

Supporting Information

Polyester Networks from Structurally Similar Monomers: Recyclable-by-Design and Upcycling to Photopolymers

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Experimental section

Materials

Dimethyl phthalate (DMPH), phthalic anhydride (PHA), allyl alcohol (allyl-OH), 1-butanol, 1-hexanol, lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), rubidium carbonate (Rb_2CO_3), cesium carbonate (Cs_2CO_3), diallyl phthalate (DAPH), diethyl phthalate, phthalate chloride, sodium sulfate, diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO), 1,2-cyclohexanedicarboxylic anhydride, 1,3,5-Trimethoxybenzene (TMB), and 2-ethyl-4-methylimidazole (EMI) were purchased from Sigma-Aldrich. Pentaerythritol tetra(3-mercaptopropionate) (PETMP) was donated by Bruno Bock. Diglycidyl phthalate (DGPH) was donated by Nagase under the tradename EX-721. Diglycidyl 1,2-cyclohexanedicarboxylate was purchased from TCI. All other chemicals were used as received without additional purification.

General procedure of epoxy-anhydride polymerization

The PHA, DGPH, and PHMEA (if needed) were mixed based on the stoichiometric ratios given in Table 1. The mixture was heated to approximately 150 °C and was subsequently, subjected to SpeedMixer® at 3000 rpm for 30 s to obtain homogeneity. EMI (1 wt% with respect to the monomers) was then added to the mixture. Note that whenever the PHA crashed out from the mixture, additional heating and speed-mixing was employed. The resin was cast into various silicone molds and was kept in an oven at 130 °C for 2 h. For cyclohexane dicarboxylate systems, the resin was kept in an oven at 80 °C for 5 h. Resin was made in batches that varied from 1g to 25g.

General procedure of synthesizing phthalic mono-ester mono-acid

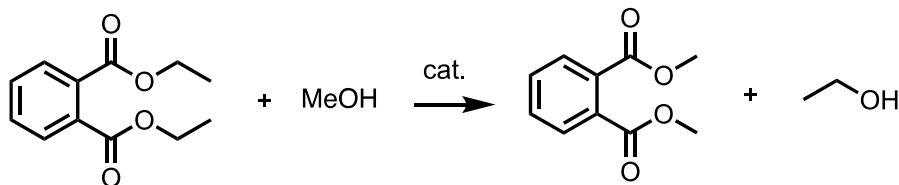
To a 250 mL round bottom flask, 7.4 g PHA (50 mmol) and 50 mL of an alcohol reagent were added. The flask was then equipped with a condenser with an N_2 balloon and was submerged in an oil bath. The mixture was kept at 80 °C with rigorous magnetic stirring overnight. No catalyst or other reagents were employed. The mono-ester product was isolated by removing the alcohol reagent by a rotary evaporator and subsequently, put under a high vacuum. The product was found sufficiently pure without further purification. This procedure has been applied using methanol, ethanol, and 1-butanol.

General procedure of degradation by transesterification reactions

Discs were cast from resin into a silicone mold with a diameter of 10 mm and a thickness of 2 mm. The polymer samples were weighed and then submerged in 10 mL methanol or allyl alcohol with 0.5 g K_2CO_3 as catalyst for a saturated solution. For degradation experiments comparing the different carbonate salts, the molar ratio of methanol to salt was fixed at 1:400. Excess solvent and catalyst were used to show proof of concept, as the solubility of K_2CO_3 in the chosen

solvents was lower than 0.05 g/mL. At each time point, samples were taken out of the solution and were weighed after physically drying the surface with a Kim wipe.

Procedure of small-molecule transesterification reactions



Scheme 1: Transesterification of Diethyl Phthalate via methanol

A group 1 carbonate salt catalyst (i.e. Na₂CO₃, K₂CO₃, Rb₂CO₃, or Cs₂CO₃), diethyl Phthalate, and methanol were mixed in molar ratios of 1:20:400. The solutions were kept at room temperature and were magnetically stirred. Samples of the solution were taken at various times to monitor the conversion of diethyl phthalate via ¹H NMR. The effectiveness of the catalysts was compared to the control group, which had no catalyst included in the methanol solution.

