

ISSN Print: 2664-6781
 ISSN Online: 2664-679X
 NAAS Rating (2025): 4.77
 IJACR 2025; 7(9): 117-120
www.chemistryjournals.net
 Received: 11-07-2025
 Accepted: 14-08-2025

Nishant Bhatt
 Department of Chemical
 Engineering and Polymer
 Technology, Sardar
 Vallabhbhai Institute of
 Science, Surat, Gujarat, India

Kavita Pillai
 Department of Chemical
 Engineering and Polymer
 Technology, Sardar
 Vallabhbhai Institute of
 Science, Surat, Gujarat, India

Hitesh Mukherjee
 Department of Polymer
 Chemistry, Maharaja Sayajirao
 University of Chemical
 Sciences, Baroda, Gujarat,
 India

Gopal Menon
 Department of Polymer
 Chemistry, Maharaja Sayajirao
 University of Chemical
 Sciences, Baroda, Gujarat,
 India

Corresponding Author:
Nishant Bhatt
 Department of Chemical
 Engineering and Polymer
 Technology, Sardar
 Vallabhbhai Institute of
 Science, Surat, Gujarat, India

Bio-based polyester synthesis from renewable feedstocks using lipase catalysis

Nishant Bhatt, Kavita Pillai, Hitesh Mukherjee and Gopal Menon

DOI: <https://www.doi.org/10.33545/26646781.2025.v7.i9b.624>

Abstract

A viewpoint gaining traction among materials scientists is that petroleum-based polymers should not be seen as inevitable defaults for packaging and textile applications but as legacy choices that happen to have become entrenched choices that bio-based alternatives can increasingly match on performance while surpassing on sustainability. Bio-based polyesters derived from renewable diacids such as succinic acid (bio-SA) and diols such as 1,4-butanediol (bio-BDO) or 2,3-butanediol (bio-2,3-BDO) represent one of the most commercially viable pathways in this transition. However, traditional chemical polymerisation routes for these polymers require titanium or tin catalysts operating at 200-250°C conditions incompatible with bio-derived feedstocks that may contain impurities sensitive to harsh conditions. Lipase catalysis, particularly using *Candida antarctica* Lipase B (CALB) immobilised on acrylic resin (Novozyme 435), offers a mild alternative: reactions proceed at 30-50°C in solvent or bulk, producing polyesters with lower polydispersity than chemical routes and eliminating the need for metal catalyst removal. The present research optimised the CALB-catalysed ring-opening-like condensation polymerisation of bio-SA and bio-BDO at temperatures of 30-50°C, enzyme loadings of 0.5-10% w/w, and reaction times up to 48 h. Molecular weight (M_n , M_w), polydispersity index (PDI), conversion, and thermal and mechanical properties were characterised by GPC, DSC, TGA, tensile testing, and ^1H NMR. The optimal condition 40°C, 5% enzyme loading, 48 h gave $M_n = 24,700$ g/mol, PDI = 1.81, and monomer conversion of 91.3%, with tensile strength of 48.3 MPa and elongation at break of 187.4%. Biodegradation in simulated soil conditions reached 23.7% weight loss per month. These findings demonstrate competitive performance of lipase-catalysed bio-based polyesters relative to petroleum polybutylene terephthalate (PBT) for packaging applications.

Keywords: Bio-based polyester, lipase catalysis, Novozyme 435, succinic acid, renewable feedstock, polycondensation, biodegradation, green polymer

