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Facile and Highly Efficient Strategy for Synthesis of Functional Polyesters via Tetramethyl Guanidine Promoted Polyesterification at Room Temperature

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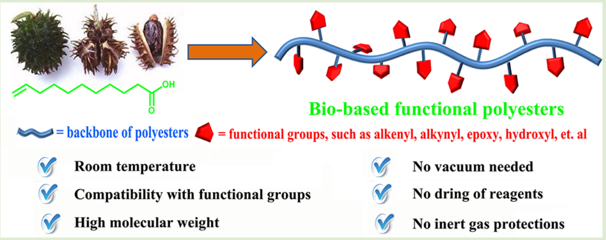
Supporting Information



ABSTRACT: A facile and highly efficient strategy for the synthesis of functional polyesters from 10-undecenoic acid, which is abundantly available and derived from ricin oil, has been successfully achieved using 1,1,3,3-tetramethyl guanidine (TMG) as a promoter at room temperature. The experimental results indicate that high molecular weight polyesters have been obtained and a variety of functional groups, such as alkenyl, alkynyl, nitro, epoxy, hydroxyl, and bromoisobutyrate, can be incorporated as pendant groups. The structures of the obtained polymers were demonstrated by ^{1}H and ^{13}C NMR spectroscopy and their thermal properties were studied by DSC and TGA.

Recently, more and more attention has already been focused on replacing the entire or part of the conventional petroleum-based monomers and polymers with those made from renewable biobased raw materials, such as natural oils.[1−10] Polyester as one of the most promising families of polymers based on renewable resources has a wide range of applications including fibers, plastics, films, and clothes. So far, there have been a number of papers published on the synthesis of polyesters from renewable resources, where the biobased polyesters were mainly synthesized via the conventional esterification reaction of diols with dicarboxylic acids or transesterification with dicarboxylates,[11−20] combining with the acyclic diene metathesis (ADMET) polymerization[21,22] or the thiol−ene click reaction.[23,24] The catalytic ring-opening polymerization of macrolactones[25] was also reported for the synthesis of biobased polyesters. However, these polymerizations are often conducted under rigorous conditions such as high temperature, high vacuum, and long reaction time. On the other hand, synthesis of functional polyesters containing reactive groups, such as hydroxyl, nitro, epoxy, alkenyl, and alkynyl groups, has drawn much attention due to their promising applications in biomedical, optoelectronic, and catalytic fields.[26−28] However, up to now, there are a few reports[29−31] published on the preparation of biobased polyesters with these functional groups. The main reason is that the functional groups are generally unstable under the conventional polyesterification condition. Therefore, it is still a challenge to prepare polyesters containing various pendant functional groups. There is no doubt that new strategies under mild conditions are much desired for preparation of novel functional polyesters based on renewable sources.

There are few reports on the synthesis of polyesters via the reaction of dicarboxylic acid salts with dihalides.[32,33] Recently, we have demonstrated that the esterification reaction of carboxylic acids with organic halides could be efficiently performed with excellent yield of carboxylic esters at room temperature using 1,1,3,3-tetramethyl guanidine (TMG) as a promoter.[34,35] Herein, this method was extended to synthesize the biobased polyesters with various functional pendant groups via the TMG promoted polyesterification of dicarboxylic acids with organic dihalides in a mild and protection-free process.

10-Undecenoic acid, an abundantly available renewable organic compound, which can be obtained by heating ricinoleic acid under vacuum,[36] was used as starting material to prepare two dicarboxylic acid monomers, 11,11′-(ethane-1,2-diylbis(sulfanediyl))diundecanoic acid (C1) and 11-((carboxymethyl)thio)undecanoic acid (C2) via the thiol−ene click reaction of 10-undecenoic acid with ethane-1,2-dithiol and 2-mercaptoacetic acid, respectively,[23,24] as shown in Scheme 1. Then, condensation polymerization of diacid monomer C1 with dihalide monomer 1,4-bis(bromomethyl)benzene was conducted as a model reaction in DMF at room temperature using TMG as the promoter. The process of the polymerization was very simple. The dicarboxylic acid and TMG were first mixed in DMF at room temperature, and then the dihalide was added. After stirring for 3 h, the product was obtained as a white solid by precipitating the reaction mixture into methanol