General procedure of preparing thiol-ene photopolymer

Diallyl phthalate and PETMP were mixed in stoichiometric amount between thiol groups and alkene groups, and subsequently, 1 wt% TPO (with respect to the total monomers) was added. The mixture was homogenized by using a SpeedMixer®. The mixture was cast in silicone molds with the desired geometry. The casted resin was exposed to 405 nm light by an Anycubic Wash and Cure Station for 30 m.

Characterization methods

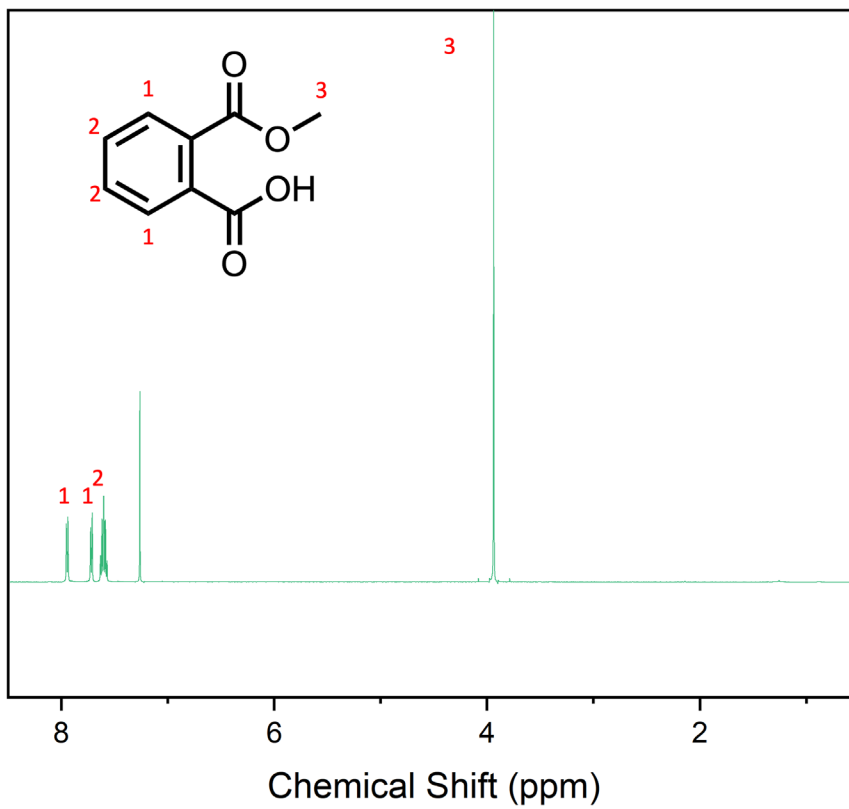
Dynamic Mechanical Analysis (**DMA**) tests were conducted on a TA DHR-20 with oscillatory force applied in the axial direction. Rectangular bars of 30 mm x 5 mm x 1 mm (LxWxT) were fabricated by curing in a silicone mold. The samples were tested with 0.1% axial strain at a frequency of 1 Hz, ramping from 40 °C to 200 °C at 3 °C/min. An axial gap limit of 3 mm was set. Glass transition temperature (T_g) was determined by the highest point on the tan δ curve. Rubbery modulus was determined by the storage modulus (E') at T_g + 40 °C. The samples were tested within 24 hours after being annealed at 150 °C for at least 1 h.

Differential Scanning Calorimetry (**DSC**) tests were conducted on a NETZSCH 3500 Sirius. Samples underwent three heat-cool cycles and the T_g was determined using the second heating cycles. The temperature ramped from 40 °C to 200 °C at 10 °C/min.

