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## Novel hydrolytically stable Lewis acidic ionic liquid catalyst system for polybutylene succinate (PBS) synthesis†

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Poly(butylene succinate) (PBS) is considered to be a potential bio-alternative for petroleum-based polymers due to its environmentally benign nature and biodegradability. Despite its various advantages, its low thermal stability and lack of high molecular weight required for industrial applications restrict its implementation on a commercial scale. The synthesis of high molecular weight PBS remains a challenging task due to the hydrolytic instability of the catalyst as well as the thermal sensitivity of PBS. Herein, we report a Lewis acidic ionic liquid (LAIL) as a novel, mild, efficient and hydrolytically stable catalyst system for the synthesis of high molecular weight PBS. Further, the thermal stability of the PBS synthesized using the novel catalyst is found to be higher than the corresponding polymer synthesized using a conventional catalyst.

## Introduction

The petrochemical revolution in the last decade led to the development of various commercially important polymers such as polyethylene, polystyrene, polypropylene and poly(vinyl chloride) from fossil fuels.<sup>1</sup> Moreover, their low cost and excellent mechanical properties have championed these polymers as the material of choice for various applications such as electrical and electronics, automobiles, food packaging, pipe and fittings, personal hygiene, cosmetics, building and construction, and pharmaceuticals.<sup>2</sup> However, the durability and non-biodegradability of fossil fuel-based polymers has led to increased plastic pollution in the environment.<sup>3</sup> In recent years, the design and synthesis of environmentally friendly polymers as an alternative to petroleum-based polymers have gained considerable interest among scientists in both academia and

the industry.<sup>4</sup> As a result, various bio-based polymers have been developed and have found commercial applications in replacing petroleum-based polymers.<sup>5</sup> Among the various bio-based polymers, polybutylene succinate (PBS) has gained considerable interest as a potential bio-alternative due to its comparable physical and mechanical properties as those of polyolefins.<sup>6</sup>

However, its high cost coupled with a lack of high molecular weight required for industrial application restricts its commercialization.<sup>7</sup> Extensive research is being carried out to broaden the application of PBS by improving its mechanical and thermal properties *via* chemical and physical methods.<sup>8</sup> Generally, the synthesis of PBS involves two steps: esterification or *trans*-esterification followed by polycondensation reactions, which are carried out at high temperatures, usually 230–250 °C under vacuum (Scheme 1).<sup>9</sup> Significant efforts have already been made towards the development of mild and efficient catalysts in synthesizing high molecular weight PBS. As a result, various catalyst systems have been reported in the literature for the synthesis of PBS.<sup>8</sup>

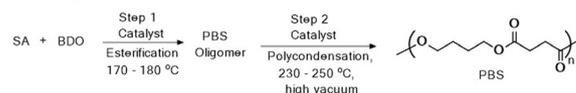
However, among the various catalysts explored, titanium-based catalysts exhibit better catalytic activity than other Lewis acid catalysts. Thus, titanium alkoxides (titanium tetrabutoxide (TBT) and titanium tetraisopropoxide (TTIP)) are the most widely used catalyst for the synthesis of PBS as well as its copolymers, and the order of efficiency is found to be Ti » Zr ~ Sn > Hf > Sb > Bi.<sup>9</sup> However, titanium-based catalysts are

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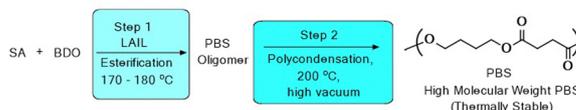
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## Conventional Synthesis:



## New Synthesis:



Scheme 1 Novel hydrolytically stable catalyst for the synthesis of PBS.



more sensitive to moisture/water, and hence the addition of catalyst during the polycondensation step exhibited higher activity than adding the catalyst during the esterification step. This clearly indicates the sensitivity of titanium-based catalysts towards water, the by-product formed during the reaction.<sup>9a</sup>

Moreover, PBS is thermally sensitive and the high temperature required for the polycondensation reaction restricts the synthesis of high molecular weight PBS, as it undergoes various side reactions including degradation.<sup>10</sup> Thus, the synthesis of high molecular weight PBS from dicarboxylic acids and diols remains a challenging task due to the thermal sensitivity of PBS and hydrolytic instability of the catalyst. Thus, the development of efficient and hydrolytically stable catalysts for the synthesis of high molecular weight PBS is much sought after. Herein, we report a novel mild, efficient and hydrolytically stable (Lewis acidic ionic liquid) catalyst system for the synthesis of high molecular weight PBS.

