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Supplementary material

SUPPLEMENTARY MATERIAL TO

Porous amphiphilic biogel from a facile chemo-biosynthetic route

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The observed ^{1}H-NMR spectrum for neat mcl-PHA, shown in Fig. S-1, matched previously published reports.[1–5] The signal at 2.5 ppm was assigned to α-position methylene (CH_2) group bonded to carbonyl (C=O) group, whereas the β-position methine (CH) was found at 5.2 ppm (Fig. S-1).

The remaining hydrogen atoms represent the side chain of the hydroxy fatty acid; the methylene protons were found at 1.3 ppm and the terminal methyl group (CH_3) at 0.9 ppm (Fig. S-1).

Another side reaction that leads to additional acrylate monomers, thereby increasing structural complexity of the copolymer, is the (partial) hydrolysis of GDD, as shown in Fig. S-2.

The terminal species with benzene ring plays a key role as a radical to attack an alkenyl group of the available GDD monomer, acrylate monomer, or mcl-PHA chain with alkenyl group. The β-carbon of the new species will be covalently bound to the α-carbon of the next (Fig. S-4). When a radical attacks the β-carbon of an acrylic system *vis-à-vis* acrylates such as GDD and its derivatives, and olefin-terminated PHA, the resulting radical is resonance-stabilized by the carbonyl group. The delocalization of the unpaired electron, as shown in Fig. S-3, reduces the energy of the intermediate and is responsible for the regioselective connection of α- to β-carbons.[6]

The ^{13}C-NMR spectrum for PHA has been reported previously.[7] In this study, the solid-state ^{13}C-NMR spectrum is shown in Figure S-5. Since the major

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parts of the biogel are virtually insoluble in any organic solvent, solid-state NMR analysis was initially conducted for the structural analysis of the PHA-*g*-GDD copolymer (Fig. S-5).

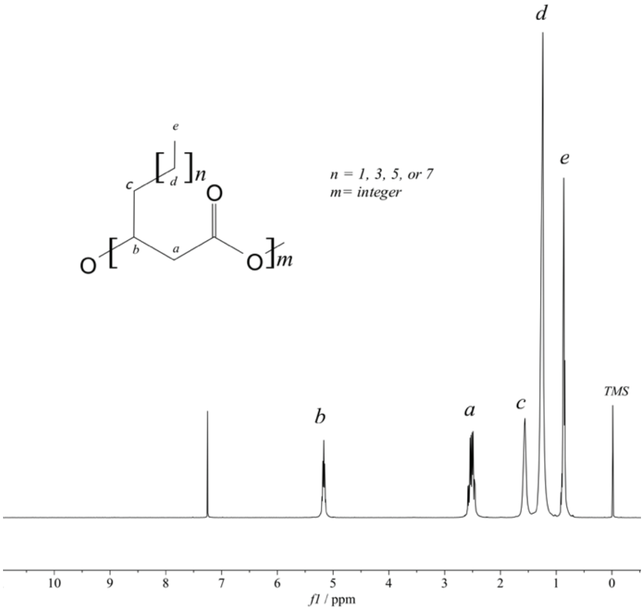


Fig. S-1. ^{1}H-NMR spectrum for neat mcl-PHA.

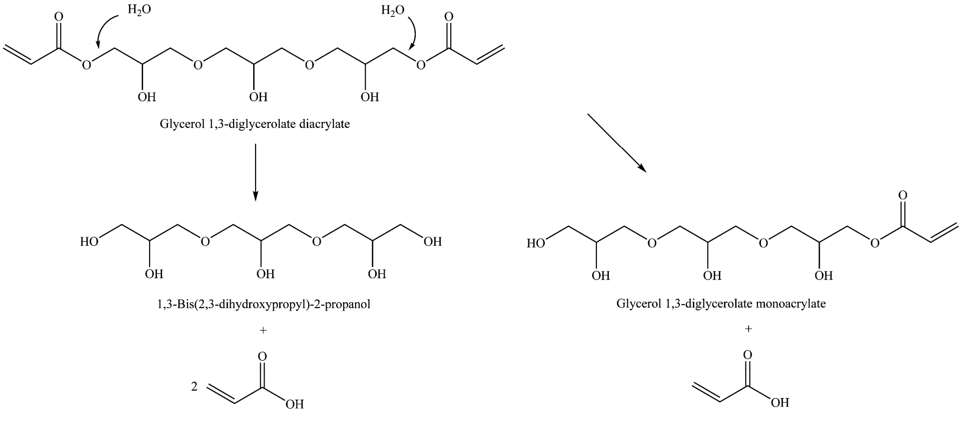


Fig. S-2. Thermal degradation of GDD to produce acrylate monomers *via* hydrolysis.