Fourier transform infrared spectroscopy (**FT-IR**) spectra were collected on a Nicolet iS50 spectrometer equipped with a single-bounce Smart iTR Attenuated Total Reflectance (ATR) setup. DTGS-KBr was used as the detector, and the air was used as the background. Spectra

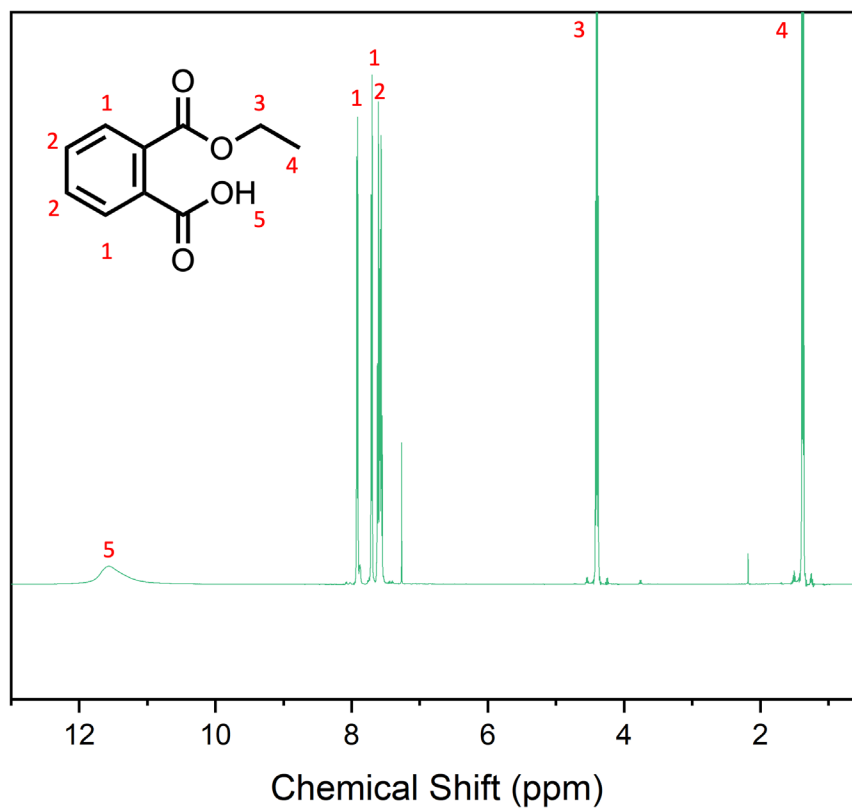
were collected from 4000 cm^{-1} to 600 cm^{-1} . Polymer samples were made into a thin film to achieve sufficient contact with the ATR window.

^1H NMR spectra were collected on a Bruker Avance NEO 500 MHz. CDCl_3 was used as the solvent for all spectra collected. 1,3,5-Trimethoxybenzene was used as an internal standard to calculate yield of DMPH and DAPH from degraded polymers.



