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via transesterifications**

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La(III)-Catalysed degradation of polyesters to monomers via transesterifications†

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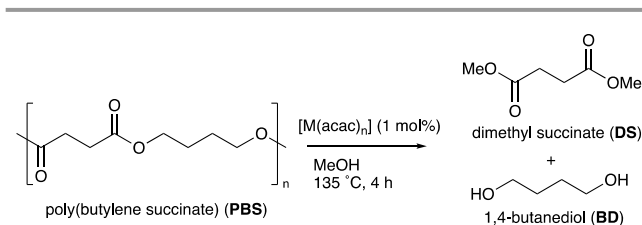
Tris(acetylacetonato)lanthanum(III) (1 mol%) catalyses the degradation of poly(butylene succinate) ($M_w = 90,700$) by transesterification in MeOH at 90 °C for 4 h, thus affording dimethyl succinate (>99% yield) and 1,4-butanediol (93% yield). Moreover, the quantitative degradations of poly(ethylene adipate), poly(ethylene terephthalate) and poly(butylene terephthalate) are also reported.

Responsible consumption and production are targets of global sustainable goals (SDGs). Nevertheless, waste-related plastic pollution both on land and in the ocean is a current social problem that needs to be urgently addressed. A large amount of polyesters is consumed on a daily basis, and the disposal of polyester waste is an urgent problem that requires to be resolved.^{1,5} The chemical degradation of polyesters is achieved by alkaline hydrolysis, aminolysis/ammonolysis and acid hydrolysis; however, a significant excess of acid or base and high temperature are normally required.² While efficient catalysts for the transesterification reactions of low-molecular-weight esters have been developed,^{3–10} polyester degradation by transesterification has been relatively unexplored. Wood and co-workers recently reported zinc acetate-catalysed methanolysis of poly(lactic acid).¹¹ Tanaka, Nakajima and co-workers reported the degradation of poly(ethylene terephthalate) (PET) catalysed by LiOMe (5 mol%) under ambient conditions. However, this method required a considerable amount of dimethyl carbonate to capture the ethylene glycol formed.¹² The efficiency was limited in the absence of dimethyl carbonate. Moreover, Duan and co-workers reported the electrocatalytic degradation of PET to

terephthalic acid and potassium diformate; however, this method required the prior hydrolysis of PET using 2 M of KOH aq.¹³ A catalytic system of zinc acetate/4-dimethylaminopyridine (15 mol%) was documented for degradation of PET with ethylene glycol at 180 °C,¹⁴ and [Hf(OTf)₄]/Pd/C-catalysed hydrogenative degradation of PET at 265 °C under H₂ (0.1 MPa) was developed.¹⁵ A review of catalytic systems for PET degradation has recently been reported.¹⁶

Research on the transesterification of polyester for degradation has become a significant research focus. The importance to this approach is the catalyst. This study focused

Table 1 Degradation of poly(butylene succinate) catalysed by [M(acac)_n]^a



Entry	Catalyst	Dimethyl succinate (%)	1,4-Butanediol (%)
1	[La(acac) ₃]	>99	93
2	[Ti(acac) ₄]	>99	93
3	[Mn(acac) ₂]	>99	90
4	[Mn(acac) ₃]	>99	96
5	[Fe(acac) ₃]	99	95
6	[Ru(acac) ₃]	4	4
7	[Co(acac) ₂]	94	84
8	[Co(acac) ₃]	93	83
9	[Al(acac) ₃]	25	27
10	w/o cat.	12	11

^aReaction conditions: poly(butylene succinate) [$M_w = 90,700$, $M_n = 21,000$, PDI = 4.3, $n = 527$] (117 mg, 0.680 mmol relative to the formula weight of constitutional repeating unit), [M(acac)_n] (0.00691 mmol), MeOH (5 ml), at 135 °C for 4 h in a 20 mL autoclave, under a nitrogen atmosphere. The degradation products were estimated by GLC analysis based on dibenzyl (10 mg, 0.0543 mmol) as an internal standard.

