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Mendeleev Commun., 2022, **32**, 351–353

Mendeleev Communications

Aryloxy ‘biometal’ complexes as efficient catalysts for the synthesis of poly(butylene adipate terephthalate)

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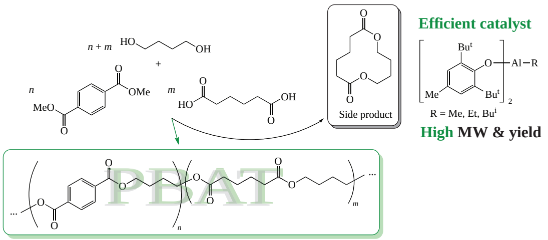
DOI: 10.1016/j.mencom.2022.05.020

A comparative study of catalytic activity of aryloxy complexes of Mg, Zn and Al in the synthesis of poly(butylene adipate terephthalate) demonstrated the preference of Al-based catalyst containing two bulky substituents in *ortho*-position of phenol ligand in terms of higher values of PBAT MW and lower yields of cyclic diester side product.



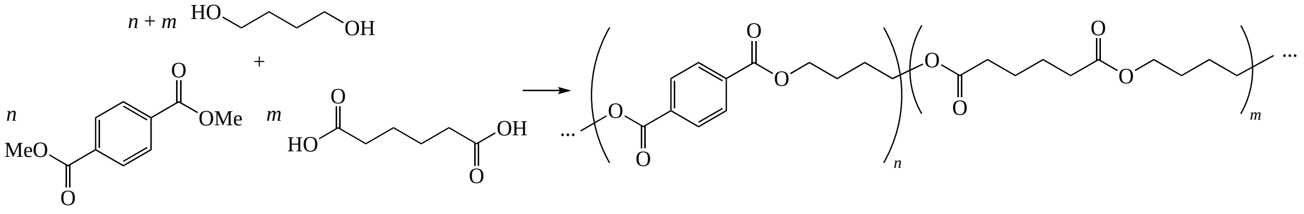
Keywords: aluminum complexes, biodegradable polymers, biometals, esterification, phenates, polycondensation, PBAT, polyesters.

In recent years, high resistance to biodegradation has limited the use of low-cost and accessible plastics such as polyolefins and polyethylene terephthalate (PET) in disposable package and other common applications.[1] Actual alternative is the use of biodegradable plastics that represent polyesters accessible *via* polycondensation or ring-opening polymerization (ROP).[2–7] The most of polyesters are far below polyolefins by mechanical characteristics, however the product of polycondensation of butane-1,4-diol, adipic acid and terephthalic acid, polybutylene adipate terephthalate (PBAT), represents biodegradable polyester that can compete with conventional polyolefins and PET in respect of strength and elasticity.[8–11] Excellent mechanical characteristics of PBAT naturally caught the researchers’ attention with regard to biomedical use of this biodegradable polymer.[12–20]

The synthesis of PBAT is based on the reaction of butane-1,4-diol with adipic acid and terephthalic acid (or dimethyl terephthalate) in the presence of acidic catalyst (Scheme 1).[11] Usually, the method involves two-stage processing. The first is the formation of relatively low MW copolymer at 150–180 °C and reduced pressure with removing water and MeOH by distillation, while the second is the synthesis of high MW polycondensation product at 240–250 °C and 0.1–0.5 Torr. The key success criteria in PBAT synthesis is M_n value of 50 kDa. However, the use of high temperatures at the second stage limits the biomedical potential of PBAT because thermaly induced free radical processes and degradation with a formation of unsaturated compounds may result in by-products with unpredictable toxicity.[21,22]

It is believed that the only substantial side reaction during PBAT synthesis is the formation of tetrahydrofuran (THF) as a result of acid-catalyzed intramolecular etherification of butane-1,4-diol,[11] and that was why butane-1,4-diol is commonly loaded in excess. The formation of THF does not affect the adipate/terephthalate ratio in copolymers obtained. The second possible side reaction, decarboxylation of terephthalic acid, is not observed (no additional signals of aromatic protons in ^{1}H NMR spectra of copolymers).

