

Supporting Information

Highly Efficient Strategies towards Sustainable Monomers and Polymers Derived from Fatty Acids via Tetramethylguanidine Promoted Esterification

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Experimental

Synthesis of fatty acid monomer M3

As illustrate in Scheme 2, methacrylate anhydride was used to synthesis M3. M (3.51 g, 10 mmol), methacrylate anhydride (1.49 mL, 10 mmol), and DMAP (20 mg) were mixed in a 25 mL round bottom flask. The reaction was allowed to performed at 60 °C under nitrogen protection overnight. After that, 3 mL of THF and 1.5 mL of DI water was added to quench the unreacted anhydride. Then the product was mixed with 10 mL 10 % sodium bicarbonate, stirred for 2h. The mixture was then moved to a separation funnel and extracted with dichloromethane. The organic phase was passed through a silica column to remove the inhibitors and dried under vacuum to obtain 3.64 g of M3

Synthesis of fatty acid monomer M4

As shown in Scheme 2, M was acrylated via acryloyl chloride to synthesis M4. A typical preparation procedure is as follows: 7.01g M, 12 mL dichloromethane, and 3.47 mL TEA were mixed in a 3-neck flask with a magnetic stir bar. 2.02 mL

Acryloyl chloride in 4 mL dichloromethane was added dropwise into the solution in an ice/water bath. When the addition process was completed, the mixture was left to warm up at room temperature, and the reaction was allowed to proceed for 12 h. Then, the product was transferred to 150 mL separation funnel, washed thrice with 10 % brine, followed by 0.2 % sodium bicarbonate. The organic phase was transferred a round bottom flask and dried with magnesium sulfate and filtrated. Solvents were removed under reduced pressure to obtain 7.42 g M4.

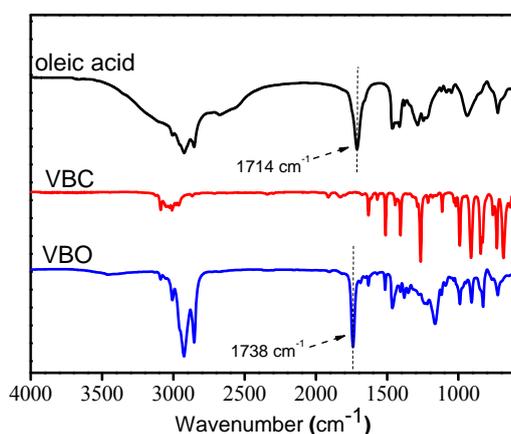


Figure S1 FT-IR spectra of oleic acid, VBC, and VBO.

Rheological Properties of PVBO prepared via the three strategies

It is well known that the rheological properties of a polymer can be affected by molecular architecture. PVBO was purified and dried before the rheological measurements. Figure S2 shows the changes in the storage modulus (G') and loss modulus (G'') as functions of angle frequency (ω) for PVBO prepared by the different strategies, respectively. For PVBO prepared via strategies 1 and 2, the G'' values were higher than the G' value in the whole frequency range of the experimental window,

indicating a typical liquid-like behavior. For PVBO prepared via strategy 3, the slope of G' crossed through that of G'' , indicating a transition from solid-like to liquid-like behaviors. These results demonstrate that all PVBO samples exhibited thermoplastic behavior. Moreover, the storage modulus of PVBO prepared via strategy 3 was much higher than those of strategies 1 and 2, owing to the presence of physical cross-links induced by the hard segments. Figure S2 also shows that the mechanical properties of the fatty acid-based polymers are affected by the fatty acid side groups. The storage modulus is regulated by controlling the degree of esterification. Moreover, the storage modulus of PVBO prepared via strategy 1 was higher than that of strategy 2 due to the higher molecular weight.

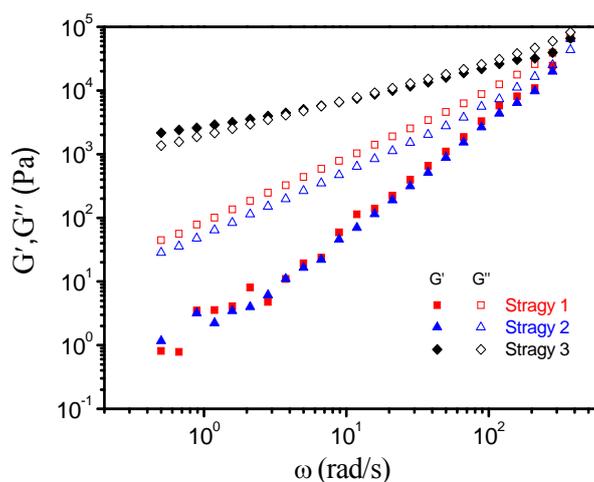
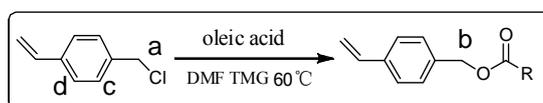


Figure S2. Changes in the storage modulus, G' , and loss modulus, G'' , as functions of angular frequency, ω , for PVBO prepared via the different strategies.

