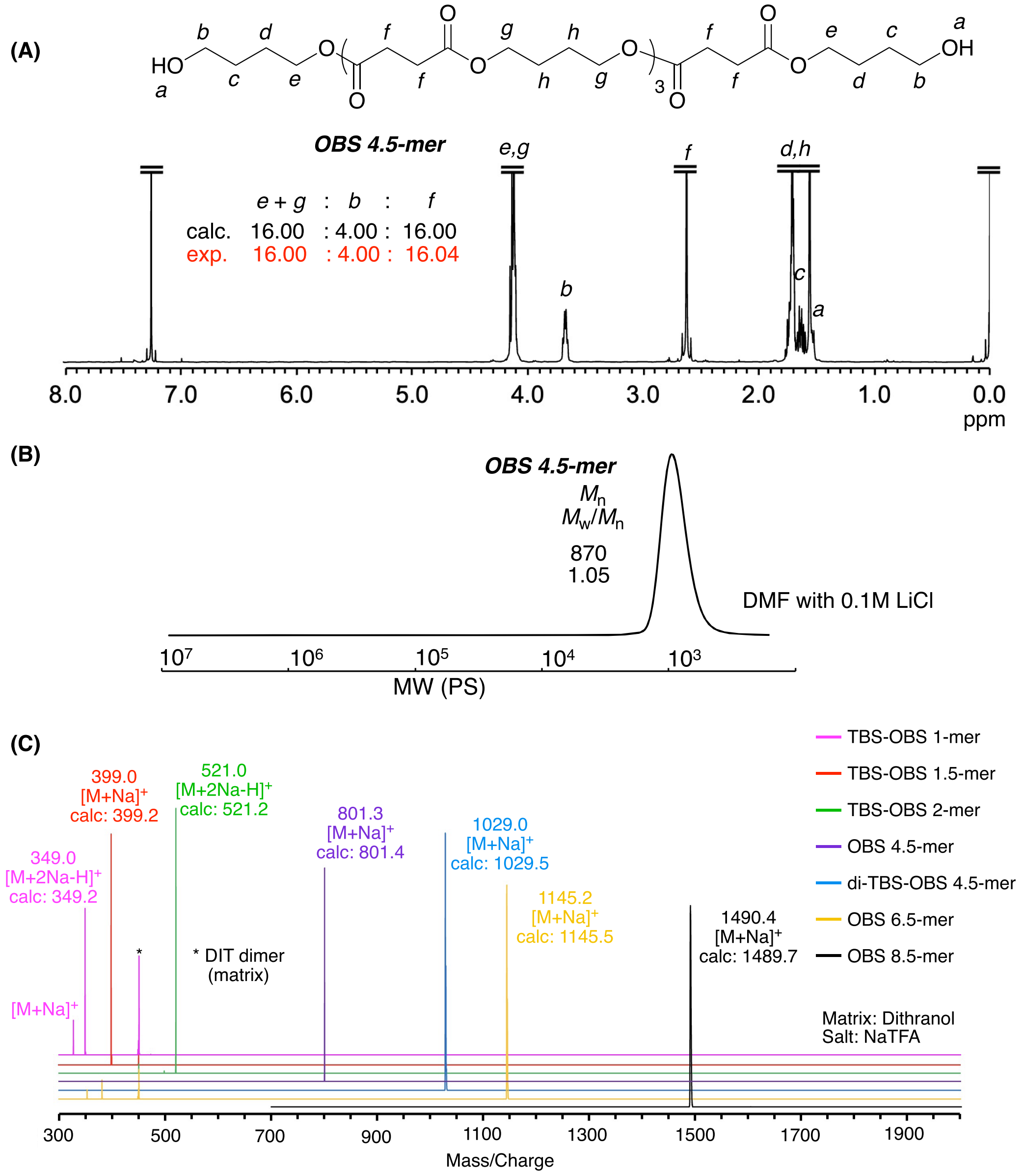
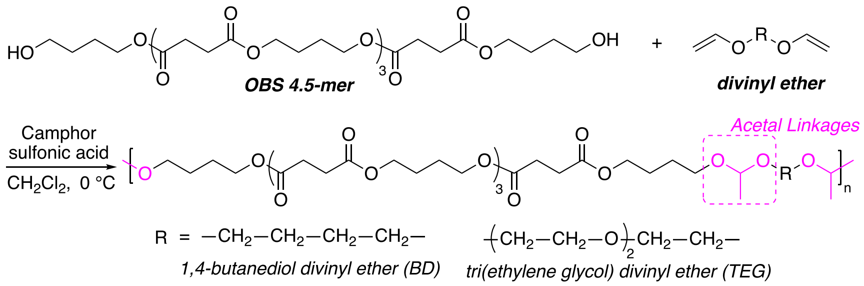


Figure 1. ^1H NMR spectrum ($CDCl_3$, r.t.) (A) and SEC chromatogram (B) of dihydroxy OBS 4.5-mer. Stacked MALDI-TOF mass spectra of each of the discrete OBS oligomers before and after deprotection (C).

Scheme 2. Acid-Catalyzed Solution Polyaddition of OBS 4.5-mer and Divinyl Ethers



mass spectra of the final oligomers closely match the calculated values, indicating the presence of the expected number of repeat units and chain ends (see also Figure S3). The dihydroxy oligomers showed good solubility in halogenated solvents such as chloroform and dichloromethane but had poor solubility in most of the nonhalogenated solvents at room temperature, presumably due to their crystalline nature. Also, the solubility of the oligomers decreases with the increase in their molecular weight.

Polyaddition of Dihydroxy Oligo(butylene succinate)s with Divinyl Ethers. OBS 4.5-mer was polymerized with equimolar divinyl ethers in the presence of an acid catalyst using

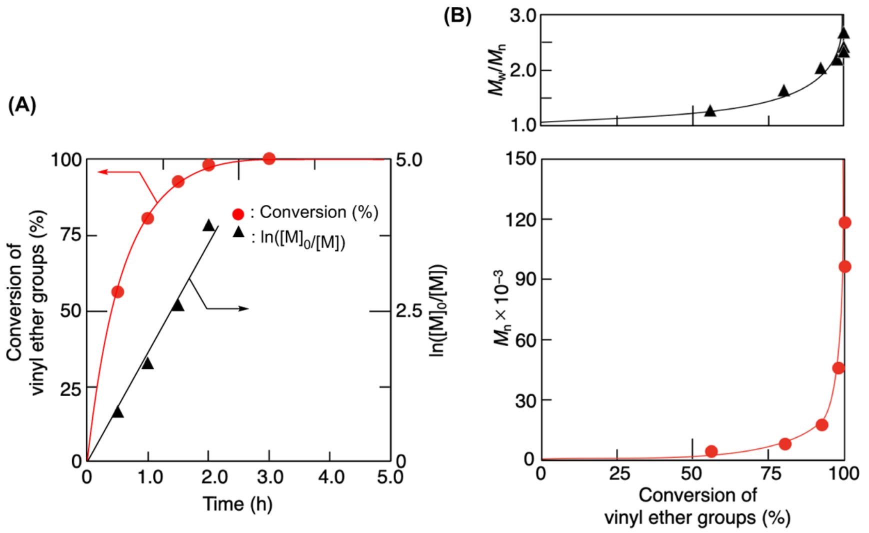


Figure 2. Kinetics of the polyaddition of OBS 4.5-mer and 1,4-butanediol divinyl ether: conversion of vinyl ether groups vs time (A) and M_n vs conversion of vinyl ether groups (B).