## Results and discussion

In recent years, ionic liquids have gained considerable attention in catalysis. Various ionic liquids (LAIL) have been developed and proven to be more efficient than conventional catalysts in various organic transformations.<sup>11</sup> To the best of our knowledge, the use of ionic liquids has not yet been explored for the synthesis of PBS. Thus, it is in our interest to explore a few Lewis acidic ionic liquids for the synthesis of PBS. Recently, a hydrolytically stable Lewis acidic ionic liquid was developed using choline chloride and the metal salts of Sn and Zn, especially for the Diels Alder reaction.<sup>12</sup> It is in our interest to explore this catalyst system for the synthesis of PBS.

Thus, ionic liquids based on Sn and Zn were prepared using choline chloride and BMIMCl (1-Butyl-3-methylimidazolium chloride) by following a reported procedure.<sup>12</sup> The synthesized catalyst was examined for its catalytic efficiency with respect to conventional catalyst such as titanium tetrabutoxide, titanium tetraisopropoxide, stannous chloride *etc.*, and the results are summarized in Table 1 (entry 1–12). The reported method was optimized and using the optimized synthetic method, PBS with  $M_n$ ,  $M_w$  and PDI values of about  $1.84 \times 10^4 \text{ g mol}^{-1}$ ,  $4.68 \times 10^4 \text{ g mol}^{-1}$  and 2.53, respectively, were synthesized.<sup>9a</sup> Further,

the optimized reaction condition was used to screen the efficiency of other catalyst systems (using 0.02 mol%) for the synthesis of PBS (Table 1).<sup>13</sup>

Interestingly, the ionic liquid prepared using choline chloride and  $\text{SnCl}_2$  exhibited better catalytic activity than the conventional catalysts (Table 1, entry 5). However, the ionic liquid prepared using zinc chloride exhibited moderate activity (Table 1, entry 6 and 8). From the experimental results, it is very clear that choline chloride-based ionic liquids are found to be more efficient in producing relatively high molecular weight PBS than the corresponding BMIMCl-based ionic liquids (Table 1, entry 5–8). Further, the reaction of succinic acid and butanediol in the presence of BMIMCl, ChCl, [BMIM][HSO<sub>4</sub>] and phosphomolybdic acid (PMA) resulted in the isolation of polymers with low molecular weight (Table 1, entry 9–12).

Furthermore, the influence of Lewis acid concentration in the ionic liquids was investigated and the results are summarized in Table 2. Since ChCl-based Lewis acidic ionic liquids exhibited better catalytic activity than the corresponding BMIMCl-based ionic liquids, a systematic investigation was carried out to understand the influence of temperature and the concentration of metal halides in ChCl-based Lewis acidic ionic liquids. An increase in the concentration of metal halides in the ChCl-based ionic liquids resulted in increased catalytic activity by reducing the reaction time required for the reaction (Table 2, entry 3); however, further increase in the concentration of Lewis acid in the catalyst system resulted in the lowering of the thermal stability of the polymer (Table 2, entry 9). Interestingly, the choline chloride-based Lewis acidic ionic liquid catalyst system was found to produce high molecular weight PBS even at low temperatures (200 °C) (Table 2, entry 6).

To understand the hydrolytic stability of the ChCl-based Lewis acidic ionic liquid catalyst system, PBS synthesis was carried out by adding the catalyst before and after the esterification reaction (Table 3, entry 1–6). Interestingly, no significant changes in catalytic activity were observed for the newly synthesized ChCl:SnCl<sub>2</sub> catalyst system, which clearly indicates the hydrolytic stability of the catalyst. Whereas, conventional titanium based catalyst exhibited reduced catalytic activity by adding the catalyst before esterification reaction, which clearly elucidates the hydrolytic instability of the catalyst system