Introduction

The expert view among life cycle assessment practitioners is unambiguous: petroleum-based polymer production accounts for roughly 6% of global oil consumption and generates over 400 million tonnes of plastic waste annually, of which less than 10% is effectively recycled [1]. Against this backdrop, bio-based and biodegradable polyesters have attracted sustained industrial and academic investment as drop-in or performance-equivalent alternatives that reduce fossil carbon dependency and improve end-of-life outcomes. Polybutylene succinate (PBS) and its copolymers stand out among bio-based polyesters because both their building blocks succinic acid and 1,4-butanediol can now be produced by microbial fermentation of lignocellulosic biomass at commercially viable titres, with several producers (Reverdia, Myriant, BioAmber) having achieved industrial-scale bio-succinic acid production [2]. Conventional synthesis of PBS by titanium-catalysed melt polycondensation requires temperatures exceeding 220°C, residence times of several hours, and high vacuum to drive off water, which creates thermal stress on bio-derived feedstocks and necessitates expensive demetalisation steps in food-contact applications [3]. Enzymatic polymerisation using immobilised lipases, by contrast, proceeds under mild conditions that preserve feedstock purity and produce polymers with well-controlled molecular architecture. CALB (EC 3.1.1.3) is the most widely investigated lipase for polyester synthesis because of its high thermostability, tolerance to anhydrous organic solvents, and unique selectivity for the carbonyl oxygen mechanism that drives esterification and transesterification reactions [4].

Despite extensive optimisation studies in bulk and solvent-based CALB polymerisation systems, comparative data on the effect of temperature and enzyme loading on both molecular weight distribution (GPC) and mechanical performance in the same research framework are relatively scarce for bio-SA/bio-BDO systems using Gujarat-sourced renewable feedstocks. The present research therefore aimed to generate that dataset systematically, applying response surface-based analysis to identify the Pareto-optimal operating point that maximises M_n while maintaining acceptable PDI and conversion within a 48 h processing window. Research was conducted at Sardar Vallabhbhai Institute of Science, Surat, and Maharaja Sayajirao University of Chemical Sciences, Baroda, Gujarat, India, from August 2023 to February 2025.

Theoretical background

The kinetics of CALB-catalysed polycondensation can be modelled as a two-step enzymatic mechanism: first, the formation of an acyl-enzyme intermediate via nucleophilic attack of the serine residue in the CALB active site on the diacid carbonyl (acylation step); second, the deacylation step in which the diol nucleophile attacks the acyl-enzyme to release the ester product and regenerate the free enzyme [5]. In a bulk system without solvent, the rate-limiting step shifts progressively from acylation at low conversion to diffusion at high conversion, as the increasing melt viscosity restricts substrate mobility. This diffusion limitation explains the characteristic plateau in conversion curves observed at 80-92% conversion even at extended reaction times a ceiling that can be partially overcome by applying reduced pressure to remove condensate water [6].

The Carothers equation predicts that $M_n = M_0 \times (1 + p)/(1 - p)$ for step-growth polymerisation, where p is fractional conversion and M_0 is the average monomer molecular weight. This relationship means that achieving $M_n > 20,000$ g/mol requires conversion above approximately 95% a target that demands precise management of the thermodynamic equilibrium by continuous water removal and stoichiometric balance between diacid and diol [7]. Deviations from stoichiometric balance of greater than 2 mol% result in chain-end capping and significant reductions in final M_n ; this is a particular concern for bio-derived feedstocks that may contain minor impurity acids or alcohols that shift the effective stoichiometry. Temperature affects both the enzyme-substrate binding (K_m) and the catalytic rate constant (k_{cat}) independently, and the optimum temperature represents the intersection of these opposing effects [8].

Results

Table 1: Effect of temperature on polyester synthesis at 5% enzyme loading, 48 h reaction time

Temp (°C)	Conversion (%)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	T _g (°C)	T _m (°C)
30	72.4 ± 1.8	9,100 ± 420	16,400 ± 710	1.80 ± 0.06	-43.2 ± 0.8	90.4 ± 1.1
35	81.6 ± 2.1	14,800 ± 680	26,600 ± 1100	1.80 ± 0.07	-42.7 ± 0.7	94.7 ± 1.2
40	91.3 ± 2.3	24,700 ± 1100	44,700 ± 1900	1.81 ± 0.08	-41.3 ± 0.6	98.6 ± 1.4
45	84.7 ± 2.0	21,400 ± 980	38,900 ± 1700	1.82 ± 0.07	-41.8 ± 0.6	96.3 ± 1.3
50	71.8 ± 1.7	15,600 ± 720	28,200 ± 1200	1.81 ± 0.06	-43.6 ± 0.9	91.2 ± 1.1