However, the synthesis of PBAT may be accompanied by the formation of stable[†] cyclic diester, 1,6-dioxacyclododecane-7,12-dione (DCDD, Figure 1). This compound was first obtained by the reaction of adipic acid with butane-1,4-diol catalyzed by dibutyltin dilaurate,[23] but it was not characterized properly.[‡] The formation of volatile cyclic diester reduces the yield of PBAT and leads to a change in copolymer composition, however this and other similar side reactions during the synthesis of polyesters have been usually ignored.[9,11,24–26]



Scheme 1

[†] The molecular structure of DCDD was optimized using PRIRODA program and moderate torsional stress detected.

[‡] Colourless crystals, mp 94 °C. For ^{1}H, ^{13}C NMR and FT-IR spectra of DCDD, see Online Supplementary Materials.

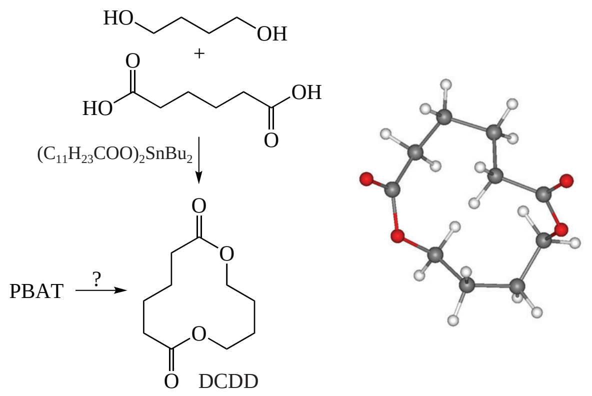


Figure 1 The formation and molecular structure of 1,6-dioxacyclododecane-7,12-dione.

Table 1 The synthesis of PBAT (data for the second stage, 240–245 °C, 6 h).[a]

Entry	Catalyst	$M_n/10^3$	$Đ_M$	[adipate]/[terephthalate] ratio
1	**1**	5.5	2.15	1.21
2	**2**	19.4	2.25	1.17
3	**3a**	51.4	2.19	1.14
4	**3b**	49.8	2.07	1.12
5	**3c**	52.5	2.23	1.15
6	**4a**	33.0	2.05	1.07
7	**4b**	43.9	2.07	1.10
8	$Ti(OBu)_4$	51.2	2.09	1.07

[a] Characteristics for the starting oligomer: $M_n = 5.4 \times 10^3$, $Đ_M = 2.15$, [adipate]/[terephthalate] ratio = 1.21.

Titanium(IV) tetrabutoxide is typically used as a catalyst for the second, the most essential, stage of the synthesis of high-MW PBAT. At this high-temperature stage, its use cannot prevent side reactions. Assuming the similarity of (trans)esterification in the synthesis of PBAT and formation of polyesters *via* coordination ROP, we proposed that aryloxy complexes of ‘biometals’ (Mg, Al, Zn), that are active catalysts of the ROP of cyclic esters,[27–36] may be useful in the synthesis of PBAT, particularly in view of the ability of phenolates to act as inhibitors of free radical processes.

In this study, we prepared the sample of low-MW PBAT by 12 h polycondensation of butane-1,4-diol, adipic acid and dimethyl terephthalate at 170–180 °C in the presence of $Ti(OBu)_4$ catalyst. This copolymer was used as the starting material for our further experiments on the synthesis of high-MW PBAT at higher temperatures. These experiments were conducted in the presence of aryloxy complexes **1**,[33] **2**,[37] **3a–c**,[38] **4a**,[39] **4b**[40] (Figure 2) and $Ti(OBu)_4$, the catalyst efficiency was evaluated by M_n of PBAT obtained (Table 1).

During experiments with metal phenates, we synthesized slightly coloured PBAT samples. The analysis of M_n and dispersity $Đ_M$ of the copolymers (SEC data) has shown that high degree of polymerization had been achieved when using Al complexes with 2,6-di-*tert*-butyl-4-methylphenate (BHT) **3a–c** (see Table 1, entries 3–5). In the case of Al complexes with less sterically hindered phenates **4a** and **4b**, the target value of M_n was not achieved, whereas BHT complexes **1** and **2** (entries 2, 3) had proved ineffective. Another substantial observation related to the formation of DCDD. The latter was detected in all experiments, but its content was seemingly lower when complexes **3a–c** were used as catalysts. Since all experiments were based on the same low-MW copolymer, the relative amount of the diester by-product could be estimated by the analysis of the composition of high-MW copolymer obtained using ^{1}H NMR spectroscopy, by the comparison of the integral intensities of signals relating to phthalate and adipate fragments (Figure 3, δ = 8.1 and 2.3 ppm, respectively). The comparison of ^{1}H NMR spectra of copolymers (see Section S2 in the Online Supplementary Materials) clearly demonstrates higher adipate content in copolymers synthesized with the use of **3a–c** catalysts. It should also be noted that increase in [adipate]/[terephthalate] ratios correlate with increase in M_n values. This result is not so surprising when keeping in mind higher reactivity of aliphatic diesters in polycondensation in comparison with terephthalate.[41]