**Table 1** Synthesis of PBS using various Lewis and Brønsted acid catalysts

S. No.	Catalyst <sup>a</sup>	Temp. (°C) (Time)	$M_n$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	PDI	$T_m$ (°C)	$T_c$ (°C)	$T_d$ (°C)
1	Ti(OBu) <sub>4</sub>	230 (6.5 h)	18 536	46 870	2.53	77	112	368
2	Ti(O <sup><i>i</i></sup> Pr) <sub>4</sub>	230 (6.5 h)	14 855	41 354	2.78	73	110	365
3	SnCl <sub>2</sub>	230 (6 h)	18 427	50 868	2.76	77	114	370
4	ZnCl <sub>2</sub>	230 (8 h)	10 226	32 226	3.15	70	112	360
5	ChCl:SnCl <sub>2</sub> (1:1)	230 (7 h)	21 874	57 957	2.65	78	115	379
6	ChCl:ZnCl <sub>2</sub> (1:1)	230 (7 h)	19 289	41 483	2.15	74.8	112.7	358
7	BMIM:SnCl <sub>2</sub> (1:1)	230 (7 h)	15 923	38 160	2.41	72.6	112.6	362
8	BMIM:ZnCl <sub>2</sub> (1:1)	230 (7 h)	9654	27 058	2.81	71.4	110.81	354
9	BMIMCl	230 (7 h)	2286	10 740	4.70	—	—	—
10	ChCl	230 (7 h)	7758	18 278	2.36	—	—	—
11	[BMIM][HSO <sub>4</sub> ]	230 (7 h)	3065	7271	2.37	—	—	—
12	PMA	230 (7 h)	1113	1884	1.69	—	—	—

<sup>a</sup> 0.02 mol% catalyst was used for the reaction;  $T_d$ : onset degradation temperature.



Table 2 Effect of the concentration of catalyst and temperature on PBS synthesis

S. No.	Catalyst <sup>a</sup>	Temp. (°C) (Time)	$M_n$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	PDI	$T_m$ (°C)	$T_c$ (°C)	$T_d$ (°C)
1	BMIM:SnCl <sub>2</sub> (1:2)	230 (7 h)	18 057	42 907	2.38	75	112	368
2	BMIM:ZnCl <sub>2</sub> (1:2)	230 (7 h)	12 365	31 623	2.56	74.6	111	362
3	ChCl:SnCl <sub>2</sub> (1:2)	230 (6 h)	31 988	72 624	2.27	77	115	383
4	ChCl:ZnCl <sub>2</sub> (1:2)	230 (7 h)	14 902	41 472	2.78	75	113	364
5	ChCl:SnCl <sub>2</sub> (1:1)	200 (8 h)	21 840	56 826	2.60	77	114	378
6	ChCl:SnCl <sub>2</sub> (1:2)	200 (7 h)	21 609	73 031	3.38	76	115	389
7	ChCl:ZnCl <sub>2</sub> (1:1)	200 (8.5 h)	12 365	31 623	2.56	75	112	354
8	ChCl:ZnCl <sub>2</sub> (1:2)	200 (7.5 h)	15 823	37 960	2.39	75	111	358
9	ChCl:SnCl <sub>2</sub> (1:3)	230 (5 h)	21 902	72 990	3.33	77	114	368

<sup>a</sup> 0.02 mol% catalyst was used for the reaction.

Table 3 Hydrolytic stability of the Lewis acidic ionic liquids

S. No.	Catalyst <sup>e</sup>	Time	$M_n$ (g mol <sup>-1</sup> )	$M_w$ (g mol <sup>-1</sup> )	PDI	$T_m$ (°C)	$T_c$ (°C)	$T_d$ (°C)
1 <sup>a</sup>	Ti(OBu) <sub>4</sub>	7 <sup>c</sup>	18 536	46 870	2.53	77	112	362
2 <sup>a</sup>	ChCl:SnCl <sub>2</sub> (1:1)	7 <sup>c</sup>	21 874	57 957	2.65	77.6	115	379
3 <sup>a</sup>	ChCl:SnCl <sub>2</sub> (1:2)	6 <sup>d</sup>	31 988	72 624	2.27	77	115	389
4 <sup>b</sup>	Ti(OBu) <sub>4</sub>	5 <sup>c</sup>	19 074	50 271	2.64	81	114	366
5 <sup>b</sup>	ChCl:SnCl <sub>2</sub> (1:1)	7 <sup>c</sup>	21 732	57 272	2.64	78	115	382
6 <sup>b</sup>	ChCl:SnCl <sub>2</sub> (1:2)	6 <sup>d</sup>	31 448	73 104	2.32	78	115	394