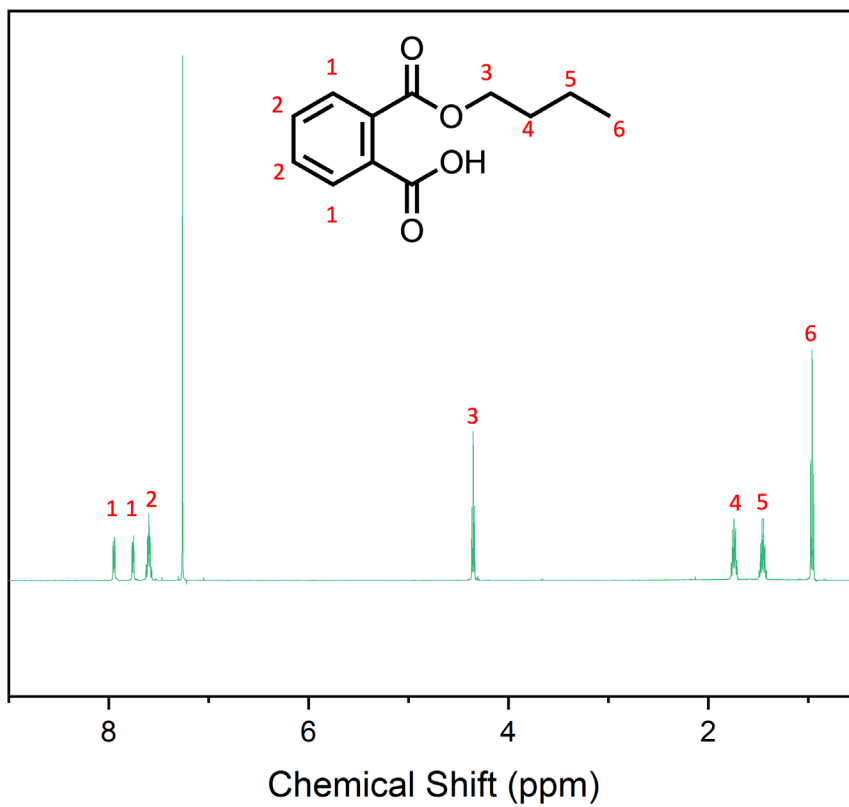
Peak #	Chemical Shift (ppm)	Integral
1	7.94	0.99
1	7.72	0.98
2	7.60	2.08
3	3.94	3

Figure S1. ¹H NMR of monomethyl phthalate in CDCl₃ with respective peaks and integrals.



Peak #	Chemical Shift (ppm)	Integral
1	7.91	0.97
1	7.70	0.97
2	7.58	2.05
3	4.39	2.00
4	1.37	3.00
5	11.56	0.95

Figure S2. ¹H NMR of monoethyl phthalate in CDCl₃ with respective peaks and integrals.



Peak #	Chemical Shift (ppm)	Integral
1	7.94	0.98
1	7.76	0.97
2	7.60	2.00
3	4.35	2.00
4	1.74	2.14
5	1.45	2.15
6	0.96	3.11

Figure S3. ¹H NMR of monobutyl phthalate in CDCl₃ with respective peaks and integrals.