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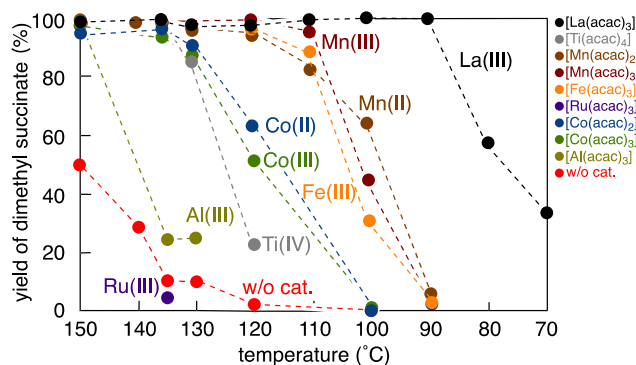
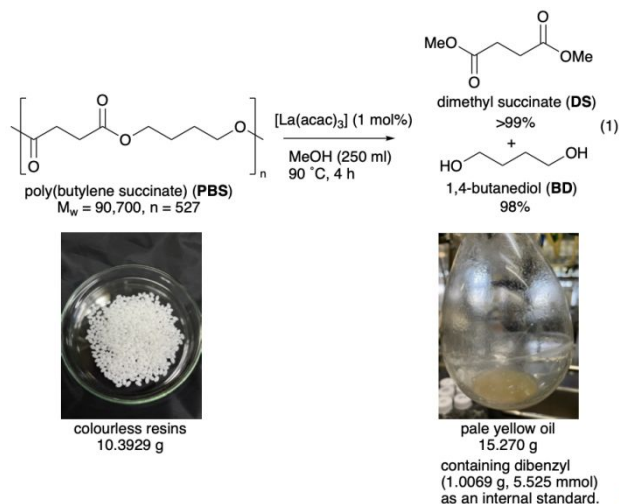


Fig. 1. Dependence of the catalytic activity on the reaction temperature for the degradation of poly(butylene succinate). Reaction conditions: poly(butylene succinate) [$M_w = 90,700$, $M_n = 21,000$, $PDI = 4.3$, $n = 527$] (117 mg, 0.00129 mmol based on the M_w , 0.680 mmol relative to the formula weight of constitutional repeating unit), $[M(acac)_n]$ (0.00691 mmol, 1 mol%), MeOH (5 ml), for 4 h in a 20 ml autoclave, and the degradation products were estimated by GLC analysis using dibenzyl (10 mg, 0.054 mmol) as an internal standard.

on metal acetylacetonates with the general formula, $[M(acac)_n]$ (acac: acetylacetonato) as robust and soluble Lewis acids. For examples, $[Ru(acac)_3]$ catalyses the esterification of low-molecular-weight acyl compounds^{17,18} and reductive etherifications;¹⁹ furthermore, $[Fe(acac)_3]$ has been reported to be a transesterification catalyst for methyl benzoate.²⁰ This study reports the degradation of certain polyesters using transesterification catalysed by $[La(acac)_3]$.