<sup>a</sup> Catalyst added during the esterification step.<sup>13a</sup> <sup>b</sup> Catalyst added during the polycondensation step.<sup>13b</sup> <sup>c</sup> Temperature of the polycondensation reaction: 230 °C. <sup>d</sup> Temperature of the polycondensation reaction: 200 °C. <sup>e</sup> 0.02 mol% ppm catalyst used for the reaction.

Table 4 Trace metal analysis of the final polymer

S. No	Catalyst used for polymerization	Metal content in the final polymer (ppm)
1	Ti(OBu) <sub>4</sub>	225
2	SnCl <sub>2</sub>	212
3	ZnCl <sub>2</sub>	230
4	ChCl:SnCl <sub>2</sub> (1:2)	96
5	ChCl:ZnCl <sub>2</sub> (1:2)	108

Table 5 Thermal stability of the Lewis acidic ionic liquids<sup>a</sup>

S. No	Catalyst	Weight loss (%) <sup>a</sup>
1	ChCl	2.50
2	BMIMCl	38.98
3	ChCl:SnCl <sub>2</sub> (1:2)	0.94
4	ChCl:ZnCl <sub>2</sub> (1:2)	1.68
5	BMIMCl:SnCl <sub>2</sub> (1:2)	0.45
6	BMIMCl:ZnCl <sub>2</sub> (1:2)	0.91

<sup>a</sup> Thermal stability studies at 250 °C for 30 min.

during PBS synthesis (Table 3, entry 1 & 4). Further, thermal stability of the PBS produced using stannous chloride-based ionic liquids was found to be higher than that of the corresponding polymer produced using the zinc-based ionic liquids and titanium-based catalysts (Tables 1 and 2).

It is reported in the literature, that the residual catalyst present in the final polymer results in the degradation of the corresponding polymer at higher temperatures.<sup>9a</sup> Trace metal analysis clearly indicates that the metal catalyst present in the final polymer (PBS) produced using Lewis acidic ionic liquids is very low when compared to the polymer produced using the corresponding metal chloride catalysts (Table 4). The removal of catalyst is found to be more effective in the case of polymerizations carried out using Lewis acidic ionic liquids compared to those with conventional metal chloride catalysts. Moreover, this resulted in the increased thermal stability of the final polymer produced using Lewis acidic ionic liquids (Table 4).

Finally, from the thermal studies, it is evident that all the synthesized ionic liquid catalysts are more stable at 250 °C (temperature required for polycondensation reaction)

(Table 5, entry 1–6). Even choline chloride is found to be stable at 250 °C (Table 5, entry 1). However, the stability of BMIMCl was found to be very low (61%) at 250 °C (Table 5, entry 2). Interestingly, the corresponding ionic liquids synthesized using BMIMCl are found to be more stable at 250 °C (Table 5, entry 5 and 6). This increased stability of the BMIMCl-based Lewis acidic ionic liquids is believed to be due to the self-association of quaternary ammonium salts (QASs) (hydrogen bond acceptor) and metal halides (hydrogen bond donor) to form complexes, which leads to an increase in the thermal and chemical stability of the ionic liquids.

## Conclusion

A novel Lewis acidic ionic liquid catalyst has been developed for the synthesis of high molecular weight PBS. The newly developed catalyst is found to be mild and more efficient than the corresponding conventional titanium-based catalysts. Moreover, the catalyst is found to be hydrolytically stable and the polymer (PBS) produced by the catalyst exhibits higher thermal



stability. In addition, choline chloride-based ionic liquids are more efficient than the corresponding imidazolium-based ionic liquids towards PBS synthesis. Furthermore, removal of the catalyst from the final polymer is found to be relatively easy using the Lewis acidic ionic liquid-based catalyst system for PBS synthesis, which in turn led to increase in thermal stability of the final polymer. We strongly believe that this development of a hydrolytically stable Lewis acidic ionic liquid-based catalyst system will find wider application in the synthesis and commercialization of bio-based polyesters, especially PBS.

