Integration of Renewable Cellulose and Rosin towards Sustainable Copolymers by "Grafting From" ATRP

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Supplementary Information

Synthesis of Resin Acid-Derived (Meth)acrylate Monomers (MAHDA and AHDA).
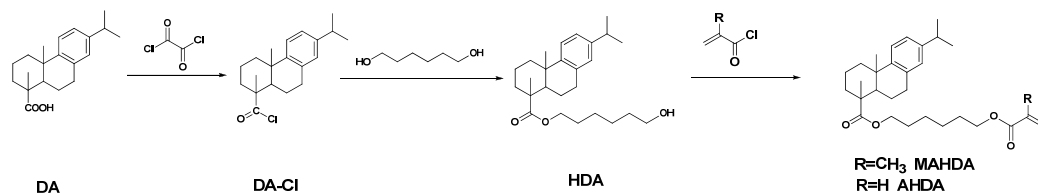
Dehydroabietic acid (DA) (1.0 g, 0.0033 mol) was dissolved in 30 mL dichloromethane (DCM) and added to a round-bottom flask. Oxalyl chloride (0.60 mL, 0.0055 mol) was injected and stirred at 25 °C for 4 h. After the removal of unreacted oxalyl chloride by vacuum distillation, the DA chloride (DA-Cl) was obtained. 50 mLTetrahydrofuran (THF), 1,6-hexanediol (4.03 g, 0.033 mol) and dimethylaminopyridine (DMAP) (4.10 g, 0.033 mol) were then added into the flask. The mixture was stirred at 50 °C for 12 h. The solution was filtered to remove the 4-(dimethylamino)phenol hydrochloride (DMAP·HCl) salt and added dropwise to petroleum ether. The solution was filtered

again and washed with dilute HCl solution. After the removal of solvent under vacuum, 1.01g hydroxylhexyl dehydroabieticcarboxylate (HDA) was obtained.[1]