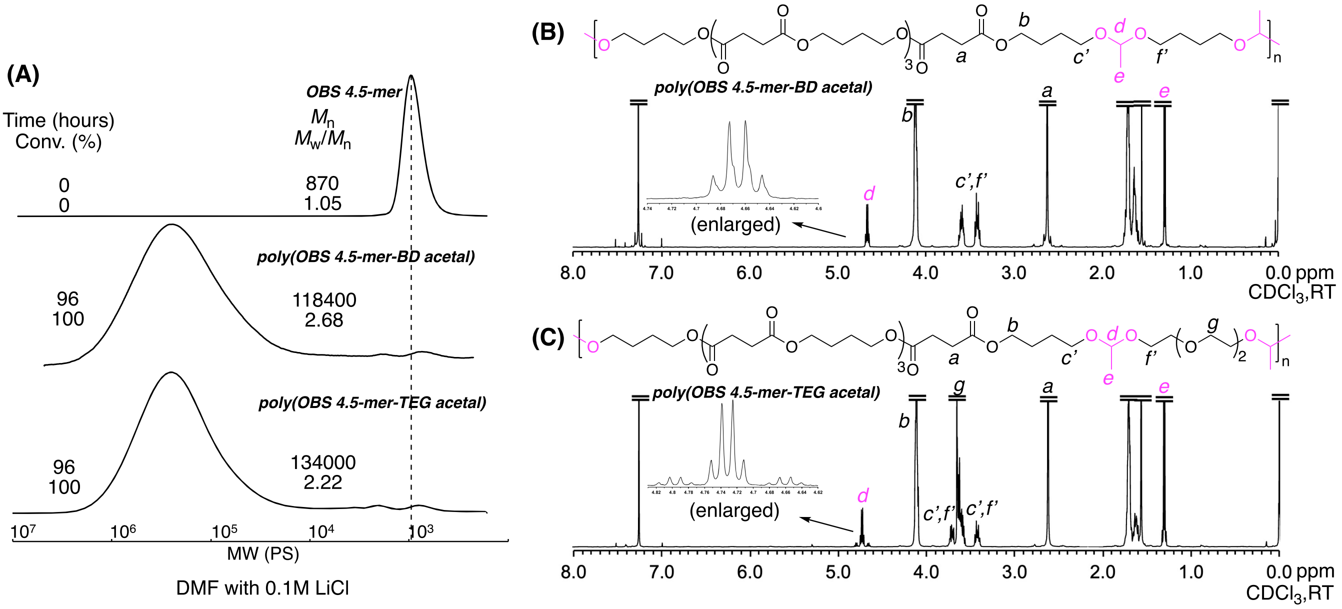


Figure 3. SEC curves of OBS 4.5-mer and polymers after reprecipitation (A). ^{1}H NMR spectra of poly(4.5-mer-BD acetal) after reprecipitation (B) and poly(OBS 4.5-mer-TEG acetal) after reprecipitation (C).

dichloromethane as a solvent at 0 °C (Scheme 2). Camphor sulfonic acid was used to catalyze the step-growth polyaddition of hydroxyl groups of the oligomer to the vinyl ether groups of the divinyl ethers. The polymerization was carried out under relatively dilute conditions (∼150 mM) because of the decreased solubility of the oligomers at 0 °C. Despite the partial solubility of the OBS 4.5-mer, polyaddition with divinyl ethers proceeded smoothly, and the reaction mixture slowly turned clear during the polymerization. The polymerizations were quenched by neutralizing the acid catalyst with excess of saturated aqueous $NaHCO_3$ solution. Further workup was carried out under basic or neutral conditions to avoid any cleavage of acetal linkages, and precipitation of the polymers in *n*-hexane yielded white fibrous solids.

The kinetics of the polymerization of OBS 4.5-mer and 1,4-butanediol divinyl ether (BD) was studied by analyzing the conversion of vinyl ether groups and the molecular weights of the aliquots taken at predetermined intervals using ^{1}H NMR and SEC analysis, respectively. The conversion of vinyl ether groups with time was determined by monitoring the area under the peaks of the vinyl ether protons with respect to the succinate protons from the ^{1}H NMR spectrum of the aliquots (Figure 2B). Characterization of the aliquots using SEC analysis determined the molecular weights corresponding to vinyl ether conversion (Figure 2C, Figure S4). Efficient polymerization to furnish high-molecular-weight polyacetals was observed even with low reaction temperature (0 °C) and low loading of camphor sulfonic acid catalyst (0.15 mol %). More specifically, conversion of the divinyl ether reached nearly 100% in 3 h of the reaction, resulting in the formation of poly(OBS 4.5-mer-BD acetal) with high molecular weight (M_n ∼100 kDa). The polymerization was carried out for 96 h, which led to a slight increase in the molecular weight of the polymer.

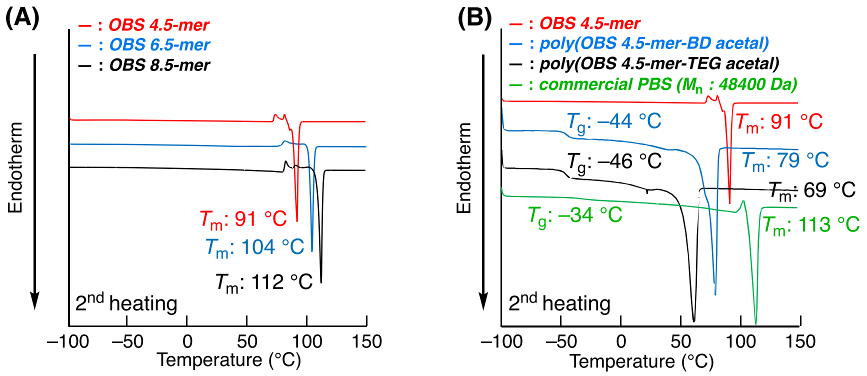


Figure 4. DSC traces: OBS oligomers (A) and OBS 4.5-mer and polymers (B).