## Author contributions

Conceptualization and investigation – K. S. Savitha Gowda; methodology and consultation – Dr M. Senthil Kumar; project administration and supervision – Prof. Dr R. L. Jagadish; writing – original draft – K. S. Savitha Gowda; review and editing – Dr M. Senthil Kumar and Prof. Dr R. L. Jagadish.

## Conflicts of interest

There are no conflicts of interest to declare.

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## References

- (a) A. Gandini, in *Biocatalysis in Polymer Chemistry*, ed. K. Loos, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011, pp. 1–33; (b) O. Platnieks, S. Gaidukovs, V. K. Thakur, A. Barkane and S. Beluns, *Eur. Polym. J.*, 2021, **161**, 110855; (c) S. A. Rafiqah, A. Khalina, A. S. Harmaen, I. A. Tawakkal, K. Zaman, M. Asim, M. N. Nurrazi and C. H. Lee, *Polymers*, 2021, **13**, 1436; (d) M. J. Mochane, S. L. Magagula, J. S. Sefadi and T. C. Mokhena, *Polymers*, 2021, **13**, 1200; (e) F. Xiao, G. Fontaine and S. Bourbigot, *Polym. Degrad. Stab.*, 2021, **183**, 109466; (f) G.-Z. Yin and X.-M. Yang, *J. Polym. Res.*, 2020, **27**, 38; (g) Bioplastics market development update 2021, <https://www.european-bioplastics.org/news/publications/>.
- (a) M. K. Huda and I. Widiastuti, *J. Phys.: Conf. Ser.*, 2021, **1808**, 012015; (b) A. L. Andrady and M. A. Neal, *Philos. Trans. R. Soc., B*, 2009, **364**, 1977–1984.
- I. Vroman and L. Tighzert, *Materials*, 2009, **2**, 307–344.
- (a) S. Spierling, E. Knupffer, H. Behnsen, M. Mudersbach, H. Krieg, S. Springer, S. Albrecht, C. Herrmann and H. J. Endres, *J. Cleaner Prod.*, 2018, **185**, 476–491; (b) Q. Zhang, M. Song, Y. Xu, W. Wang, Z. Wang and L. Zhang, *Prog. Polym. Sci.*, 2021, **120**, 101430; (c) S. Rameshkumar, P. Shaiju, K. E. O'Connor and R. B. Padamati, *Curr. Opin. Green Sustainable Chem.*, 2020, **21**, 75–81; (d) W. Sikorska, M. Musioł, B. Zawidlak-Węgrzyńska and J. Rydz, *Adv. Polym. Technol.*, 2021, 6695140.
- (a) J. Xu and B. H. Guo, *Biotechnol. J.*, 2010, **5**, 1149–1163; (b) G. Guidotti, M. Soccio, V. Siracusa, M. Gazzano, E. Salatelli, A. Munari and N. Lotti, *Polymers*, 2017, **9**, 724; (c) F. De Santis, V. Volpe and R. Pantani, *Polym. Eng. Sci.*, 2016, **57**, 306–311; (d) P. Scarfato, L. D. Maio, M. R. Milana, S. Giamberardini, M. Denaro and L. Incarnato, *Food Addit. Contam., Part A: Chem., Anal., Control, Exposure Risk Assess.*, 2017, **34**, 1730–1742; (e) V. V. Jost, *EXPRESS Polym. Lett.*, 2018, **12**, 429–435; (f) A. Z. Naser, I. Deiab and B. M. Darras, *RSC Adv.*, 2021, **11**, 17151; (g) C. Vilela, A. F. Sousa, A. Fonseca, A. Serra, J. Cohello, C. Freire and A. Silvestre, *Polym. Chem.*, 2014, **5**, 3119–3141; (h) European Bioplastics conference, bioplastics market development update 2021, [https://docs.europeanbioplastics.org/publications/market\\_data/Report\\_Bioplastics\\_Market\\_Data\\_2021\\_short\\_version.pdf](https://docs.europeanbioplastics.org/publications/market_data/Report_Bioplastics_Market_Data_2021_short_version.pdf).
- (a) E. Pollet and L. Averous, Production, chemistry and properties of polyhydroxyalkanoates, in *Biopolymers – New Materials for Sustainable Films and Coatings*, ed. D. Plackett, John Wiley & Sons, Ltd, Chichester, 2011, pp. 65–86. (accessed February 16, 2016); (b) L. Av\_erous, *J. Macromol. Sci., Part C: Polym. Rev.*, 2004, **44**, 231–274; (c) M. Gigli, M. Fabbri, N. Lotti, R. Gamberini, B. Rimini and A. Munari, *Eur. Polym. J.*, 2016, **75**, 431–460.
- L. Aliotta, M. Seggiani, A. Lazzer, V. Gigante and P. Cinelli, *Polymers*, 2022, **14**, 844.
- (a) K. S. Savitha, B. R. Paghadar, M. Senthil Kumar and R. L. Jagadish, *Polym. Chem.*, 2022, **13**, 3562–3612; (b) S. Y. Hwang, E. S. Yoo and S. S. Im, *Polym. J.*, 2021, **44**, 1179–1190; (c) Y.-R. Tang, Y. Zhang, Y. Liu, B.-H. Guo and J. Xu, *J. Compos. Biodegrad. Polym.*, 2020, **8**, 45–60.
- (a) N. Jacquell, F. Freyermouth, F. Fenouillot, A. Rousseau, J. P. Pascault, P. Fuertes and R. Saint-Loup, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 5301–5312; (b) X. Kong, H. Qi and J. M. Curtis, *J. Appl. Polym. Sci.*, 2014, **131**, 40579; (c) D. N. Bikiaris and D. Achilias, *Polymer*, 2006, **47**, 4851–4860; (d) C. Zhu, Z. Zhang, Q. Liu, Z. Wang and J. Jin, *J. Appl. Polym. Sci.*, 2003, **90**, 982–990; (e) K. Y. Choi and K. B. McAuley, in *Step-growth polymerization in Polymer Reaction Engineering*, ed. J. M. Asua, Blackwell Publishing, Oxford, UK, 2007, ch. 7, pp. 273–314.
- S.-F. Lu, M. Chen and C. H. Chen, *J. Appl. Polym. Sci.*, 2012, **123**, 3610–3619.
- (a) A. S. Amarasekara, *Chem. Rev.*, 2016, **116**, 6133–6183; (b) R. Ratti, *Adv. Chem.*, 2014, 729842.
- A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.*, 2001, 2010–2011.
- Literature method was standardized by repeating the PBS synthesis in triplicates. Concordant values of Mn, Mw and PDI clearly indicates the repeatability and reproducibility of the synthetic procedure, which was further used to evaluate the efficiency of Lewis acidic ionic liquid catalyst system towards the synthesis of PBS. (a) **General method for the**