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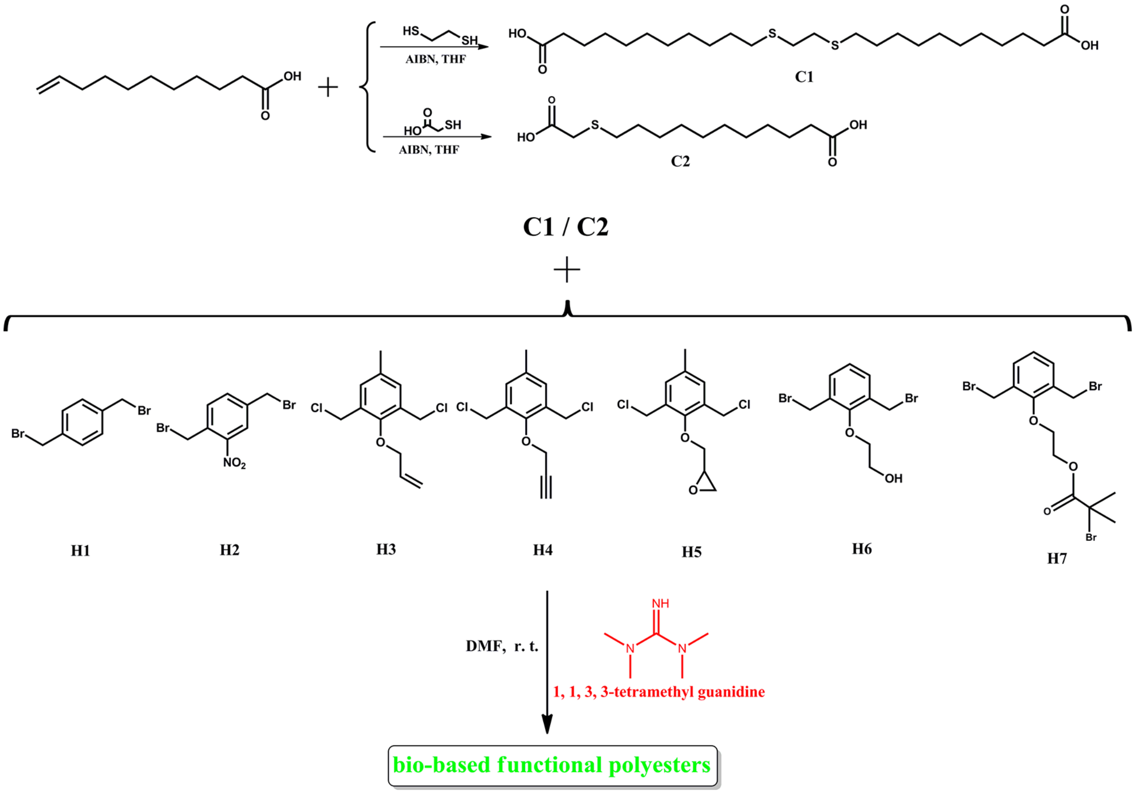
Scheme 1. Synthesis of Biobased Functional Polyesters via the TMG Promoted Polyesterification Reaction at Room Temperature