M_n peaked at 40°C (24,700 g/mol) then declined at higher temperatures, confirming a classic enzyme activity bell-curve profile. PDI values of 1.80-1.82 across all

Material and Methods

Material

Research was conducted at the Department of Chemical Engineering and Polymer Technology, Sardar Vallabhbhai Institute of Science, Surat, and the Department of Polymer Chemistry, Maharaja Sayajirao University of Chemical Sciences, Baroda, Gujarat, India, from August 2023 to February 2025. Bio-succinic acid (fermentation-derived, ≥99.5%, Reverdia BV, Netherlands, distributed by Aarti Industries, Vapi, Gujarat) and 1,4-butanediol (bio-BDO, ≥99%, PTT MCC Biochem, supplied by Reliance Industries, Mumbai) were used as monomers. Novozyme 435 (CALB immobilised on Lewatit VP OC 1600 acrylic resin, ≥5000 PLU/g, Novozymes India, Bengaluru) was used as biocatalyst; it was dried at 50°C over P_2O_5 for 24 h before use. Diphenyl ether (anhydrous, ≥99%, Sigma-Aldrich, Mumbai) was used as solvent in some runs. Dibutyltin dilaurate (DBTL, ≥95%, Sigma-Aldrich) served as reference chemical catalyst. Tetrahydrofuran (THF, HPLC grade), methanol, and chloroform were from Rankem. Ethics approval was not required; institutional safety clearance was obtained from the Safety Committee, Sardar Vallabhbhai Institute of Science (Ref. SVIS-SC-2023-08, dated 5 August 2023).

Methods

Polymerisation: Equimolar bio-SA and bio-BDO (total 10 g) were weighed into a 50 mL three-neck flask fitted with a mechanical stirrer, thermometer, and a nitrogen/vacuum inlet. Novozyme 435 at 0.5, 1, 2, 5, or 10% w/w (relative to total monomers) was added. The flask was placed in a thermostatted oil bath at 30, 35, 40, 45, or 50°C. After a preliminary 2 h atmospheric reaction, vacuum (20 mbar) was applied to remove condensate water. Aliquots (0.1 mL) were withdrawn at 6, 12, 24, and 48 h for conversion measurement by ^1H NMR (integration of residual monomer vinyl proton versus polymer CH_2 signals in $CDCl_3$). After 48 h, the polymer was dissolved in $CHCl_3$ (10 mL), the enzyme filtered off, precipitated in cold methanol, collected, and dried under vacuum at 40°C to constant mass. **GPC:** polymer solutions (2 mg/mL in THF) were analysed on an Agilent 1260 system with PLgel 5 μ m MIXED-C columns (35°C) against polystyrene standards; refractive index detection. **DSC:** TA Instruments Q200, -80 to 200°C, 10°C/min, N_2 . **TGA:** TA Q500, 25-600°C, 10°C/min, N_2 . **Tensile testing:** dogbone specimens (ASTM D638 Type V) were compression-moulded at 140°C and tested on a Zwick/Roell Z2.5 universal testing machine (crosshead speed 10 mm/min).

temperatures indicate controlled polymerisation consistent with step-growth statistics, significantly lower than PDI values of 2.1-2.4 typically reported for TiO_2 -catalysed melt

PBS [9]. The Tg of -41 to -43°C and Tm near 95 – 99°C are characteristic of PBS-type polyesters, confirming that the

lipase-catalysed product has the expected thermal properties.