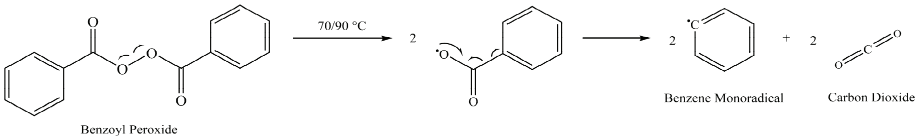


Fig. S-3. BPO dissociation prior to the initiation step during grafting commencement.

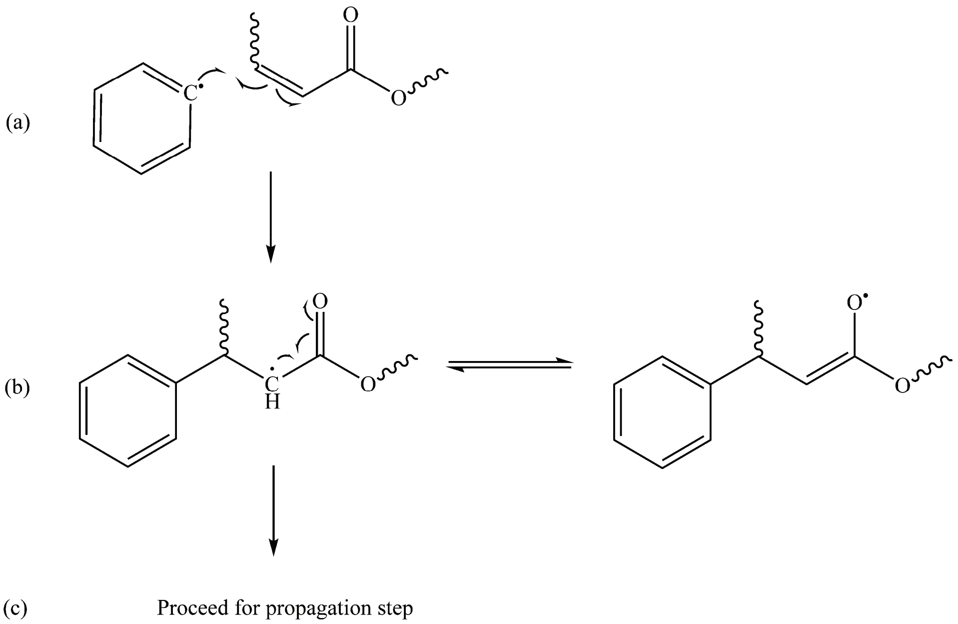
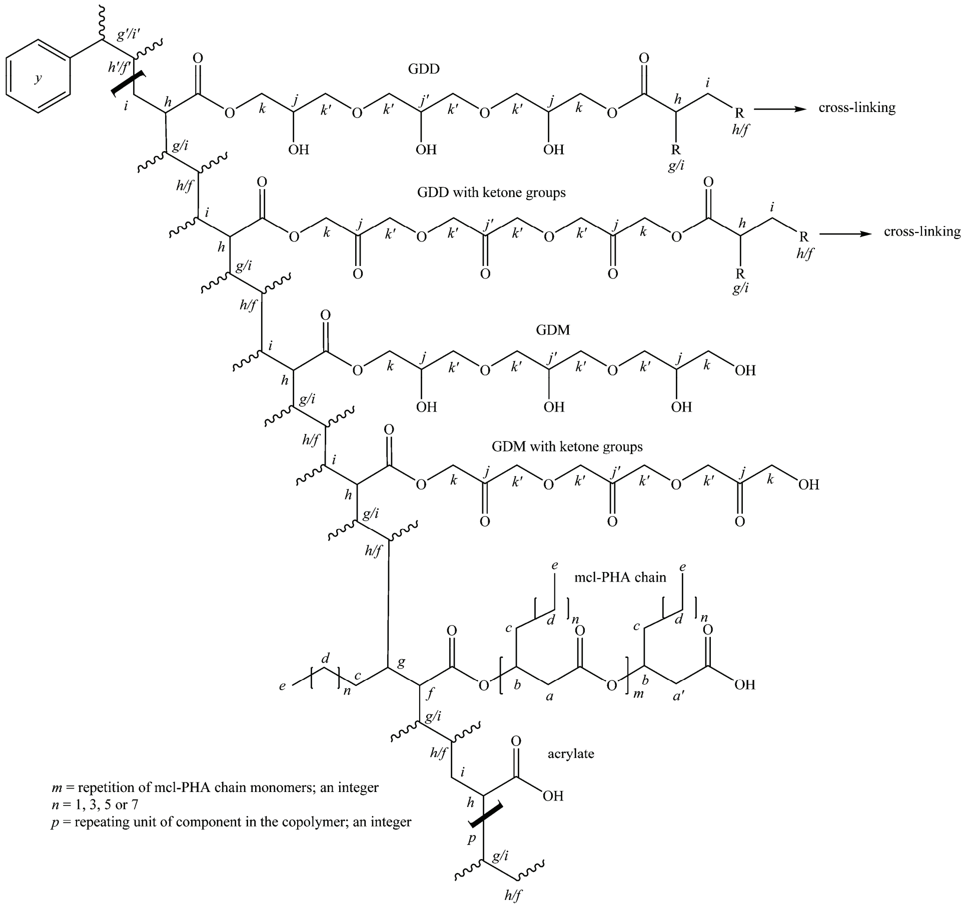