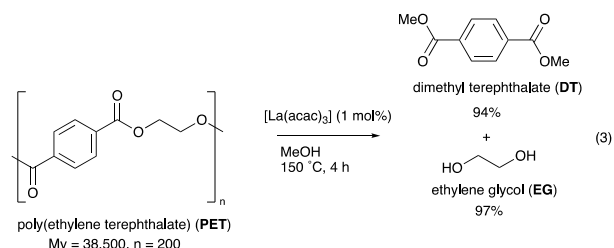
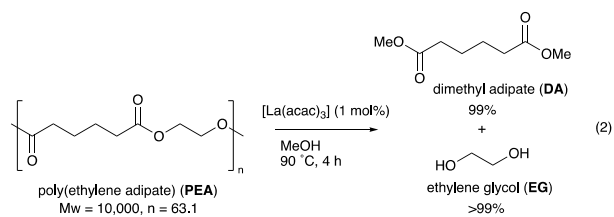
The degradation of poly(butylene succinate) (PBS), a commodity polyester used in large quantities, was examined. The molecular structure was determined by X-ray analysis.²¹ The degradation of PBS (Mitsubishi Chemical: BioPBS®, $M_w = 90,700$, 0.680 mmol, resin size of 2.0 x 2.0 x 5.0 mm³) was performed in MeOH (5 ml) at 135 °C for 4 h catalysed by a number of $[M(acac)_n]$ (1 mol%) under a nitrogen atmosphere (0.1 MPa at room temperature) in an autoclave (20 ml). Table 1 lists a summary of the catalyst screening. In the presence of $[La(acac)_3]$ (1 mol%), the quantitative formation (>99%) of dimethyl succinate (DS) occurred, and 1,4-butanediol (BD) was formed in 93% yield (Entry 1). We achieved similar quantitative degradations of PBS by $[Ti(acac)_4]$, $[Mn(acac)_2]$, $[Mn(acac)_3]$ and $[Fe(acac)_3]$ (Entries 2-5). $[Co(acac)_2]$ and $[Co(acac)_3]$ demonstrated high catalytic activities (Entries 7-8). However, $[Ru(acac)_3]$ (Entry 6) and $[Al(acac)_3]$ (Entry 9) showed low catalytic activity. In the absence of a catalyst, DS and BD were formed only in 12% and 11% yields, respectively, and the resins were recovered (Entry 10).

With these promising results, this study then evaluated the dependence of the catalytic activity of $[M(acac)_n]$ on the reaction temperature for PBS degradation (Fig. 1). The catalyst concentration and reaction time were fixed at 1 mol% and 4 h, respectively. Among these catalysts, the difference in activity became clearer at 110 °C, the melting point of PBS,²² and $[La(acac)_3]$ afforded DS quantitatively, even at 90 °C. This indicates that $[La(acac)_3]$ can degrade PBS even below the polymer's melting point. However, the catalytic activity of $[La(acac)_3]$ decreased at temperatures below 80 °C. PBS with a



higher molecular weight ($M_w = 125,000$) could be degraded quantitatively at 90 °C. Okano and co-workers reported the transesterification of a low-molecular-weight ester, ethyl benzoate, catalysed by $[La(OiPr)_3]$ in refluxing MeOH,⁴ and Ishihara and co-workers reported the transesterification of low-molecular-weight carboxylic esters, dimethyl carbamates and methyl carbamates, using $[La(OiPr)_3]$ /monomethyl diethylene glycol as a catalyst under azeotropic conditions.⁸ The results show that a La(III) species are effective in transesterifying a polyester. The degradation of PBS was performed in an air using commercial MeOH as-received for the reaction using $[La(acac)_3]$ (1 mol% at 90 °C) giving DS (>99%) and BD (98%) (ESI). This is an advantage of $[La(acac)_3]$ for a practical use. Note that when $[Mn(acac)_2]$ and $[Mn(acac)_3]$ were used for comparison, the catalytic activity was significantly affected by air or incorporated water (ESI).