HDA (0.40 g, 1.0 mmol), triethylamine (TEA) (0.24 g, 2.5 mmol), 0.00010 g hydroquinone and 50 mL THF were added into 250 mL round-bottom flask. Methacryloyl chloride or acryloyl chloride (1.2mmol)was then added dropwise to the flask and stirred at room temperature for 10 h. The solution was filtered to remove the Triethylamine Hydrochloride (TEA·HCl) salt and extracted with petroleum ether. The petroleum ether solution was then washed with NaOH (8 wt% in water). After the removal of solvent under vacuum, MAHDA or AHDA was obtained.[1]
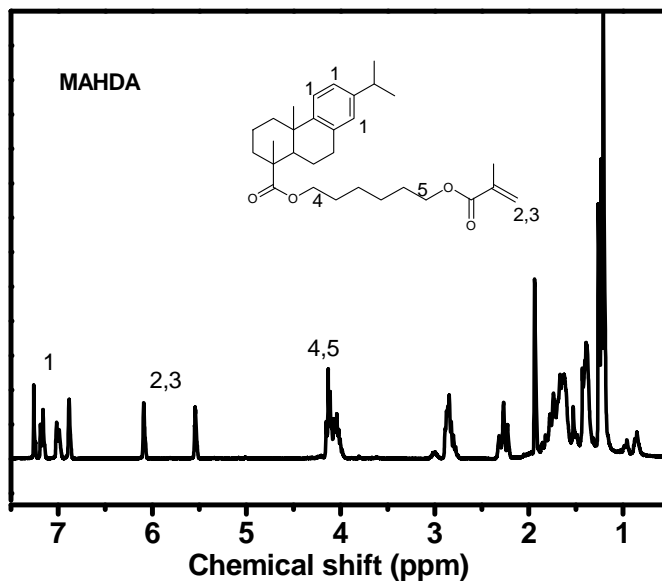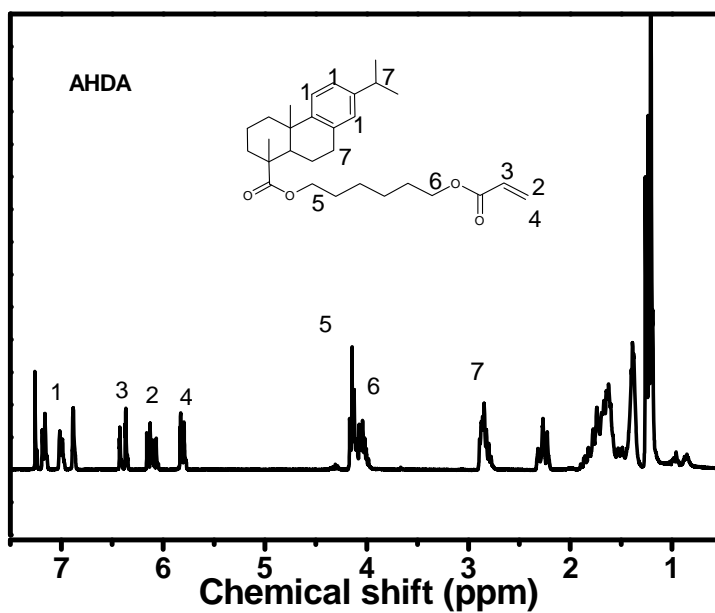
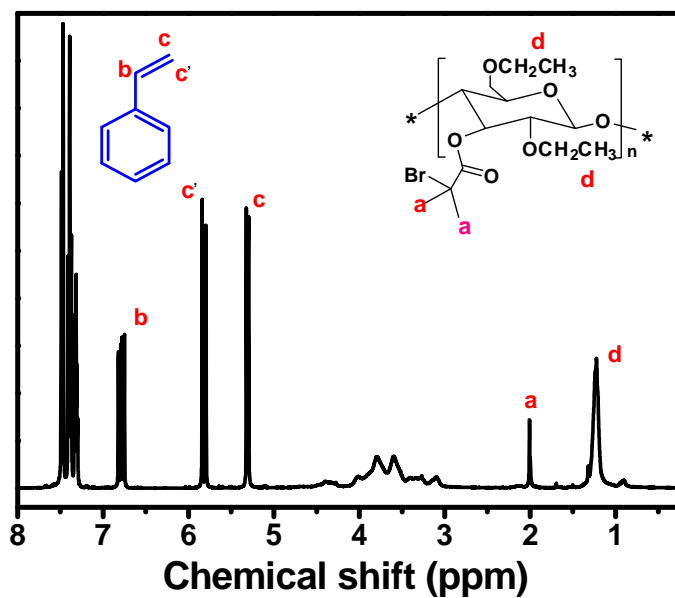**Figure S1.** ^{1}H NMR spectra of MAHDA and AHDA in CDCl$_3$.

Figure S2. ^{1}H NMR spectrum for calculation of bromoisobutyryl ester moiety in EC in CDCl$_3$.
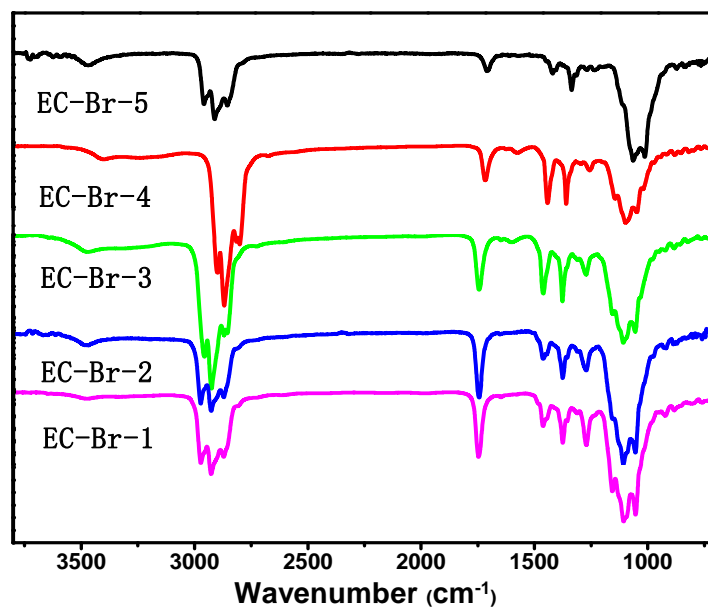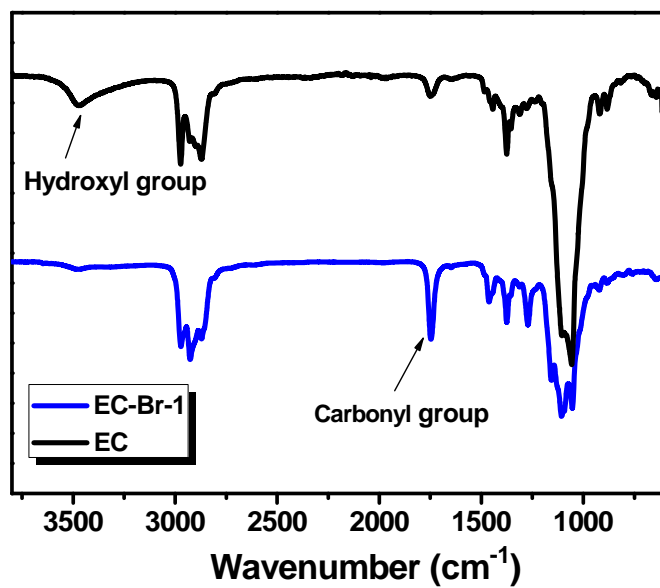
Figure S3. FT-IR spectra of EC and EC macroinitiators.