$$\text{Degree of esterification} = \frac{I_a}{I_d} \times 100\%$$



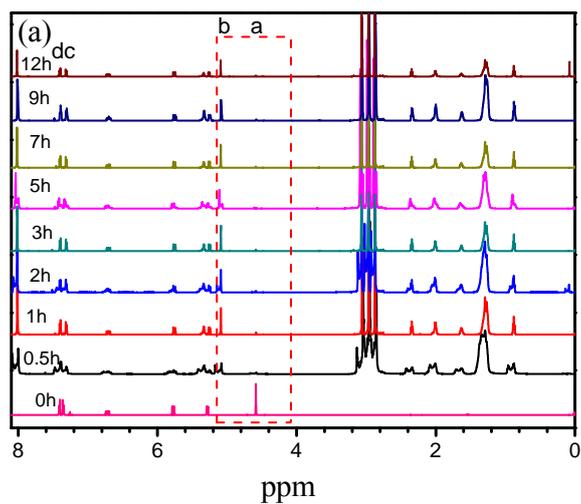


Figure S3 ^1H NMR spectra (CDCl_3 , 600 MHz) of TMG promoted esterification reaction of VB with oleic acid at different reaction time (strategy 1).

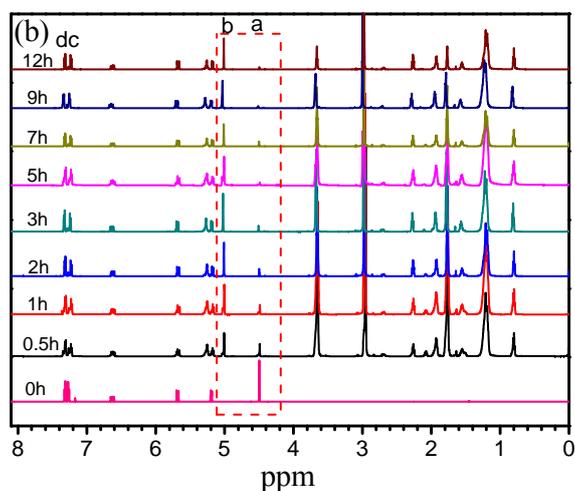
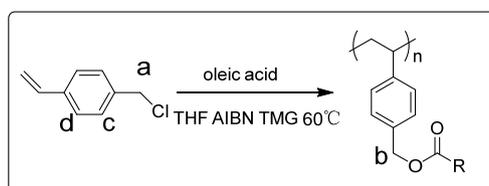
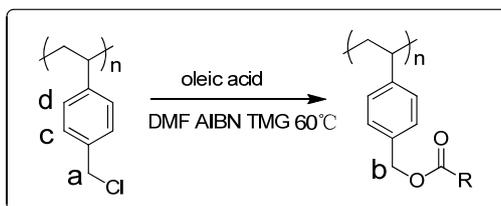


Figure S4 ^1H NMR spectra (CDCl_3 , 600 MHz) of the esterification of fatty acids with halogenated compounds promoted by TMG at different reaction time (strategy 2).



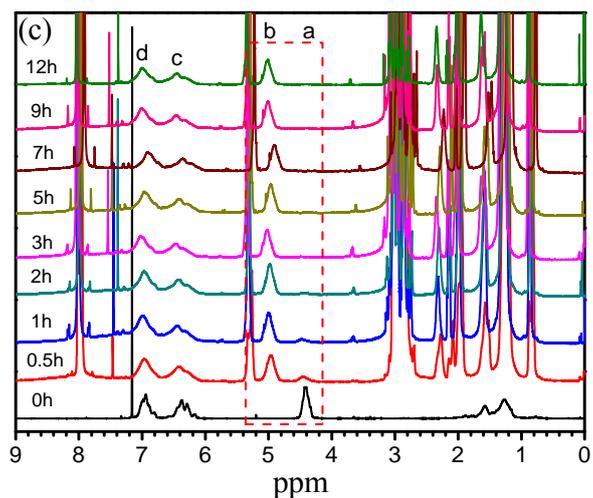


Figure S5 ^1H NMR spectra (CDCl_3 , 600 MHz) of the TMG promoted esterification reaction of PVB with oleic acid at $60\text{ }^\circ\text{C}$ at different reaction time (strategy 3).

Table S1. Esterification of oleic acid with halogenates towards various monomers.

Entry	Reactant 1	Reactant 2	Product	Solvent	Yield
1	Oleic acid			DMF	73%
2	Oleic acid			DMF	77%
3	Oleic acid			DMF	81%
4	Oleic acid			DMF	71%
5				None	98%
6				DCM	94%

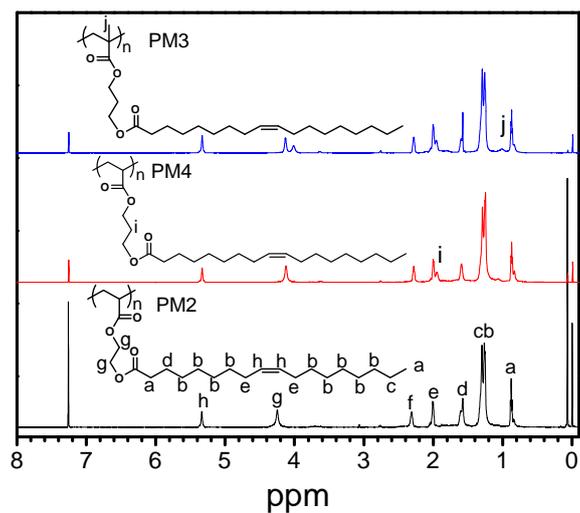


Figure S6. ^1H NMR spectra (CDCl₃, 600 MHz) of PM2, PM3, and PM4.