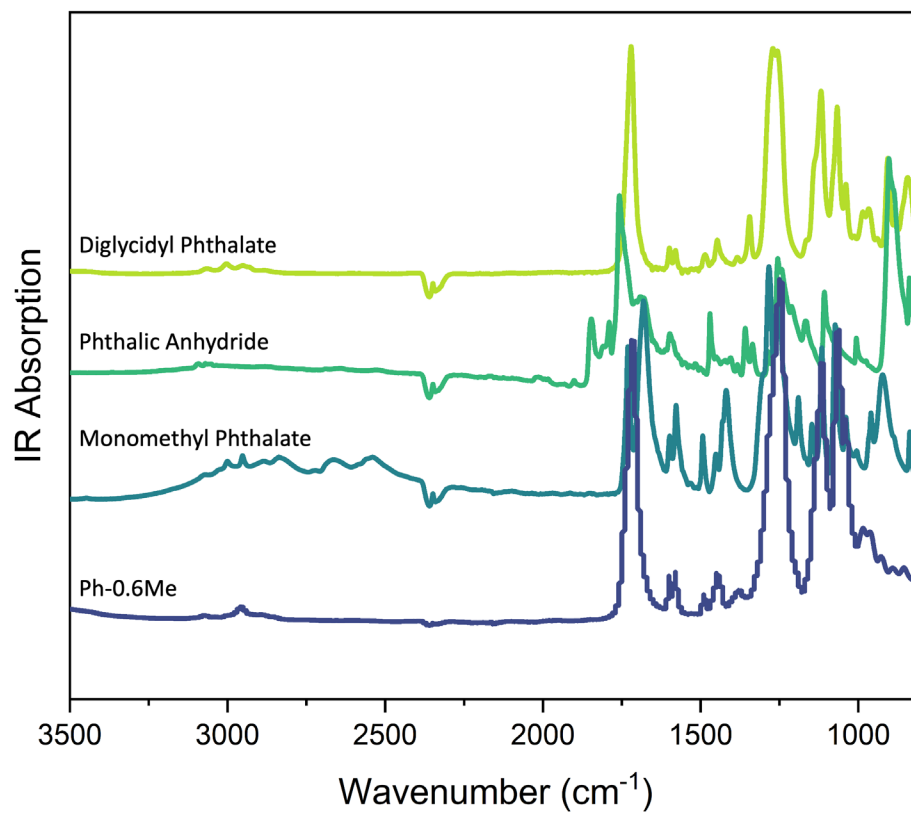


Figure S4. FT-IR spectrum of monomers and the resulting polymer for the tertiary DGPH-PHA-PHMEA system.

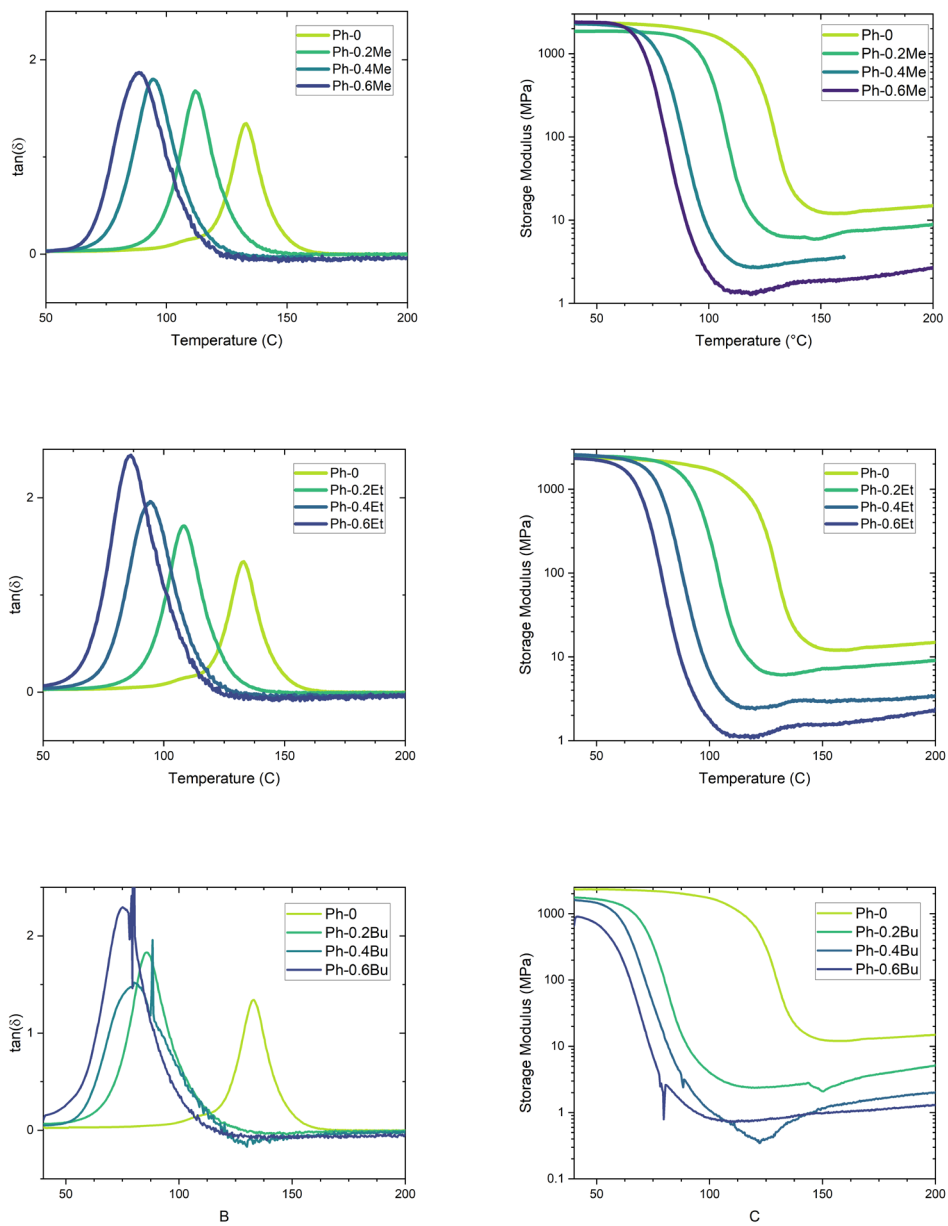


Figure S5. Entailed DMA data of PH-Me (top), PH-Et (middle), and PH-Bu (bottom) systems, including both $\tan \delta$ (left) and storage modulus (right).