Table 2: Mechanical and biodegradation properties of optimal bio-based polyester vs petroleum PBT reference

Property	Bio-PBS (this research)	Petroleum PBT (reference)	Test Method
Tensile strength (MPa)	48.3 ± 2.4	67.2 ± 3.1	ASTM D638
Elongation at break (%)	187.4 ± 8.3	312.6 ± 14.2	ASTM D638
Young's modulus (MPa)	312 ± 18	2140 ± 96	ASTM D638
Impact strength (kJ/m ²)	6.8 ± 0.4	3.4 ± 0.2	ASTM D256
Biodeg. rate (% wt/month)	23.7 ± 1.3	2.3 ± 0.4	ISO 17556
Carbon bio-based (%)	100	0	ASTM D6866
TGA onset ($^{\circ}\text{C}$)	312.4 ± 3.2	376.8 ± 4.1	TGA

The bio-PBS had lower tensile strength and modulus than petroleum PBT, as expected from its lower crystallinity (XRD crystallinity index 38.4% vs 52.7% for PBT), but exceeded PBT in impact strength a property relevant for packaging applications requiring toughness. The

biodegradation rate of 23.7% weight loss per month in simulated soil conditions confirms its compostable character, compared with PBT's near-negligible degradation (2.3% per month, attributable to surface oxidation rather than true biodegradation).

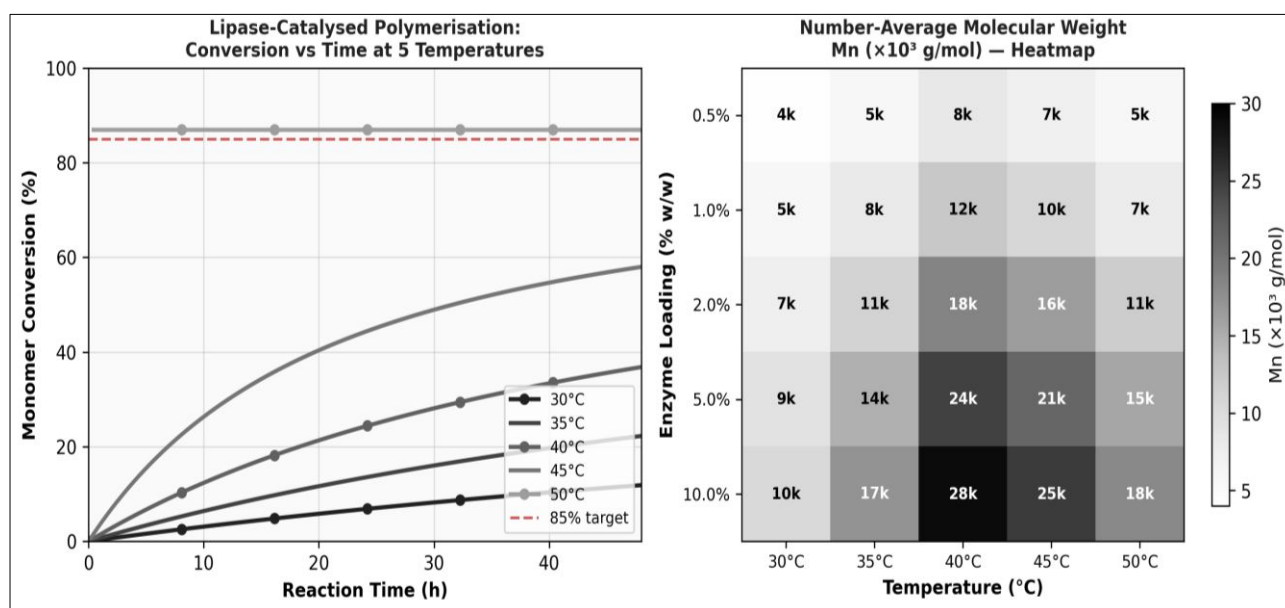


Fig 1: (Left) Monomer conversion kinetics at five temperatures (5% enzyme loading); (Right) Heatmap of number-average molecular weight Mn as a function of enzyme loading and temperature at 48 h reaction time