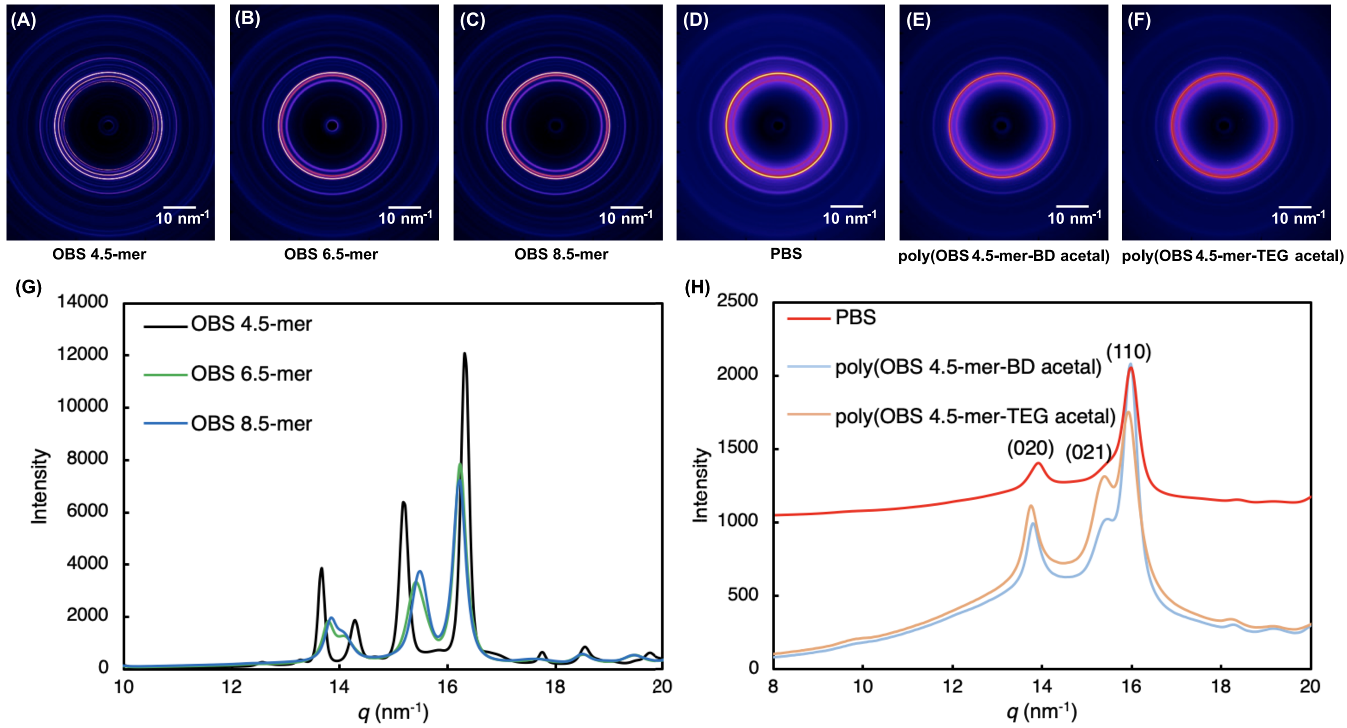


Figure 5. WAXS 2D patterns of the OBS oligomer and polymers (A–F). WAXS 1D profiles of OBS oligomers (G) and polymers with assigned Braggs peaks (H). Scattering vector, q, is denoted here as $q = 4\pi \sin(\theta)/\lambda$, where 2θ and λ are scattering angle and wavelength of X-ray.

SEC analysis of poly(OBS 4.5-mer-BD acetal) after precipitation in *n*-hexane revealed the formation of high-molecular-weight polymers with the number-average molecular weight over 100 kDa (Figure 3A). The low-molecular-weight oligomers present in the SEC curves of the final polymers were presumably cyclic oligomers formed as a result of the relatively low monomer concentration. The presence of main chain acetal linkages in the polymers was indicated by the appearance of characteristic ^{1}H NMR peaks, namely, a quartet at 4.70−4.63 ppm and a doublet at 1.32−1.27 ppm (Figure 3B). Conversion of the hydroxy groups of the OBS 4.5-mer to acetal groups resulted in a slight upfield shift of the methylene protons alpha to hydroxy groups. The formation of a pair of multiplets with complex splitting patterns in the ^{1}H NMR of the polymers was observed because the pairs of methylene protons adjacent to the acetal oxygens are diastereotopic.[52] Overall, these analyses indicated the successful formation of a high-molecular-weight PBS analogue with acetal linkages in the backbone.

The acetal-forming polyaddition of diols and divinyl ethers was performed with different combinations of monomer pairs. Polymerization of higher-molecular-weight OBS oligomers was attempted to obtain poly(OBS-acetal)s with longer OBS segments. Unfortunately, in the polymerizations of OBS 6.5-mer and OBS 8.5-mer with 1,4-butanediol divinyl ether, their reaction mixtures remained turbid and yielded only low-molecular-weight oligomers as shown by the SEC analysis (Figures S5 and S6). This observation must be attributed to the poor solubility of the 6.5-mer and 8.5-mer of the OBS in both organic solvents and monomers. Polyaddition of shorter OBS 4.5-mer with a more hydrophilic divinyl ether, tri(ethylene glycol) divinyl ether (TEG), was also carried out under similar conditions to furnish high-molecular-weight poly(OBS 4.5-mer-TEG acetal) (Figure 3A,C).

Thermal and Mechanical Properties. We studied the thermal stability of OBS oligomers and poly(OBS-acetal)s using TGA. According to the 5% mass loss temperature, T_{d5}, determined from TGA curves, OBS 4.5-mer, OBS 6.5-mer, and OBS 8.5-mer were found to be thermally stable with T_{d5} > 300 °C (Figure S7A). The conversion of OBS 4.5-mer into acetal containing polyesters increased their T_{d5} by over 40 °C compared to that of OBS 4.5-mer, closely matching the high thermal stability of commercial PBS (Figure S7B).[2]

The crystalline properties of the oligomers and polymers were characterized by DSC analysis. Unlike commercial PBS, OBS 4.5-mer, OBS 6.5-mer, and OBS 8.5-mer did not show any glass transition within the temperature range of −100 to 150 °C, indicating the lack of an observable amorphous fraction in the oligomers (Figure 4). All of the oligomers showed very sharp melting transitions, with the melting temperature being the highest for the OBS 8.5-mer due to it having the longest chain length. Like commercial PBS, the oligomers also showed cold crystallization exotherms while heating, indicating the transition of thermally less stable crystallites to more stable crystalline forms.[53] When OBS 4.5-mer was polymerized with divinyl ethers, the resulting polymers exhibited PBS-like semicrystalline properties with well-defined glass transitions and sharp melting transitions as shown in Figure 4B. Compared to the low-molecular-weight OBS 4.5-mer, entangled polymer chains in poly(OBS 4.5-mer-acetal)s can restrict chain mobility and crystallization of OBS segments from melt in a stable configuration.[54] This could be one of the reasons for the observation of a lower melting temperature in poly(OBS 4.5-mer-acetal)s compared to OBS 4.5-mer. Annealing poly(OBS 4.5-mer-BD acetal) and poly(OBS 4.5-mer-TEG acetal) at 40 and 31 °C, respectively, slightly increased their enthalpy of melting (Table S1). Both of the polymers showed the same enthalpy of melting of 52 J/g from the DSC analysis due to the presence of identical crystallizable segments. Poly(OBS 4.5-mer-BD acetal) had a higher T_m and T_c compared to those of poly(OBS 4.5-mer-TEG acetal) despite both of the polymers sharing the same crystallizable segments. The presence of more polar tri(ethylene glycol) spacers could exhibit a dilution effect on OBS crystallites in the latter, leading to a depression in melting temperature. Also, the lower T_c suggests that the tri(ethylene glycol) spacers could have an inhibitory effect on the crystallization of the OBS segments. The polymers could be molded easily by hot pressing above their T_m values to give translucent films (Figure S8). As mentioned above, OBS 6.5-mer and OBS 8.5-mer afforded only oligomers, of which the thermal properties could not be evaluated appropriately.