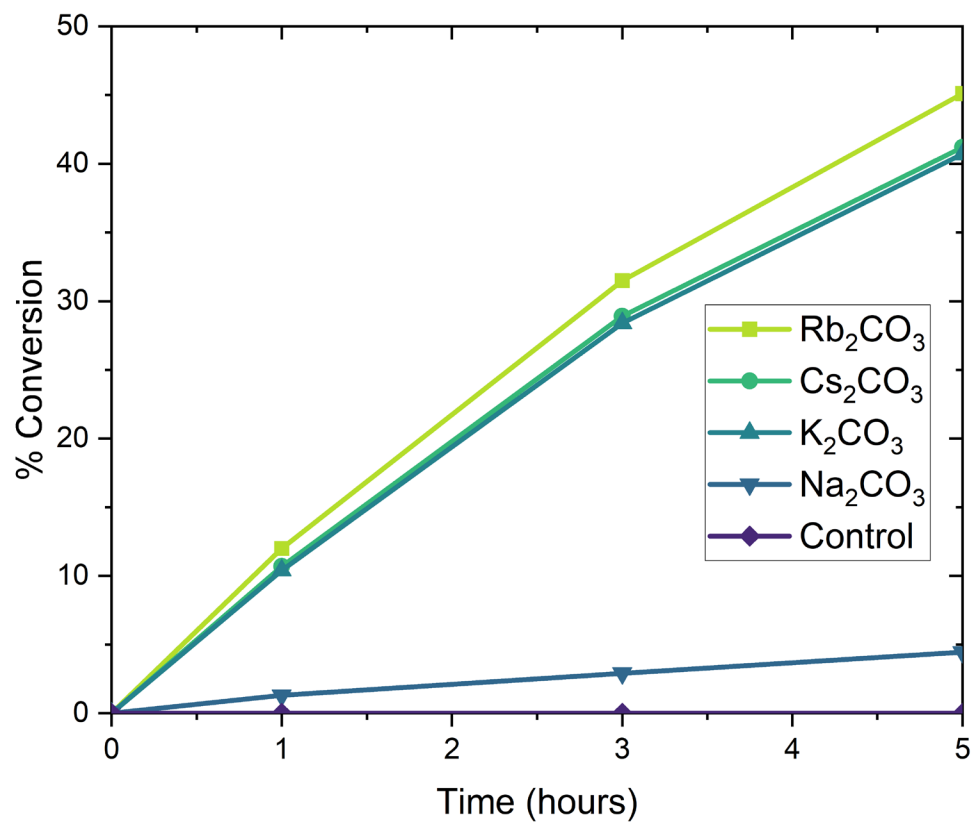


Figure S6. Conversion of diethyl phthalate in methanol using various group 1 carbonate salts. Samples for ¹H NMR were collected at various times to calculate conversion. Control group solution included no catalyst.

