Supporting Information

Environmentally benign synthesis of saturated and unsaturated aliphatic polyesters via enzymatic polymerization of biobased monomers derived from renewable resources

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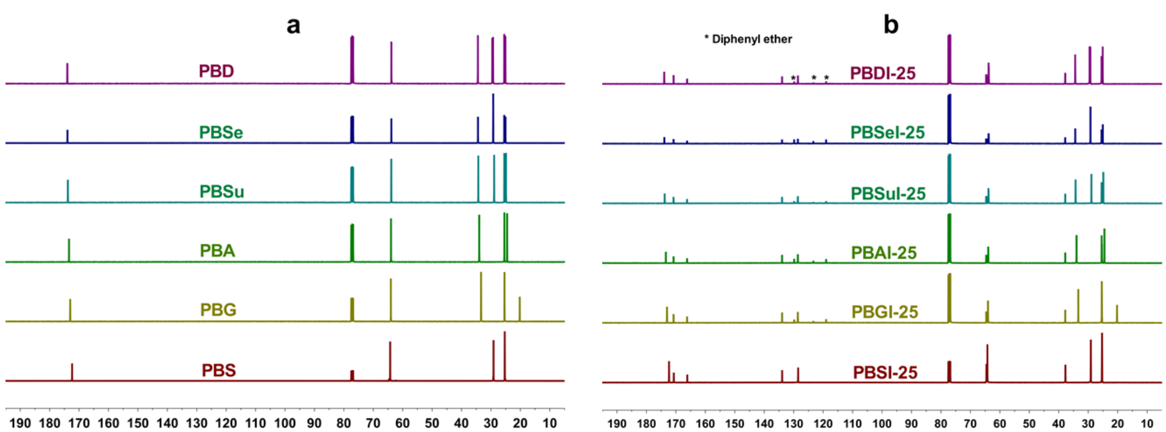

Figure S1. Representative ^{13}C-NMR spectra of the obtained aliphatic polyesters: (a) saturated aliphatic polyesters; and (b) unsaturated aliphatic polyesters containing around 25 % itaconate. PBS = poly(butylene succinate); PBG = poly(butylene glutarate); PBA = poly(butylene adipate); PBSu = poly(butylene suberate); PBSe = poly(butylene sebacate); PBD = poly(butylene dodecanedioate) (PBD); PBSI = poly(butylene succinate-*co*-itaconate); PBGI = poly(butylene glutarate-*co*-itaconate); PBAI = poly(butylene adipate-*co*-itaconate); PBSuI = poly(butylene suberate-*co*-itaconate); PBSeI = poly(butylene sebacate-*co*-itaconate); PBDI = poly(butylene dodecanedioate-*co*-itaconate).

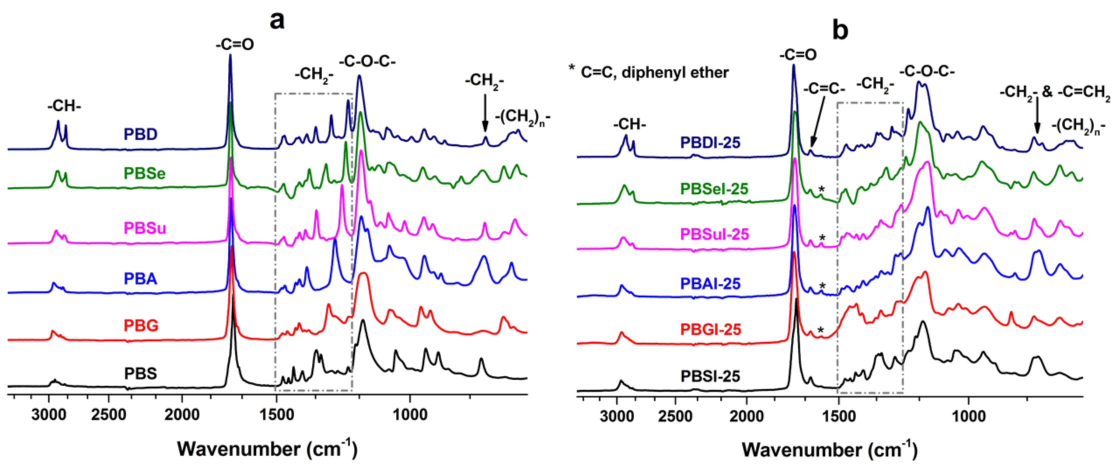

Figure S2. Representative ATR-FTIR spectra of the obtained aliphatic polyesters: (a) saturated aliphatic polyesters; and (b) unsaturated aliphatic polyesters containing around 25 % itaconate.