Additionally, tensile tests revealed that poly(OBS 4.5-mer-BD acetal) has a maximum strength of 20.6 MPa and an elongation of 753% at the break (Figure S9). This study indicates that the PBS derivatives with periodic acetal linkages have a thermoplastic nature and mechanical characteristics comparable to those of PBS (yield strength = 29.6 MPa, elongation at break = 283%).[55]

Synchrotron X-ray Characterization. OBS oligomers and poly(OBS 4.5-mer-acetal)s were analyzed using wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) to study their structural characteristics (Figure 5, Figure S10).[56,57] The presence of broad periodic peaks in the WAXS pattern of the OBS oligomers suggests the formation of large well-defined crystallites. Interestingly, WAXS patterns of poly(OBS 4.5-mer-BD acetal) and poly(OBS 4.5-mer-TEG acetal) resemble each other and also that of PBS, presumably due to the presence of similar crystallizable oligo(butylene succinate) segments as shown in Figure 5. Their resemblance in crystal structure enabled the assignment of Braggs peaks of the polyacetals by comparing their WAXS data against the well-characterized WAXS data of PBS.[58,59]

Peak deconvolution of one-dimensional (1D) WAXS profiles of polymers allowed us to calculate the degree of crystallinity (χ_c) of samples (Figure S11A−C).[60] The long period (L_p) and lamellar thickness (d_c) of the polymers were evaluated from the (1D) SAXS profiles using the one-dimensional electron-density correlation function ($K(z)$) (Figure S11D).[61−63] The summary of the WAXS and the SAXS analysis of the polymers is listed in Table 1. It is interesting to note that the polyacetals share a similar degree of crystallinity, long period, and lamellar thickness despite having acetal spacers of different lengths. These observations suggest that the length of the acetal spacer might not have a strong influence over the packing of the OBS segments. However, calculation of the crystallite sizes of polyacetals using Scherrer's equation showed that poly(OBS 4.5-mer-BD acetal) has larger OBS crystallites (D_{110}= 15.1 nm) when compared to poly(OBS 4.5-mer-TEG acetal) (D_{110}= 11.6 nm).[64] The presence of smaller crystallites with higher surface energy in the latter might also have contributed to the depression in the melting point observed in DSC analysis. The smaller size of the crystallites implies a higher nucleation rate and slower crystal growth rate in poly(OBS 4.5-mer-TEG acetal), suggesting the influence of tri(ethylene glycol) spacers on the kinetics of crystallization of the OBS segments.

Table 1. Summary of WAXS and SAXS Characterization of the Polymers

entry	sample name	mol. wt.[a]	χ_c (%)[b]	D_{110} (nm)[c]	L_p (nm)[d]	d_c (nm)[e]
1	poly(OBS 4.5-mer-BD acetal)	74,900 (M_n), 3.29 (M_w/M_n)	48.0	15.1	10.0	2.36
2	poly(OBS 4.5-mer-TEG acetal)	58,300 (M_n), 3.43 (M_w/M_n)	47.7	11.6	10.5	2.34
3	PBS	43,000 (M_n), 3.2 (M_w/M_n)	47.0	16.1	8.2	2.4

[a]Determined by SEC analysis of polymer films. [b]The degree of crystallinity (χ_c) was calculated from deconvoluted WAXS data.[60] [c]The crystal size was calculated from the (110) WAXS peak.[64] [d]The long period of the lamellar stacking structure was calculated from SAXS analysis.[62] [e]Lamellar thickness.[62]

Chemical and Marine Degradation Studies. The chemical degradability of poly(OBS-acetal)s under a variety of aqueous conditions as well as mild acidic conditions was studied. Powder samples of polymers were suspended in deionized water with a slightly acidic pH of 6, a phosphate buffer with a neutral pH of 7.4, and natural seawater with a slightly alkaline pH of 8 (Figure S12A). After 7 days at 40 °C, SEC analysis showed that there was only a marginal decrease in the number-average molecular weights of poly(OBS 4.5-mer-BD acetal) and poly(OBS 4.5-mer-TEG acetal) under all three conditions (Figure S12B,C). For context, the molecular weight of commercial PBS under the same conditions remained mostly unchanged even after 30 days (Figure S12D). This observation shows that the poly(OBS-acetal)s can remain stable with a long half-life under a pH ranging from 6 to 8.[65]

To demonstrate the labile nature of acetal linkages under acidic conditions, poly(OBS 4.5-mer-BD acetal) in THF was treated with aqueous HCl at room temperature (Figure 6A), and the changes in composition and molecular weight of the polymer were monitored at regular intervals by ^{1}H NMR and SEC