Determination of molar fraction of DA in EC-DA.

The moles of DA per EC-DA mass were determined according to Equation 1.

$$mol(DA)/mass(EC-DA) = \frac{1}{3\times151.12} \times \frac{A_b}{A_a} \times \frac{m_a}{m_b} \tag{1}$$

Where A_a is the ^{1}H NMR integration area (~10.1ppm) of aldehyde protons in *p*-nitrobenzaldehyde; A_b is the ^{1}H NMR integration area (6.8~7.2 ppm) of aromatic protons in DA;3 is the number of protons of aromatic ring in DA; 151.12 is the molecular weight of *p*-nitrobenzaldehyde; m_a and m_b are actual mass of *p*-nitrobenzaldehyde and EC-DA respectively.
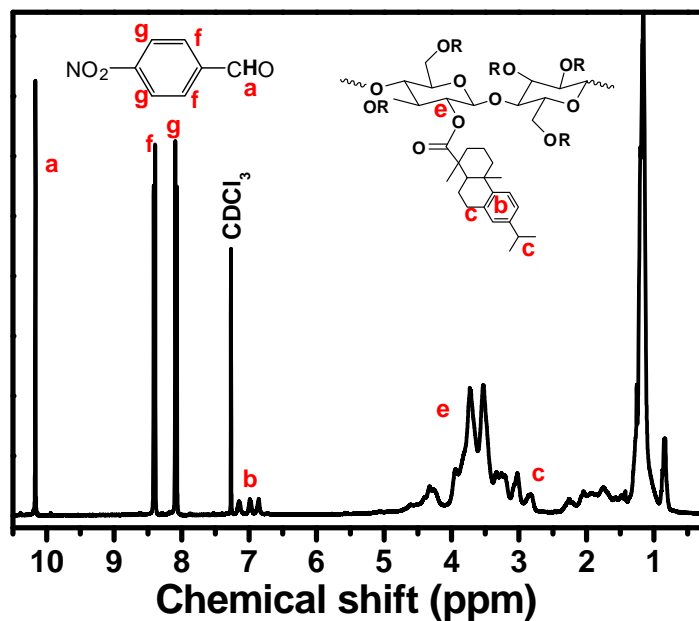