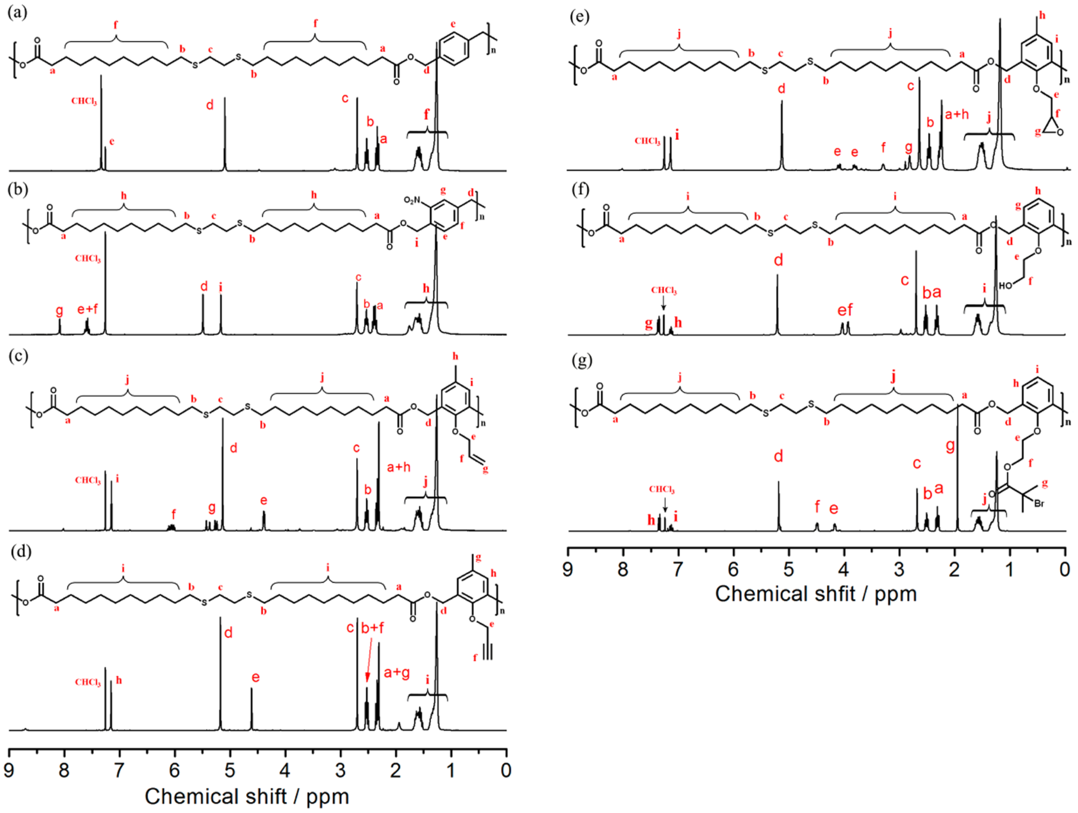


Figure 1. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of biobased functional polyesters (a) P1, (b) P2, (c) P3, (d) P4, (e) P5, (f) P6, and (g) P7 obtained via the TMG promoted polyesterification of C1 with H1−H7 at room temperature.

Table 1. Synthesis of Biobased Functional Polyesters via the TMG Promoted Esterification Reaction of Dicarboxylic Acids with Dihalides in DMF at Room Temperature[a]

polymer	dicarboxylic acid	dihalide	time (h)	yield[b] (%)	$M_{n,GPC}$ (g mol^{-1})	$M_{w,GPC}$ (g mol^{-1})	PDI[c]
P1	C1	H1	3	88	25600	64500	2.5
P2		H2	5	91	20900	46000	2.2
P3		H3	5	90	21900	34200	1.6
P4		H4	5	92	20500	38600	1.9
P5		H5	5	81	15000	26100	1.7
P6		H6	4	89	18600	33500	1.8
P7		H7	4	89	15600	24900	1.6
P8	C2	H1	3	87	19500	34100	1.7
P9		H2	5	90	18800	38200	2.0
P10		H3	5	92	20900	33300	1.6
P11		H4	5	89	12600	22000	1.7
P12		H5	4	91	6200	10600	1.7
P13		H6	4	85	12300	21000	1.7
P14		H7	4	92	17900	32300	1.8

[a] Reaction conditions: dicarboxylic acid (1 mmol), TMG (2 mmol), dihalide (1 mmol), and DMF (5 mL). [b] Determined gravimetrically. [c] Determined by GPC.

for three times. The structure of the polymer was characterized by ^{1}H and ^{13}C NMR spectroscopies, as shown in Figures 1a and S26, respectively. The molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC), as shown in Table 1. It can be clearly seen that the number-average molecular weight (M_n) is as high as 25600 g/mol, which is as high as the polyesters synthesized via the traditional esterification or transesterification condensation polymerization reported in literatures.[11−24] It is worth pointing out that the polymerization conditions in this work are very mild and readily accessible; in comparison with the conventional polyesterification, heating, vacuum, anhydrous reagents, and inert gas protections are all not required.