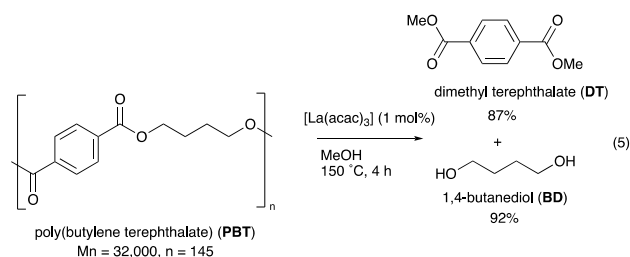
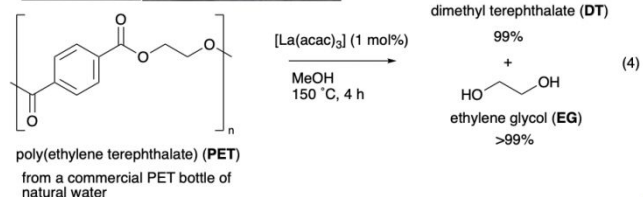
$[La(acac)_3]$ can be used for the large-scale degradation of PBS (10.3929 g, 0.1146 mmol). The quantitative degradation of PBS was achieved using $[La(acac)_3]$ (1 mol%) at 90 °C for 4 h in MeOH giving DS (>99%) and BD (98%) (eqn (1)). In this 10-gram scale PBS degradation, it was possible to reduce the solvent volume to at least 125 ml and still efficiently degrade PBS into the monomers: DS (>99%) and BD (98%), under the same conditions. These results suggest the high scalability of the present catalysis without any loss in catalytic activity. The formation of DS and BD was confirmed using ¹H NMR, with a 1/1 (mol/mol) mixture of DS/BD (1.06/1.00). The separation of the resulting DS and BD from the degraded oil was possible by first extracting DS from the monomer mixture with Et₂O and then extracting BD from the remaining solution with EtOH. The contamination of La in these monomers was analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and was found to be 13 ppm (DS) and 3600 ppm (BD), respectively, without distillation. As EtOH was required for the extraction of BD, probably some of the La complex was also extracted and would need to be purified, e.g. by distillation. The obtained DS and BD monomers could be polymerised by $[Ti(OiPr)_4]$ to give PBS. However, the catalyst recovered after the degradation of PBS showed only low activity (around 10-



12% yields, see ESI). It is not known at what stage this deactivation occurred, but the catalyst recycling is currently not possible.

[La(acac)₃] (1 mol%) catalysed the degradation of poly(ethylene adipate) (PEA) (resins from Sigma-Aldrich) at 90 °C for 4 h in MeOH to afford dimethyl adipate (EA) (99%) and ethylene glycol (EG) (>99%) (eqn (2)). Poly(ethylene terephthalate) (PET) (commercial resins for beverage bottles) was barely degraded by [La(acac)₃] (1 mol%) at 90 °C for 4 h to yield dimethyl terephthalate (DT) (1%) and EG (1%). However, [La(acac)₃] (1 mol%) degraded PET at 150 °C for 4 h to afford DT (94%) and EG (97%) (eqn (3)).^{23,55} In the absence of a catalyst under these conditions, the degradation of PET proceeded at a low rate [DT (18%) and EG (16%)]. Note that additional study will be required for the more efficient degradation of PET, but [La(acac)₃] could be used as a catalyst for degradation of PET without any additives or pretreatments with base. A PET plastic bottle of natural water available worldwide (the molecular weight unknown) could also be effectively degraded into DT (99%) and EG (>99%) under the same conditions (eqn (4)). This experiment shows that the present catalysis can be applied to a polyester material available in the world.

Poly(butylene terephthalate) (PBT) is the crystalline engineering plastics, and it is widely used for housings in electrical engineerings, automotives and households.



[La(acac)₃] (1 mol%) also catalysed the degradation of PBT at 150 °C for 4 h in MeOH to yield DT (87%) and BD (92%) (eqn (5)). In the absence of a catalyst, PBT hardly degraded under these conditions [DT (7 %) and BD (6 %)].