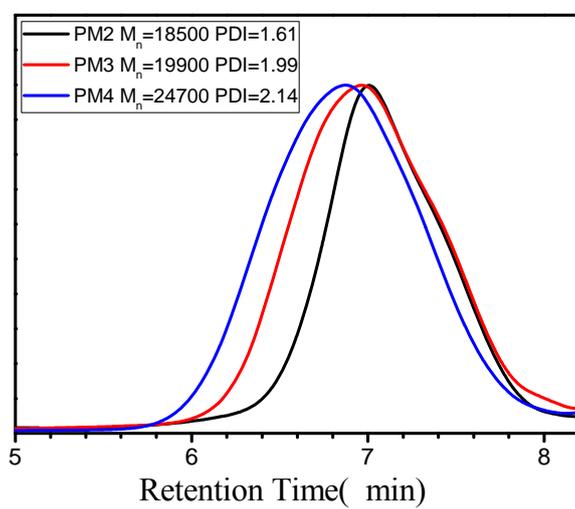


Figure S7. SEC traces for fatty acid based polymers PM2, PM3, and PM4.

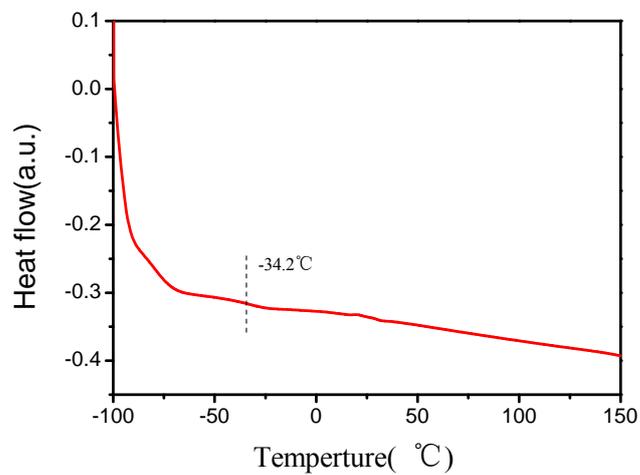


Figure S8. DSC curves of PVBO prepared by strategy 3.

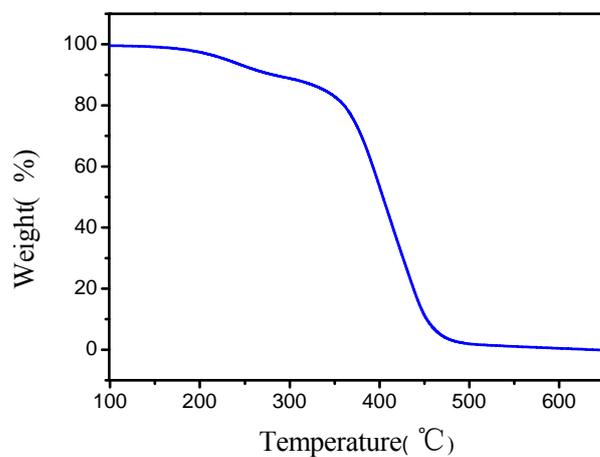


Figure S9. TGA curves of PVBO prepared by strategy 3.

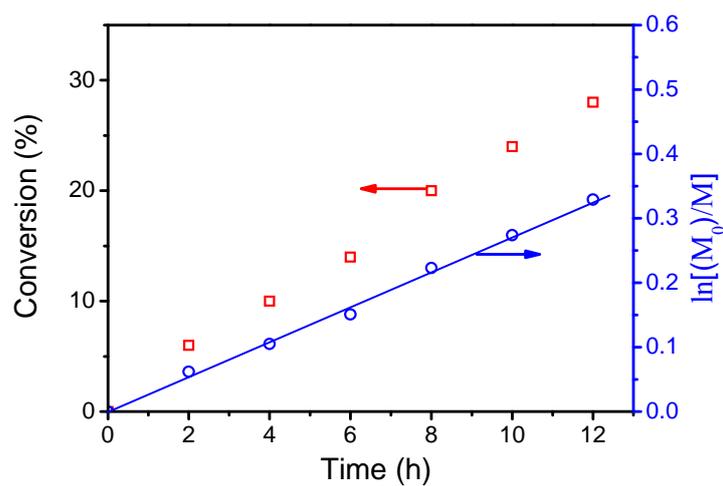


Figure S10. Semilogarithmic kinetic plot of RAFT polymerization of VBO