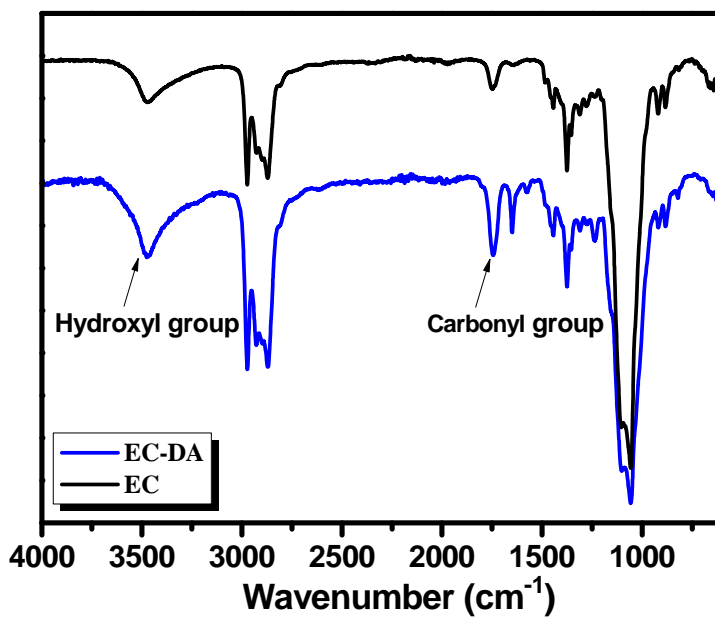**Figure S4.** ^{1}H NMR spectrum for calculation of DA ester moiety in EC in CDCl₃.

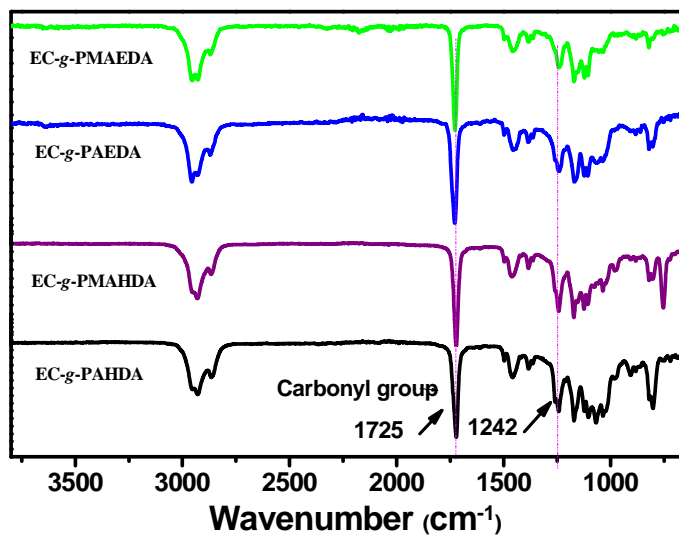**Figure S5.** FT-IR spectra of EC and EC-DA.

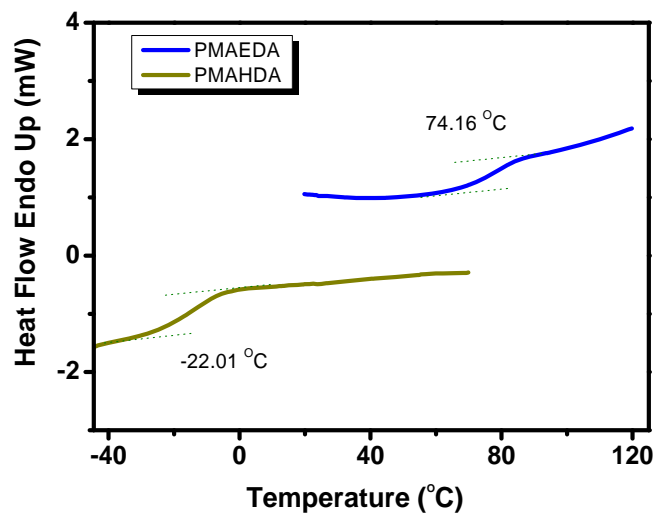**Figure S6.** FT-IR spectra of EC grafted Copolymers.

Figure S7. DSC curves for PMAEDA and PMAHDA cleaved from graft Copolymers (EC-*g*-PMAEDA (Table 2, Entry 1) and EC-*g*-PMAHDA).

Reference

1. J. Yu, Y. Liu, C. Wang, Y. Chen, J. Wang and F. Chu, *Adv. Mater. Res.*, 2013, **712**, 139-146.