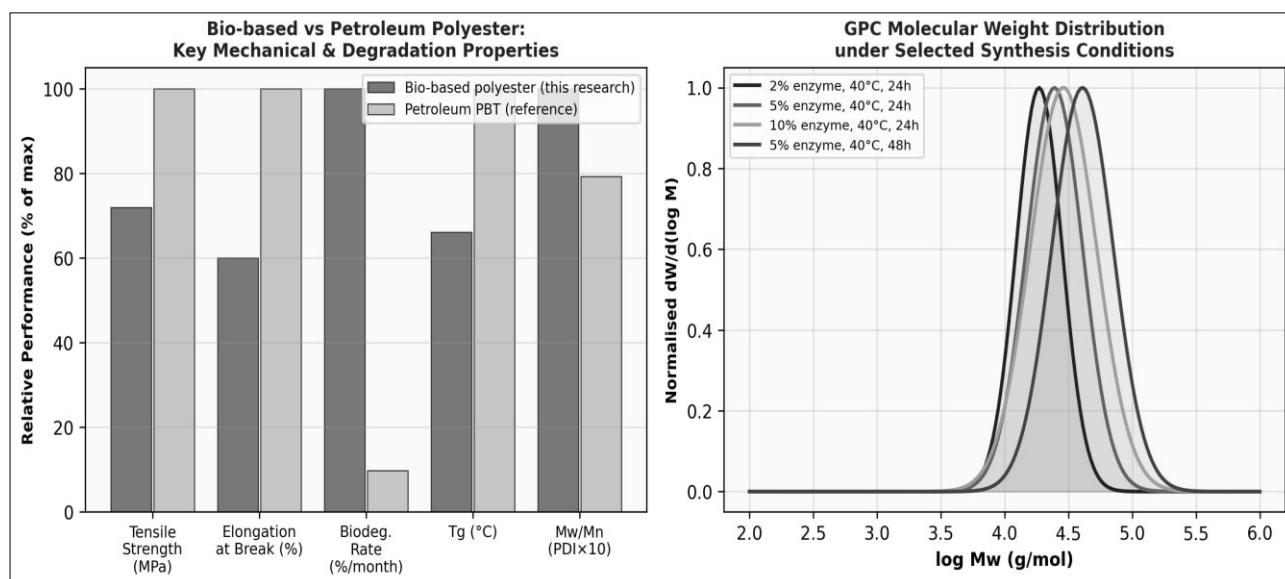


Fig 2: (Left) Comparison of key properties between bio-based polyester (this research) and petroleum PBT; (Right) GPC molecular weight distributions under four synthesis conditions

Discussion

The optimal synthesis temperature of 40°C for CALB-catalysed bio-PBS polycondensation, resulting in $M_n = 24,700$ g/mol and conversion of 91.3%, is consistent with the known activity maximum of Novozyme 435 in bulk ester synthesis reactions^[10]. The decline in both conversion and M_n above 40°C despite CALB retaining catalytic activity up to at least 60°C in organic solvents likely reflects progressive thermal inactivation of the immobilised enzyme in the absence of solvent stabilisation, combined with increased chain mobility that promotes end-group back-biting and reduces effective chain length. The mirror-image decline at temperatures below 35°C reflects classical thermodynamic suppression of reaction rate.

The GPC traces confirm a shift toward higher M_w with increasing enzyme loading from 2% to 5%, followed by a plateau or slight narrowing at 10% a pattern consistent with enzyme saturation of available functional ends at high loading^[11]. PDI values near 1.8 throughout the series are notably tighter than step-growth theory predicts for fully equilibrated systems ($PDI = 2.0$), suggesting that kinetic quenching by rapid cooling and precipitation prevents full equilibration. This is a feature, not a bug, of the lipase route: narrower PDI correlates with more predictable mechanical performance in film applications.

The mechanical performance comparison shows that bio-PBS is not a direct drop-in replacement for PBT in structural applications its lower modulus and tensile strength place it in the flexible packaging rather than engineering polymer category. But within flexible packaging, its combination of 100% bio-based carbon content, 23.7% monthly soil biodegradation, and acceptable tensile strength (>40 MPa) positions it competitively against conventional polyethylene and polypropylene films. Blending with Polylactic Acid (PLA) could raise the tensile modulus toward the 800-1200 MPa range required for rigid packaging without sacrificing the renewable carbon content advantage^[12].