Functional polyesters with pendant reactive groups, such as alkenyl, alkynyl, nitro, epoxy, hydroxyl, and bromoisobutyrate, can be expected to be promising precursors for designing and preparing useful and environmentally friendly polymer materials such as biomaterials and optical materials. However, as we know, it is very difficult to obtain these functional polyesters with unstable pendant groups by the traditional methods of polyesterification and polytransesterification under the rigorous reaction conditions. Fortunately, the TMG promoted esterification reaction can be effectively performed under very mild reaction conditions, which affords a possibility for designing and preparing functional polyesters with pendant functional groups.

In order to synthesize the functional polyesters, several organic dihalides with different functional groups, such as alkenyl, alkynyl, epoxy, hydroxyl, and bromoisobutyrate, were designed and synthesized, as shown in Scheme 1. Then, the polymerizations of the dihalide monomers with the diacid monomers C1 were performed under the same conditions used for the synthesis of P1. The experimental results indicate that the polymerizations were very successful and the designed biobased polyesters with pendant alkenyl, alkynyl, nitro, epoxy, hydroxyl, and bromoisobutyrate were obtained, respectively. The ^{1}H NMR spectra of the functional polyesters are shown in Figure 1, where the resonances of the functional groups can be clearly seen. Combining the measurement of polymer molecular weights in Table 1, it turns out that the functional polyesters have been successfully prepared via the TMG promoted polyesterification reaction.

The same strategy was also employed for the polymerization of monomer C2 with the different dihalides (H1−H7 in Scheme 1). As expected, the biobased functional polyesters were also successfully obtained with the number-average molecular weight as high as tens of thousands, as shown in Table 1. And the structures of the polyesters were also demonstrated by ^{1}H and ^{13}C NMR spectra, as shown in Supporting Information. The results further demonstrate that this strategy is facile, highly efficient, and universal for the preparation of the functional polyesters. Furthermore, the commercially available TMG can be recovered by treating with sodium hydroxide and used repeatedly.

The thermal properties of the biobased functional polyesters were investigated by DSC. As we know, aliphatic polyesters are usually crystalline or semicrystalline materials. The incorporation of aromatic rings or functional pendant groups on the backbone of polyesters generally have significant influence on the folding and stacking of the polymer chains; therefore, the melting temperature (T_m) and glass transition temperature (T_g) of the corresponding polyesters should be affected. The DSC traces of P1−P7 were shown in Figure S1. It can be observed that T_m of P1, P2, and P6 is 67, 56, and 23 °C, respectively, whereas P3−P5 and P7 are amorphous polymers without T_m, but with T_g ranging from −40 °C to −10 °C, probably due to the effect of their bulky side chains on the chain folding and stacking.

The thermal stability of the biobased functional polyesters was examined by TGA under nitrogen atmosphere. The TGA curves of the P1−P7 measured from 30−700 °C are shown in Figure S1, and the thermal decomposition data are available in Table S1, where it can be seen that the polymers P1−P7 show 5 wt % weight loss in the range of 233−317 °C, and the maximum decomposition in the range of 312−373 °C, indicating that the functional pendant groups have a significant influence on the thermal stabilities of the biobased polyesters. In addition, the thermal properties and the thermal stability of P8−P14 were also investigated, which were available in Supporting Information. All these results suggest that the functional polyesters have high thermal stability for the potential application in many areas.

In conclusion, the TMG promoted polyesterifications of the organic dihalide monomers with the diacid monomers were successfully performed at room temperature. The results demonstrate that the biobased polyesters with high molecular weight can be efficiently obtained. In comparison with the conventional polyesterification, this approach exhibits many advantages such as high efficiency and very mild reaction conditions. Moreover, a more important point is that the polymerization shows a high tolerance to variety of functional groups, thus, it has been successfully used to synthesize a series of the biobased functional polyesters with different reactive pendant groups, which can be used as promising precursors for designing and preparing new and useful polymer materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of experimental section, thermal properties, GPC traces, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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