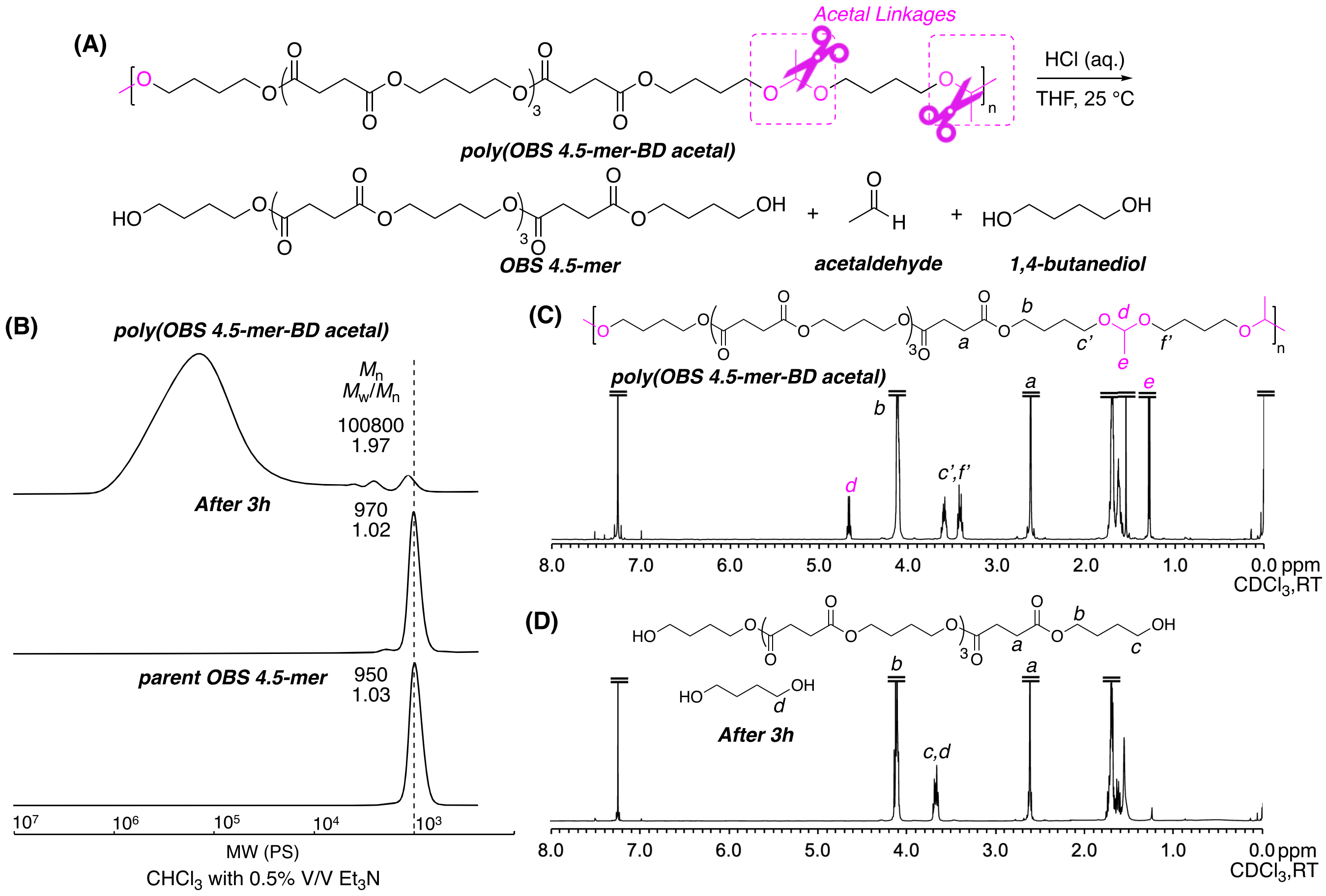


Figure 6. Acid-catalyzed selective cleavage of acetal linkage scheme (A), SEC stack plot of poly(OBS 4.5-mer-BD acetal) and hydrolysis products (B), ^{1}H NMR spectra of parent poly(OBS 4.5-mer-BD acetal) (C), and ^{1}H NMR spectrum of hydrolysis products after 3 h (D)

analysis, respectively. The cleavage of main chain acetal groups reached 25%, and the M_n of the polyacetal rapidly decreased from 100 to 6.4 kDa within just 5 min (Figure S13A,B). After 3 h, the characteristic peaks corresponding to the acetal linkages completely disappeared from the ^{1}H NMR, indicating quantitative cleavage of acetal linkages and the polymer degrading into the parent OBS 4.5-mer 1,4-butanediol, and acetaldehyde (Figure S13C). Interestingly, SEC analysis showed that the molecular weight of the recovered 4.5-mer OBS was identical to the starting oligomer, indicating the selective cleavage of acetal linkages (Figure 6B,C). Thus, the main-chain acetal linkages of the polymer could be selectively cleaved while keeping the ester groups completely intact. This approach should enable the highly efficient and rapid chemical degradation of the polymers under certain chemical stimuli.

The biodegradability in seawater was preliminarily evaluated by quantifying the amount of CO_2 generated during biodegradation using a titration method under accelerated marine conditions (Figure 7).[66−68] The OBS 4.5-mer and commercially available PBS were tested for marine biodegradability. Unlike non-marine-degradable commercial PBS, the marine biodegradation rate of the 4.5-mer obtained from OBS is comparable to that of cellulose, which shows that the degradability of the oligomers of OBS can vary significantly depending on their molecular weight. In addition, the marine biodegradability of the acetal-linked polymers poly(OBS 4.5-mer-TEG acetal) and poly(OBS 4.5-mer-BD acetal) was also evaluated. Interestingly, the more hydrophilic poly(OBS 4.5-mer-TEG acetal) showed better biodegradation, and the degradation reached almost half compared to the oligomer in 40 days, whereas poly(OBS 4.5-mer-BD acetal) was hardly biodegraded under the same conditions even with the lower M_n. Thus, the hydrophilic nature of the main chain could improve the water uptake into the polymer bulk, which probably induced

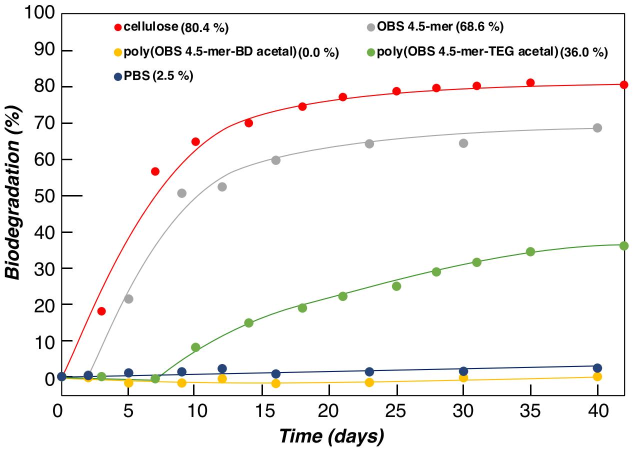


Figure 7. Biodegradability of OBS 4.5-mer, poly(OBS-acetal)s, and PBS with cellulose as positive control in extracted seawater; OBS 4.5-mer (terminal diol, FW = 778.8), poly(OBS 4.5-mer-BD acetal) (M_n = 31,500 and M_w/M_n = 2.44), poly(OBS 4.5-mer-TEG acetal) (M_n = 134,000 and M_w/M_n = 2.22), and commercial poly(butylene succinate) (PBS) (M_n = 44,000 and M_w/M_n = 2.86).

the degradation of acetal linkage to regenerate marine-degradable OBS 4.5-mer, and thus, the main-chain structure played an important role on the marine biodegradability of the polymers.[69,70]

■ CONCLUSIONS

In this work, a multigram-scale protection−deprotection strategy had been demonstrated to obtain monodisperse and discrete oligomeric butylene succinates (OBS) with hydroxy end groups. Polyaddition of OBS 4.5-mer with divinyl ethers yielded high-molecular-weight polyacetals with periodic distribution of the acetal linkages along the polymer backbone. The presence of well-defined crystallizable OBS segments joined together by acetal spacers resulted in PBS-like semicrystalline properties. The polyacetals showed slightly improved uncatalyzed hydrolytic degradability under elevated temperatures compared to commercial PBS due to the presence of more labile acetal linkages along the polymer main chain. Furthermore, these polyacetals were rapidly degraded by selective cleavage of acetal linkages under mild acidic conditions, and the recovered oligomer was identical to the parent oligomer, which was an OBS 4.5-mer. The controlled and selective degradability of the acetal linkages could be explored to efficiently degrade the polymers under mild conditions with potential chemical recyclability. Lower-molecular-weight OBS 4.5-mer has excellent marine biodegradability, unlike commercial PBS and the poly(OBS 4.5-mer-TEG acetal), which also showed relatively good biodegradation, due to the generation of more biodegradable products after the hydrolysis of acetal linkages. Therefore, this strategy could be expanded to other monomers to obtain polymers with properties similar to those of the homopolymers while being selectively degradable in response to specific chemical stimuli.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c03178.

> Detailed experimental procedures and data, including materials, measurements, synthesis, and characterization of discrete oligo(butylene succinate)s including ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, SEC, and TGA; preparation of poly(OBS-acetal)s and their characterization, including SEC curves of kinetics study; ^{1}H NMR, TGA, DSC, tensile testing, SAXS and WAXS, and SEC analysis of the chemical degradation of the polymers under different conditions (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a project (JPNP18016) commissioned by the New Energy and Industrial Technology Development Organization (NEDO). Synchrotron radiation X-ray scattering measurements were performed at the BL38B1 beamline station of the SPring-8 synchrotron facility in Japan with the approval of RIKEN (Proposal No. 20240082).