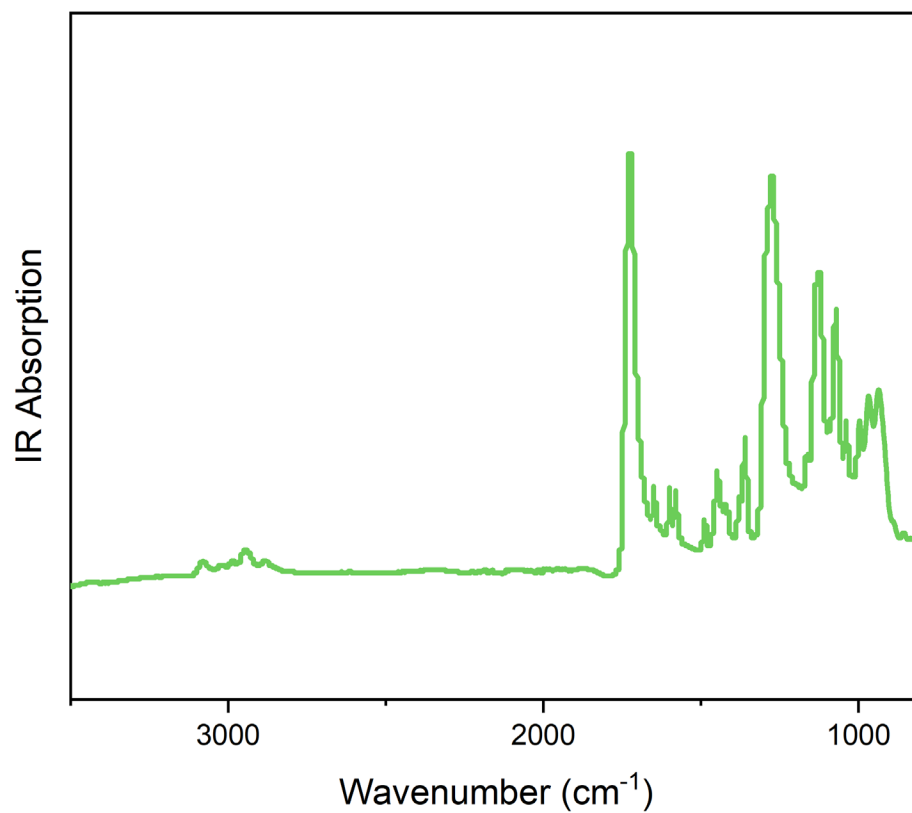
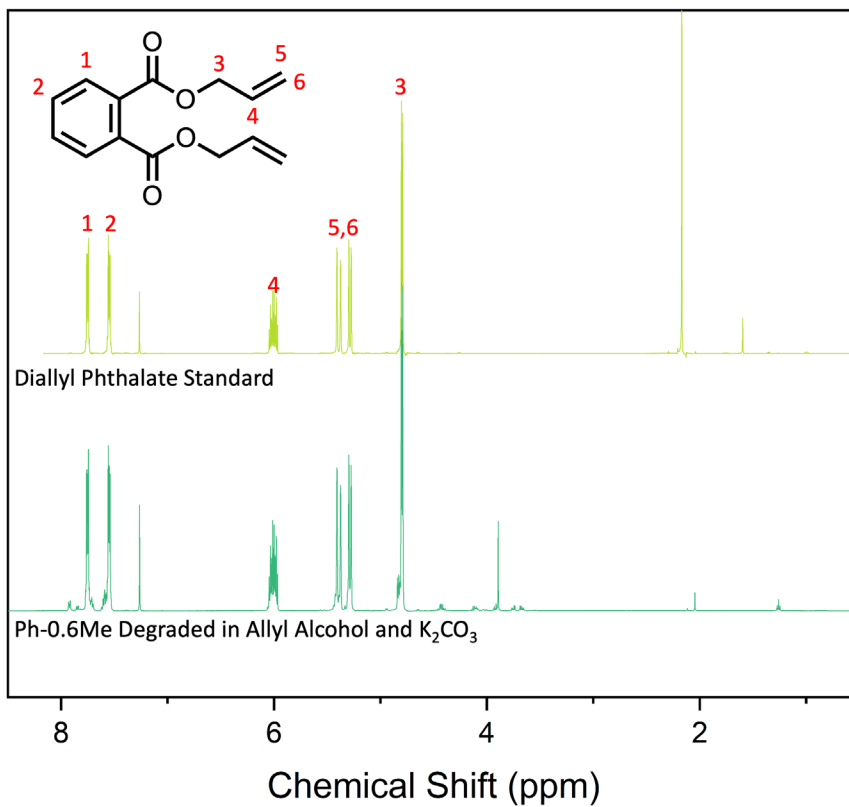