Low catalytic activity of complexes **1** and **2** in PBAT formation was not anticipated for us, considering that Mg phenolates were more active in ROP of lactones and lactides in comparison with Zn and Al phenolates.[32] The difference in M_n of copolymers also deserved attention: as can be seen from Table 1, the presence of two bulky substituent in *ortho*-positions of phenoxy ligand is necessary to achieve target M_n value of ~50 kDa (see Table 1, entries 3–5). The formation of cyclic diester DCDD, resulting in drop of the PBAT yield, was also minimal for **3a–c**. Note that DCDD was not detected during polycondensation of adipic acid with butane-1,4-diol, catalyzed by aryloxy metal complexes, in the absence of dimethyl terephthalate; this interesting observation is awaiting mechanistic explanation.

Since complexes **3a–c**, **4a**,**b** form similar catalytic species at elevated temperatures due to disproportionation,[42] it is the nature of the aryloxy ligand that impacts on the catalytic activity. In this way, the complexes **3a–c**, derivatives of BHT that is ‘generally recognized as safe’ by US FDA,[43] represent excellent catalysts for the synthesis of biomedical grade PBAT.

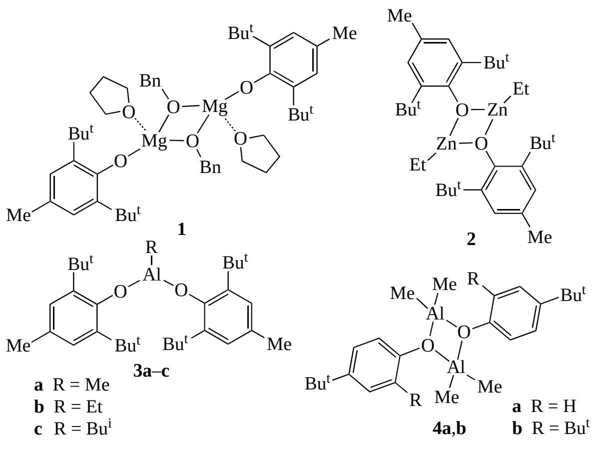


Figure 2 Aryloxy complexes of ‘biometals’ studied in the synthesis of PBAT.

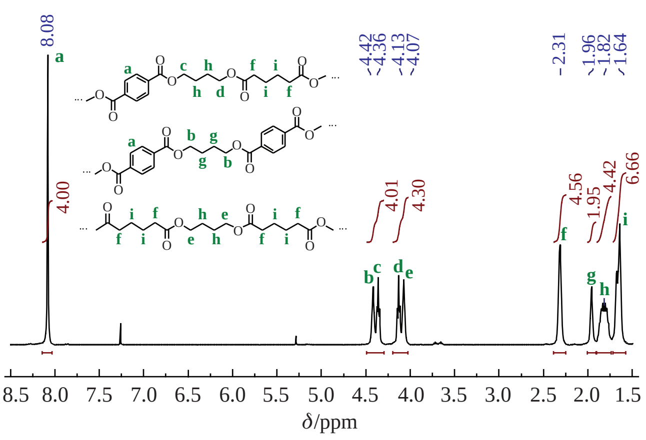


Figure 3 ^{1}H NMR spectrum of the PBAT sample (see Table 1, entry 3) with the assignment of the signals.

This work was supported by Russian Science Foundation (grant no. 21-73-30010, in part of the synthesis of catalysts and polymers) and was carried out within the State Program of TIPS RAS (in part of the polymer analysis).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.020.

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Received: 3rd November 2021; Com. 21/6747