■ REFERENCES

(1) Shi, C.; Quinn, E. C.; Diment, W. T.; Chen, E. Y.-X. Recyclable and (Bio)Degradable Polyesters in a Circular Plastics Economy. *Chem. Rev.* **2024**, *124* (7), 4393−4478.

(2) Barletta, M.; Aversa, C.; Ayyoob, M.; Gisario, A.; Hamad, K.; Mehrpouya, M.; Vahabi, H. Poly(Butylene Succinate) (PBS): Materials, Processing, and Industrial Applications. *Prog. Polym. Sci.* **2022**, *132*, No. 101579.

(3) Gigli, M.; Fabbri, M.; Lotti, N.; Gamberini, R.; Rimini, B.; Munari, A. Poly(Butylene Succinate)-Based Polyesters for Biomedical Applications: A Review. *Eur. Polym. J.* **2016**, *75*, 431−460.

(4) Zhou, H.; Hu, D.; Zhu, M.; Xue, K.; Wei, X.; Park, C. B.; Wang, X.; Zhao, L. Review on Poly (Butylene Succinate) Foams: Modifications, Foaming Behaviors and Applications. *Sustainable Materials and Technologies* **2023**, *38*, e00720−e00720.

(5) Savitha, K. S.; Ravji Paghadar, B.; Senthil Kumar, M.; Jagadish, R. L. Polybutylene Succinate, a Potential Bio-Degradable Polymer: Synthesis, Copolymerization and Bio-Degradation. *Polym. Chem.* **2022**, *13* (24), 3562−3612.

(6) Ali, Z.; Ma, J.; Sun, R.-C. Scaling-up Clean Production of Biomass-Derived Organic Acids a Step towards the Realization of Dual Carbon Goals: A Review. *Green Chem.* **2024**, *26*, 11061−11082.

(7) Kumar, V.; Kumar, P.; Maity, S. K.; Agrawal, D.; Narisetty, V.; Jacob, S.; Kumar, G.; Bhatia, S. K.; Kumar, D.; Vivekanand, V. Recent Advances in Bio-Based Production of Top Platform Chemical, Succinic Acid: An Alternative to Conventional Chemistry. *Biotechnol. Biofuels Bioprod.* **2024**, *17* (1), 72.

(8) Platnieks, O.; Gaidukovs, S.; Kumar Thakur, V.; Barkane, A.; Beluns, S. Bio-Based Poly (Butylene Succinate): Recent Progress,

Challenges and Future Opportunities. *Eur. Polym. J.* **2021**, *161*, No. 110855.

(9) Zhao, J.-H.; Wang, X.-Q.; Zeng, J.; Yang, G.; Shi, F.-H.; Yan, Q. Biodegradation of Poly(Butylene Succinate) in Compost. *J. Appl. Polym. Sci.* **2005**, *97* (6), 2273−2278.

(10) Eckel, F.; Van Opdenbosch, D.; Schandl, K. S.; Zollfrank, C. Dependency of Tensile Properties and Biodegradation on Molecular Mass during Hydrolysis of Poly(Butylene Succinate). *NPJ Mater. Degrad.* **2024**, *8* (1), 97.

(11) Nakayama, A.; Yamano, N.; Kawasaki, N. Biodegradation in Seawater of Aliphatic Polyesters. *Polym. Degrad. Stab.* **2019**, *166*, 290−299.

(12) Suzuki, M.; Ishii, S.; Ota, M.; Gonda, K.; Kashima, H.; Arai, T.; Tachibana, Y.; Takeno, H.; Kasuya, K. I. Enhancing Marine Biodegradability of Poly(Butylene Succinate) by Blending with 16-Hydroxyhexadecanoic Acid and Poly(ε-Caprolactone). *Polym. Degrad. Stab.* **2024**, *228*, No. 110912.

(13) Kimura, Y.; Fukuda, Y.; Otsu, R.; Yu, J.; Mino, S.; Misawa, S.; Maruyama, S.; Ikeda, Y.; Miyamachi, R.; Noguchi, H.; Kato, S.; Yamamoto, Y.; Sawabe, T. A Lesson from Polybutylene Succinate Plastisphere to the Discovery of Novel Plastic Degrading Enzyme Genes in Marine Vibrios. *Environ. Microbiol.* **2023**, *25* (12), 2834−2850.

(14) Larrañaga, A.; Lizundia, E. A Review on the Thermomechanical Properties and Biodegradation Behaviour of Polyesters. *Eur. Polym. J.* **2019**, *121*, No. 109296.

(15) De Jong, S. J.; van Dijk-Wolthuis, W. N. E.; Kettenes-Van Den Bosch, J. J.; Schuyl, P. J. W.; Hennink, W. E. Monodisperse Enantiomeric Lactic Acid Oligomers: Preparation, Characterization, and Stereocomplex Formation. *Macromolecules* **1998**, *31* (19), 6397−6402.

(16) Gao, M.; Leng, X.; Zhang, W.; Wei, Z.; Li, Y. A Biobased Aliphatic Polyester Derived from 10-Hydroxydecanoic Acid: Molecular Weight Dependence of Physical Properties. *Polym. Test.* **2020**, *82*, No. 106295.

(17) Barbon, S. M.; Carter, M. C. D.; Yin, L.; Whaley, C. M.; Albright, V. C.; Tecklenburg, R. E. Synthesis and Biodegradation Studies of Low-Dispersity Poly(Acrylic Acid). *Macromol. Rapid Commun.* **2022**, *43* (13), No. 2100773.

(18) Barros, J. J. P.; Boskamp, L.; Silva, I. D. S.; Jaques, N. G.; Barreto, J. V. M.; Haag, K.; Koschek, K.; Wellen, R. M. R. Renate. Biodegradation and Thermal-Oxidative Degradation of Propanediol Based Poly (Lactic Acid) Oligomers. *J. Polym. Res.* **2023**, *30* (6), 227.

(19) Kawai, F. Bacterial Degradation of Acrylic Oligomers and Polymers. *Appl. Microbiol. Biotechnol.* **1993**, *39* (3), 382−385.

(20) Gudeangadi, P. G.; Uchida, K.; Tateishi, A.; Terada, K.; Masunaga, H.; Tsuchiya, K.; Miyakawa, H.; Numata, K. Poly(Alanine-Nylon-Alanine) as a Bioplastic: Chemoenzymatic Synthesis, Thermal Properties and Biological Degradation Effects. *Polym. Chem.* **2020**, *11* (30), 4920−4927.

(21) Yoshinaga, N.; Tateishi, A.; Kobayashi, Y.; Kubo, T.; Miyakawa, H.; Satoh, K.; Numata, K. Effect of Oligomers Derived from Biodegradable Polyesters on Eco- and Neurotoxicity. *Biomacromolecules* **2023**, *24* (6), 2721−2729.

(22) Matsumoto, M.; Ito, H.; Tateishi, A.; Kobayashi, Y.; Satoh, K.; Numata, K.; Miyakawa, H. Effects of Polycaprolactone Degradation Products on the Water Flea, *Daphnia Magna*: Carbodiimide Additives Have Acute and Chronic Toxicity. *J. Appl. Toxicol.* **2023**, *43* (12), 1840−1848.