Figure S7. FT-IR spectrum of degraded Ph-0.6Me with allyl alcohol after aqueous work up



Peak #	Chemical Shift (ppm)	Integral (Standard)	Integral (Recycled)
1	7.75	2.01	1.98
2	7.55	2.05	2.06
4	6.00	2.00	2.0
5	5.39	2.03	1.88
6	5.28	2.03	1.97
3	4.79	4.20	3.61

Figure S8. ¹H NMR spectrum of degraded Ph-0.6Me with allyl alcohol after aqueous work up with respective peaks and integrals of both the degraded polymer and the internal standard.

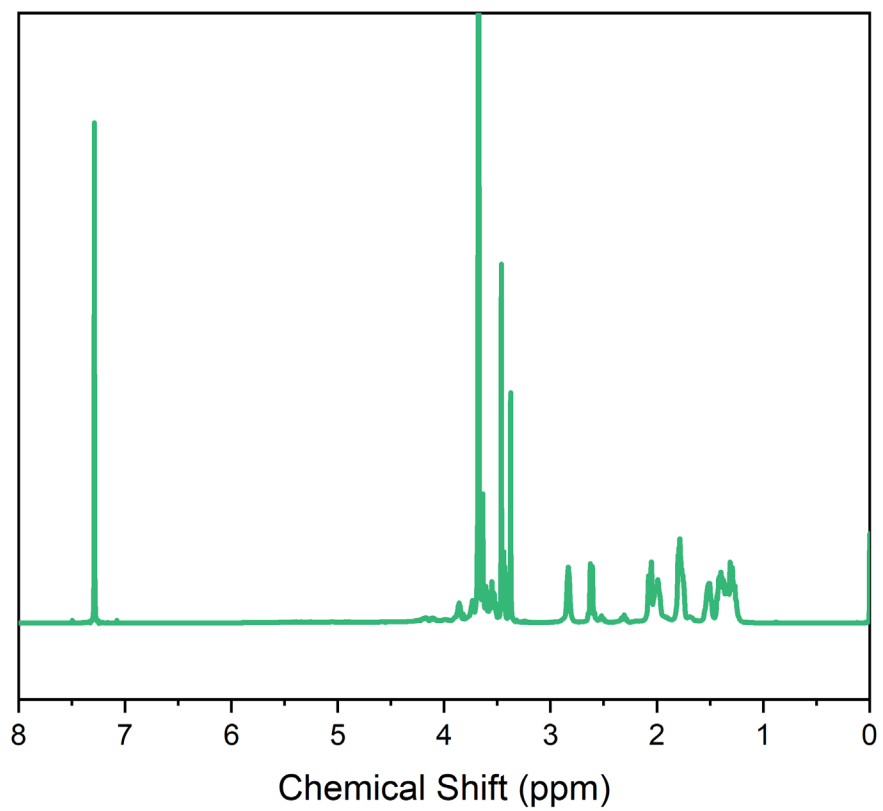


Figure S9. ^1H NMR spectrum of the degraded 1,2-cyclohexane dicarboxylate-based polymer with methanol.

Polymer	Solvent	Expected Phthalate Ester	Initial Polymer (g)	Theoretical Yield of Phthalate Ester (g)	Actual Yield of Phthalate Ester via ¹H NMR	Percent Yield (wt %)
PH-0.6Me	Methanol	DMPH	0.1746	0.1591	0.1036	65.1%
PH-0.6Me	Allyl Alcohol	DAPH	0.1999	0.2310	0.1896	82.1%
DAPH-PETMP	Methanol	DMPH	0.1100	0.0435	0.0434	99.8%

Table S1. Yields calculated via ¹H NMR spectrum using TMB as an internal standard. Degradation of polymers were performed at 23 °C using a saturated K₂CO₃ alcohol solution.