Fig. S-4. The allylic resonance involved after radical intervention on the reaction species, a) benzene radical attacked the species with alkenyl group, b) the allylic resonance shows the movement of the unpaired electron along the bonds and c) entering the propagation step.

However, the signal resolution was poor with several combined peaks, especially for the aliphatic component and the copolymer backbone chain, making it virtually impossible to decipher. The aliphatic component peaks were labelled as **A**, **A′** and **A″** across 40 ppm to 10 ppm within the spectrum.

Since ^{1}H-NMR from the main text allows for structural authentication of low molecular weight and partially soluble grafted product in deuterated chloroform, the solid-state ^{13}C-NMR further illustrating the complexity of the macromolecule with respect to the insoluble major fraction. An additional signal of minute amount of carbonyl ketone groups is available around 210 ppm on the ^{13}C-NMR spectrum, labelled as **E** indicates there was oxidation of the hydroxyl group a secondary alcohol within GDD, occurring as a side reaction due to the cascading radical reaction environment.[8] However, the distribution of the carbonyl ketone is random throughout the biogel.

A broad combined peak across 80 to 40 ppm represents carbonyl ester carbons, available in both PHA and GDD labelled as **B**, ether carbons within GDD labelled as **B′**, and *β*-carbon within PHA labelled as **B″**. In addition, initial benzene attachment is clearly visible in the ^{13}C-NMR spectrum labelled as **C** between 120 ppm to 110 ppm. On the other hand, a broad peak labelled as **D** ranging from 170 ppm to 155 ppm is believed to typically arise from carboxylic groups within PHA and GDD, while peak labelled as **D′** is attributed to the terminal carboxylic acid group of the PHA chain and acrylate component from hydrolysed GDD.



m = repetition of mcl-PHA chain monomers; an integer
n = 1, 3, 5 or 7
p = repeating unit of component in the copolymer; an integer

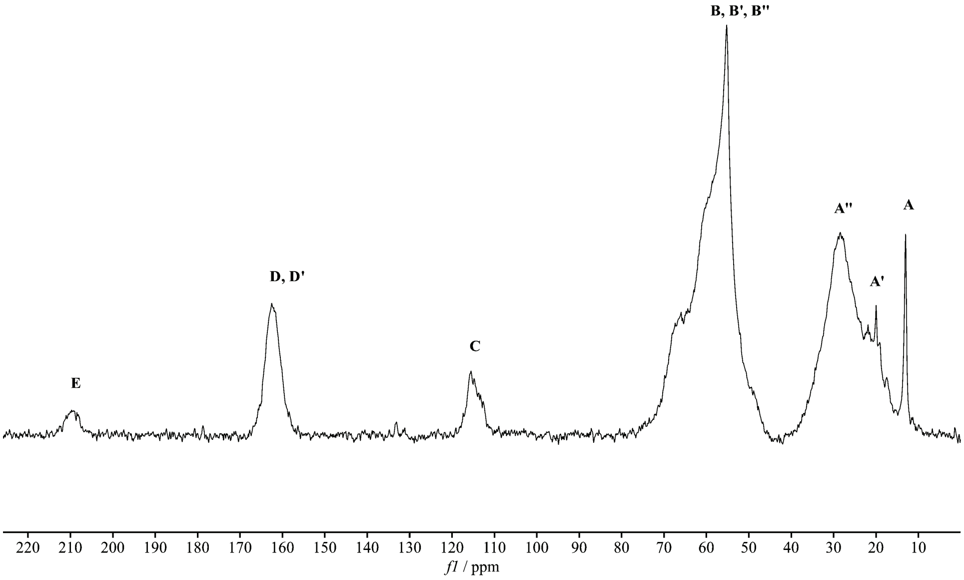


Fig. S-5. Solid state ^{13}C-NMR spectrum (bottom) with proposed general molecule of PHA-*g*-GDD biogel (top).

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