(23) Fu, C.; Huang, Z.; Hawker, C. J.; Moad, G.; Xu, J.; Boyer, C. RAFT-Mediated, Visible Light-Initiated Single Unit Monomer Insertion and Its Application in the Synthesis of Sequence-Defined Polymers. *Polym. Chem.* **2017**, *8* (32), 4637−4643.

(24) Williams, J. B.; Chapman, T. M.; Hercules, D. M. Synthesis of Discrete Mass Poly(Butylene Glutarate) Oligomers. *Macromolecules* **2003**, *36* (11), 3898−3908.

(25) Duan, S.; Yang, X.; Yang, Z.; Liu, Y.; Shi, Q.; Yang, Z.; Wu, H.; Han, Y.; Wang, Y.; Shen, H.; Huang, Z.; Dong, X.-H.; Zhang, Z. A Versatile Synthetic Platform for Discrete Oligo- and Polyesters Based on Optimized Protective Groups *Via* Iterative Exponential Growth. *Macromolecules* **2021**, *54* (23), 10830−10837.

(26) van Genabeek, B.; Lamers, B. A. G.; Hawker, C. J.; Meijer, E. W.; Gutekunst, W. R.; Schmidt, B. V. K. J. Properties and Applications of Precision Oligomer Materials; Where Organic and Polymer Chemistry Join Forces. *J. Polym. Sci.* **2021**, *59* (5), 373−403.

(27) Hakobyan, K.; Noble, B. B.; Xu, J. The Current Science of Sequence-Defined Macromolecules. *Prog. Polym. Sci.* **2023**, *147*, No. 101754.

(28) Lawrence, J.; Lee, S.-H.; Abdilla, A.; Nothling, M. D.; Ren, J. M.; Knight, A. S.; Fleischmann, C.; Li, Y.; Abrams, A. S.; Schmidt, B. V. K. J.; Hawker, M. C.; Connal, L. A.; McGrath, A. J.; Clark, P. G.; Gutekunst, W. R.; Hawker, C. J. A Versatile and Scalable Strategy to Discrete Oligomers. *J. Am. Chem. Soc.* **2016**, *138* (19), 6306−6310.

(29) Takizawa, K.; Tang, C.; Hawker, C. J. Molecularly Defined Caprolactone Oligomers and Polymers: Synthesis and Characterization. *J. Am. Chem. Soc.* **2008**, *130* (5), 1718−1726.

(30) Satoh, K.; Ishizuka, K.; Hamada, T.; Handa, M.; Abe, T.; Ozawa, S.; Miyajima, M.; Kamigaito, M. Construction of Sequence-Regulated Vinyl Copolymers via Iterative Single Vinyl Monomer Additions and Subsequent Metal-Catalyzed Step-Growth Radical Polymerization. *Macromolecules* **2019**, *52* (9), 3327−3341.

(31) Miyajima, M.; Satoh, K.; Horibe, T.; Ishihara, K.; Kamigaito, M. Multifactor Control of Vinyl Monomer Sequence, Molecular Weight, and Tacticity via Iterative Radical Additions and Olefin Metathesis Reactions. *J. Am. Chem. Soc.* **2020**, *142* (44), 18955−18962.

(32) Miyajima, M.; Satoh, K.; Kamigaito, M. Periodically Functionalized Sequence-Regulated Vinyl Polymers via Iterative Atom Transfer Radical Additions and Acyclic Diene Metathesis Polymerization. *Macromol. Chem. Phys.* **2021**, *223* (12), No. 2100426.

(33) Tsutsuba, T.; Tachibana, Y.; Shimizu, M.; Kasuya, K. i. Marine Biodegradation of Poly(Butylene Succinate) Incorporating Disulfide Bonds Triggered by a Switch Function in Response to Reductive Stimuli. *ACS Appl. Polym. Mater.* **2023**, *5* (4), 2964−2970.

(34) Paul, M. K.; Raeside, M. C.; Gutekunst, W. R. General and Mild Method for the Synthesis of Polythioesters from Lactone Feedstocks. *ACS Macro Lett.* **2024**, *13* (11), 1411−1417.

(35) Uchiyama, M.; Osumi, M.; Satoh, K.; Kamigaito, M. Thiol-Ene Cationic and Radical Reactions: Cyclization, Step-Growth, and Concurrent Polymerizations for Thioacetal and Thioether Units. *Angew. Chem.* **2020**, *132* (17), 6899−6905.

(36) Heller, J.; Barr, J. Poly(Ortho Esters)from Concept to Reality. *Biomacromolecules* **2004**, *5* (5), 1625−1632.

(37) Tomlinson, R.; Klee, M.; Garrett, S.; Heller, J.; Duncan, R.; Brocchini, S. Pendent Chain Functionalized Polyacetals That Display PH-Dependent Degradation: A Platform for the Development of Novel Polymer Therapeutics. *Macromolecules* **2002**, *35* (2), 473−480.

(38) Satoh, K.; Poelma, J. E.; Campos, L. M.; Stahl, B.; Hawker, C. J. A Facile Synthesis of Clickable and Acid-Cleavable PEO for Acid-Degradable Block Copolymers. *Polym. Chem.* **2012**, *3* (7), 1890−1898.

(39) Rostagno, M.; Price, E. J.; Pemba, A. G.; Ghiriviga, I.; Abboud, K. A.; Miller, S. A. Sustainable Polyacetals from Erythritol and Bioaromatics. *J. Appl. Polym. Sci.* **2016**, *133* (45), 44089.

(40) Pemba, A. G.; Rostagno, M.; Lee, T. A.; Miller, S. A. Cyclic and Spirocyclic Polyacetal Ethers from Lignin-Based Aromatics. *Polym. Chem.* **2014**, *5* (9), 3214−3221.

(41) Heller, J.; Penhale, H.; Helwing, R. F. Preparation of Polyacetals by the Reaction of Divinyl Ethers and Polyols. *Journal of polymer science. Polymer letters edition* **1980**, *18* (4), 293−297.

(42) Samanta, S.; De Silva, C. C.; Leophairatana, P.; Koberstein, J. T. Main-Chain Polyacetal Conjugates with HIF-1 Inhibitors: Temperature-Responsive, PH-Degradable Drug Delivery Vehicles. *J. Mater. Chem. B* **2018**, *6* (4), 666−674.

(43) Samanta, S.; Bogdanowicz, D. R.; Lu, H. H.; Koberstein, J. T. Polyacetals: Water-Soluble, PH-Degradable Polymers with Extraordinary Temperature Response. *Macromolecules* **2016**, *49* (5), 1858−1864.

(44) Fuoco, T. Degradation in Order: Simple and Versatile One-Pot Combination of Two Macromolecular Concepts to Encode Diverse

and Spatially Regulated Degradability Functions. *Angew. Chem., Int. Ed.* **2021**, *60* (28), 15482−15489.

(45) Hashimoto, T.; Ishizuka, K.; Umehara, A.; Kodaira, T. Synthesis of Polyacetals with Various Main-Chain Structures by the Self-Polyaddition of Vinyl Ethers with a Hydroxyl Function. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (22), 4053−4064.