The degradation mechanism will be reported in a future study. Nevertheless, this section provides a brief comment on the reaction mechanism. Firstly, the acac ligand contributes significantly to increase the catalytic activity. In fact, a related La(III) complex, [La(OTf)₃] (1 mol%) degraded PBS at 90 °C for 4 h to give only DS (13%) and BD (13%). Duda, Penczek and co-workers reported reversible and stepwise exchange between the acetylacetonate and butoxide on [Al(acac)₃].²⁴ A part of the acac ligand in [La(acac)₃] would remain attached during the catalysis. Secondly, the La(III) species demonstrated the least Lewis acidity among lanthanoids(III).²⁵ Therefore, the present catalytic activity is not only attributed to the Lewis acidity of [La(acac)₃]. In this connection, a related Sc(III) species, [Sc(OTf)₃] (1 mol%), which demonstrated the strongest Lewis acidity among lanthanoid complexes,²⁵ only afforded DS (7%) and BD (8%) by the degradation of PBS at 100 °C for 4 h. Thirdly, Neverov and Brown have reported the formation of a dinuclear La(III)₂(μ²-OMe)₂ species from [La(OTf)₃] in MeOH, which behaves as a Lewis acid–Lewis base dual activation catalyst for

Table 2 Effect of particle size on the initial degradation rate of PBS^a

Time (h)	Pellets		Powder	
	DS (%)	BD (%)	DS (%)	BD (%)
0.0	0	0	0	0
0.50	44	45	49	50
1.0	76	78	71	75

^aReaction conditions: poly(butylene succinate) [M_w = 136,000, M_n = 53,500, PDI = 2.54, n = 781] (117 mg, 0.000816 mmol relative to the formula weight of constitutional repeating unit), [La(acac)₃] (0.007 mmol), MeOH (5 ml), at 90 °C in a 20 mL autoclave, under a nitrogen atmosphere. The mean pellet and powder particle sizes of PBS were 2.0 × 2.0 × 5.0 mm³ and about 100 μm, respectively. The degradation products were estimated by GLC analysis based on dibenzyl (10 mg, 0.054 mmol) as an internal standard.

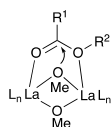


Fig. 2. A possible intermediate for the transesterification based on the Neverov and Brown's proposal. L_n stands for suitable ligands.

the present transesterification (Fig. 2),⁵ and Ishihara and co-workers also proposed the similar dinuclear species.⁸ This is a probable intermediate for the present degradation process, but because La(III) can achieve up to eight-coordination,²⁶ the details of which will be the subject of a future study.

Further information on the reaction mechanism is the effect of particle size on degradation of **PBS** below its melting point. For this purpose, **PBS** pellets were pulverised in a blade-and-mesh grinder. In the presence of $[La(acac)_3]$ (1 mol%), the degradations of **PBS** pellets (2.0 x 2.0 x 5.0 mm³) and power (about maximum particle size: 100 μ m) were stopped at 90 °C for 0.5 h and 1 h to determine the monomer yields. As shown in Table 2, there is no marked difference in the initial degradation rates between them. Further degradation mechanisms, including the quest of the active catalyst species, will be studied in due course.

The present results show that the transesterification of certain polyesters in MeOH is extremely effective for degradation. $[La(acac)_3]$ had high catalytic activity in MeOH without requiring additives. The presence of excess MeOH is believed to inhibit oligomerisation between the obtained monomers and is essential for complete degradation. This study also demonstrated the degradation of **PBS** on the 10 g-scale. This contributes to a closed-loop of plastics with chemical recycling. Complete degradation was achieved for **PEA**, **PET** and **PBT**. In particular **PET** and **PBT** are known to be almost insoluble in organic solvents except expensive hexafluoroisopropyl alcohol, but could be degraded by the transesterification in MeOH despite the in their insolubility. These results are expected to contribute to the responsible consumption and production of polyester.

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Notes and references

§ Recently, Milstein and co-workers reported hydrogenative depolymerisation of nylons and current problems in plastic recycling was described.

§§ The viscosity-average molecular weight of **PET** was calculated on the basis of the intrinsic viscosity measured in hexafluoroisopropyl alcohol ($IV = 0.80 \pm 0.02$ dl g⁻¹) and ref. 23.

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