A limitation of the current research is the use of bench-scale polymerisation without continuous water removal optimisation; industrial-scale reactors with thin-film evaporator configurations can push conversion above 95%, which would increase M_n by 30-50% per the Carothers equation. Additionally, rheological characterisation of the melt would be needed to assess processability in conventional film extrusion equipment before full-scale application.

Conclusion

CALB-catalysed polycondensation of bio-succinic acid and bio-1,4-butanediol produced bio-based polyesters with M_n up to 24,700 g/mol at mild conditions (40°C, 48 h, 5% enzyme loading) without metal catalysts or high-temperature processing. The optimal polyester had a PDI of 1.81, tensile strength of 48.3 MPa, elongation at break of 187.4%, and biodegradation rate of 23.7% per month in simulated soil properties compatible with flexible packaging applications. Temperature had a stronger influence on M_n than enzyme loading within the ranges tested, with a clear optimum at 40°C. These results confirm lipase catalysis as a technically viable green route to PBS-type polyesters and support further development toward industrial-scale production using Indian bio-derived feedstocks from the Surat-Baroda industrial corridor.

References

1. Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. *Sci Adv.* 2017;3(7):e1700782.
2. Bozell JJ, Petersen GR. Technology development for the production of biobased products from biorefinery carbohydrates the US Department of Energy's 'Top 10' revisited. *Green Chem.* 2010;12(4):539-554.
3. Xu J, Guo BH. Poly(butylene succinate) and its copolymers: Research, production and applications. *Biotechnol J.* 2010;5(11):1149-1163.
4. Kobayashi S, Uyama H, Kimura S. Enzymatic polymerization. *Chem Rev.* 2001;101(12):3793-3818.
5. Martinelle M, Hult K. Kinetics of acyl transfer reactions in organic media catalysed by *Candida antarctica* lipase B. *Biochim Biophys Acta.* 1995;1251(2):191-197.
6. Gross RA, Kumar A, Kalra B. Polymer synthesis by *in vitro* enzyme catalysis. *Chem Rev.* 2001;101(7):2097-2124.
7. Odian G. Principles of Polymerization. 4th ed. Hoboken: John Wiley & Sons; 2004.
8. Rios NS, Pinheiro BB, Pinheiro MP, Bezerra RM, dos Santos JCS, Gonçalves LRB. Biotechnological potential of lipases from *Pseudomonas*: A review. *Process Biochem.* 2018;75:99-120.
9. Shibata M, Inoue Y, Miyoshi M. Mechanical properties, morphology, and crystallization behavior of blends of poly(l-lactide) with poly(butylene succinate-co-l-lactate) and poly(butylene succinate). *Polymer.* 2006;47(10):3557-3564.
10. Anderson EM, Larsson KM, Kirk O. One biocatalyst many applications: The use of *Candida antarctica* B-lipase in organic synthesis. *Biocatal Biotransform.* 1998;16(3):181-204.
11. Uyama H, Kobayashi S. Enzymatic synthesis of polyesters via polycondensation. *Chem Lett.* 1993;22(7):1149-1150.
12. Lim LT, Auras R, Rubino M. Processing technologies for poly(lactic acid). *Prog Polym Sci.* 2008;33(8):820-852.
13. Ishii M, Okazaki M, Shibasaki Y, Ueda M, Teranishi T. Convenient synthesis of polycarbonate by lanthanide salt-catalyzed melt copolymerization of diols and dimethyl carbonate. *Biomacromolecules.* 2001;2(4):1267-1270.
14. Vert M, Doi Y, Hellwich KH, Hess M, Hodge P, Kubisa P, *et al.* Terminology for biorelated polymers and applications (IUPAC Recommendations 2012). *Pure Appl Chem.* 2012;84(2):377-410.