(46) Hashimoto, T.; Mori, H.; Urushisaki, M. Poly(Tetramethylene Ether) Glycol Containing Acetal Linkages: New PTMG-Based Polyol for Chemically Recyclable Polyurethane Thermoplastic Elastomer. *Journal of Polymer Science Part A Polymer Chemistry* **2008**, *46* (5), 1893−1901.

(47) Schara, P.; Cristadoro, A. M.; Sijbesma, R. P.; Tomović, Ž. Solvent-Free Synthesis of Acetal-Containing Polyols for Use in Recyclable Polyurethanes. *Macromolecules* **2023**, *56* (21), 8866−8877.

(48) Feng, Y.; Zhang, Z.; Yue, D.; Belko, V. O.; Maksimenko, S. A.; Deng, J.; Sun, Y.; Yang, Z.; Fu, Q.; Liu, B.; Chen, Q. Recent Progress in Degradation and Recycling of Epoxy Resin. *Journal of Materials Research and Technology* **2024**, *32*, 2891−2912.

(49) Chen, Y.-C.; Reddy, K. S. K.; Jeng, R.-J.; Lin, C.-H. Poly(Carbonate Acetal) Vitrimers with Enhanced Thermal Properties and Closed-Loop Thermal Recyclability Derived from Waste Polycarbonate-Derived Polyaldehyde and Pentaerythritol/Erythritol/D-Sorbitol. *Green Chem.* **2024**, *26* (19), 10275−10289.

(50) Mankar, S. V.; Wahlberg, J.; Warlin, N.; Valsange, N. G.; Rehnberg, N.; Lundmark, S.; Jannasch, P.; Zhang, B. Short-Loop Chemical Recycling via Telechelic Polymers for Biobased Polyesters with Spiroacetal Units. *ACS Sustainable Chem. Eng.* **2023**, *11* (13), 5135−5146.

(51) Wróblewska, A. A.; Lingier, S.; Noordijk, J.; Du Prez, F. E.; De Wildeman, S. M. A.; Bernaerts, K. V. Polyamides Based on a Partially Bio-Based Spirodiamine. *Eur. Polym. J.* **2017**, *96*, 221−231.

(52) Zhang, H.; Ruckenstein, E. Self-Polyaddition of Hydroxyalkyl Vinyl Ethers. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (20), 3751−3760.

(53) Wang, X.; Zhou, J.; Li, L. Multiple Melting Behavior of Poly(Butylene Succinate). *Eur. Polym. J.* **2007**, *43* (8), 3163−3170.

(54) Peng, F.; Cao, R.; Sun, H.; Liu, Z.; Zhang, Y.; Xu, T.; Li, L. Role of Entanglement in Polymer Crystal Growth and Melting: Molecular Dynamics Simulations. *Macromolecules* **2024**, *57* (21), 10487−10498.

(55) Wan, C.; Heeley, E. L.; Zhou, Y.; Wang, S.; Cafolla, C. T.; Crabb, E. M.; Hughes, D. J. Stress-oscillation behaviour of semi-crystalline polymers: the case of poly(butylene succinate). *Soft Matter* **2018**, *14* (45), 9175−9184.

(56) Alexander, L. E. *X-Ray Diffraction Methods in Polymer Science*; John Wiley & Sons, 1969.

(57) Tashiro, K. Crystal Structure analysis by wide-angle X-ray diffraction method. In Tashiro, K, editors. *Structural science of crystalline polymers: Basic concepts and practices*; Springer Nature Singapore; 2022. pp 1−285.

(58) Ihn, K. J.; Yoo, E. S.; Im, S. S. Structure and Morphology of Poly(Tetramethylene Succinate) Crystals. *Macromolecules* **1995**, *28* (7), 2460−2464.

(59) Ichikawa, Y.; Kondo, H.; Igarashi, Y.; Noguchi, K.; Okuyama, K.; Washiyama, J. Crystal Structures of α and β Forms of Poly(Tetramethylene Succinate). *Polymer* **2000**, *41* (12), 4719−4727.

(60) Xu, J., Guo, B. H. Microbial Succinic Acid, Its Polymer Poly(butylene succinate), and Applications. In Chen, G. Q., (eds) *Plastics from Bacteria*. Microbiology Monographs, vol *14*; Springer: Berlin, Heidelberg, 2010; pp 347−388 .

(61) Padermshoke, A.; An, Y.; Kajiwara, T.; Masunaga, H.; Kobayashi, Y.; Ito, H.; Sasaki, S.; Noguchi, H.; Kusuno, A.; Takahara, A. Photooxidation-induced Conformational Changes and Degradation Behaviors of Poly(butylene succinate) and Poly(butylene succinate-co-adipate). *J. Polym. Sci.* **2024**, *62* (16), 3794−3807.

(62) Strobl, G. R.; Schneider, M. Direct Evaluation of the Electron Density Correlation Function of Partially Crystalline Polymers. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18* (6), 1343−1359.

(63) Liu, G.; Zheng, L.; Zhang, X.; Li, C.; Jiang, S.; Wang, D. Reversible Lamellar Thickening Induced by Crystal Transition in Poly(Butylene Succinate). *Macromolecules* **2012**, *45* (13), 5487−5493.

(64) Scherrer, P. Bestimmung Der Größe Und Der Inneren Struktur von Kolloidteilchen Mittels Röntgenstrahlen. *Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl.* **1918**, *1918*, 98−100.

(65) Liu, B.; Thayumanavan, S. Substituent Effects on the PH Sensitivity of Acetals and Ketals and Their Correlation with Encapsulation Stability in Polymeric Nanogels. *J. Am. Chem. Soc.* **2017**, *139* (6), 2306−2317.

(66) Taguchi, H.; Osaka, N.; Kikuchi, T. Accelerated Evaluation of Biodegradability in Seawater by Activated Inoculum. *J. Mater. Life Soc. Jpn.* **2021**, *33*, 57−64.

(67) Ando, S.; Hirano, M.; Watakabe, L.; Yokoyama, H.; Ito, K. Environmentally Friendly Sustainable Thermoset Vitrimer-Containing Polyrotaxane. *ACS Materials Lett.* **2023**, *5*, 3156−3160.

(68) An, Y.; Padermshoke, A.; Nguyen, T. V.; Masunaga, H.; Yokoyama, R.; Yonemura, M.; Kato, D.; Kobayashi, Y.; Ito, H.; Sasaki, S.; Takahara, A. Photo-Oxidative Degradation and Biodegradation of Poly(Ether-*Block*-Amide) Multiblock Copolymers. *ACS Applied Polymer Materials* **2024**, *6* (10), 6140−6149.

(69) Ma, C.; Xu, L.; Xu, W.; Zhang, G. Degradable Polyurethane for Marine Anti-Biofouling. *J. Mater. Chem. B* **2013**, *1* (24), 3099.

(70) He, M.; Hsu, Yu-I.; Uyama, H. Superior Sequence-Controlled Poly(L-Lactide)-Based Bioplastic with Tunable Seawater Biodegradation. *Journal of Hazardous Materials* **2024**, *474*, No. 134819.