**synthesis of PBS (catalyst addition during esterification reaction):** In a clean three neck RB flask fitted with distillation assembly, succinic acid (20 g, 0.17 mol) and butane diol (16 g, 0.18 mol) was taken and stirred for 10 mins. Into this catalyst (0.02 mol%) was added and the resultant mixture was heated to 175 °C till the completion of the esterification reaction (water collected approximately 5.6 mL). After completion of the esterification reaction, polycondensation was carried out at 230 °C under vacuum (10 mmHg) to give the corresponding polymer. After completion of the polycondensation reaction, reaction mixture was cooled (80 °C) and then poured into water. The solid thus obtained was filtered, washed with acetone and dried under nitrogen to give the corresponding PBS in good yield (88%). IR (neat): 1714, 1157  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.71 (m, 4H), 2.63

(m, 4H), 4.24 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  172.3, 64.2, 29.0, 25.2. (b) **General method for the synthesis of PBS (catalyst addition during polycondensation reaction):** In a clean three neck RB flask fitted with distillation assembly, succinic acid (20 g, 0.17 mol) and butane diol (16 g, 0.18 mol) was taken and heated to 175 °C till the completion of the esterification reaction (water collected approximately 5.6 mL). After completion of the esterification reaction, catalyst (0.02 mol%) was added and the polycondensation reaction was carried out at 230 °C under vacuum (10 mmHg) to give the corresponding polymer. After completion of the polycondensation reaction, reaction mixture was cooled (80 °C) and then poured into water. The solid thus obtained was filtered, washed with acetone and dried under nitrogen to give the corresponding PBS in good yield (92%).