Table S1. Result summary: aliphatic polyesters from CALB-catalyzed two-stage polycondensation of diacid ethyl esters, dimethyl itaconate and 1,4-butanediol

	Molar Composition (%)						Molecular weight			
	Feed [a]			Co-polyester [b]			SEC [c]			
Polyester	F_D	F_I	F_B	X_D	X_I	X_B	$\bar{M}_n$ (kg/mol)	$\bar{M}_w$ (kg/mol)	*Đ* ($\bar{M}_w/\bar{M}_n$)	Yield (%)
PBS	50	0	50	50	0	50	6.0	11.5	1.92	86 [d]
PBSI-15	35	15	50	35	16	49	13.3	22.6	1.70	90 [d]
PBSI-25	25	25	50	27	24	49	11.1	16.6	1.50	87 [d]
PBSI-15	20	30	50	36	16	48	1.9	2.2	1.16	21 [e]
PBSI-15	15	35	50	41	15	44	0.5	0.5	1.00	49 [e]
PBI	0	50	50	0	68	32	0.2	0.2	1.00	35 [e]
PBG	50	0	50	49	0	51	18.0	39.1	2.17	85 [d]
PBGI-15	35	15	50	36	14	50	20.7	39.8	1.92	84 [d]
PBGI-25	25	25	50	26	24	50	19.8	37.2	1.88	82 [d]
PBGI-30	20	30	50	21	29	50	13.7	24.6	1.80	76 [d]
PBGI-35	15	35	50	16	34	50	11.8	23.5	1.99	70 [d]
PBA	50	0	50	50	0	50	46.8	94.0	2.01	89 [d]
PBAI-15	35	15	50	36	15	50	24.6	57.9	2.35	84 [d]
PBAI-25	25	25	50	26	25	49	30.0	55.3	1.84	86 [d]
PBAI-30	20	30	50	21	30	49	20.1	33.7	1.68	78 [d]
PBAI-35	15	35	50	17	33	50	15.6	30.3	1.94	68 [d]
PBSu	50	0	50	50	0	50	18.0	37.6	2.09	87 [d]
PBSuI-15	35	15	50	36	14	50	19.4	38.7	1.99	84 [d]
PBSuI-25	25	25	50	26	24	50	20.2	34.3	1.70	87 [d]
PBSuI-30	20	30	50	22	28	50	23.2	46.9	2.02	77 [d]
PBSuI-35	15	35	50	16	34	50	15.8	25.4	1.61	70 [d]
PBSe	50	0	50	50	0	50	21.5	39.5	1.84	94 [d]
PBSeI-15	35	15	50	34	18	48	21.1	38.0	1.80	84 [d]
PBSeI-25	25	25	50	26	24	50	22.5	41.6	1.85	81 [d]
PBSeI-30	20	30	50	20	31	49	18.7	30.1	1.61	79 [d]
PBSeI-35	15	35	50	17	34	49	11.3	29.1	2.58	66 [d]
PBD	50	0	50	49	0	51	12.4	26.3	2.12	88 [d]
PBDI-15	35	15	50	34	18	48	17.3	39.2	2.27	87 [d]
PBDI-25	25	25	50	26	25	49	20.3	34.6	1.70	80 [d]
PBDI-30	20	30	50	22	28	50	21.9	47.6	2.17	82 [d]
PBDI-35	15	35	50	17	33	50	24.2	49.5	2.05	82 [d]

[a] F_D, F_I, F_B: molar percentage of diacid ethyl ester, dimethyl itaconate, and 1,4-butanediol fed into enzymatic polymerization; [b] X_D, X_I, X_B: molar percentage of diacid ethyl ester units, itaconate units and butanediol units in the obtained aliphatic polyesters, calculated from ^{1}H-NMR; [c] The number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$), and dispersity (*Đ*, $\bar{M}_w/\bar{M}_n$) were determined by SEC in chloroform; [d] Isolated yield. The final products were precipitated in cold methanol (-20 °C); [e] Isolated yield. The final products were precipitated in hexane (r.t.).

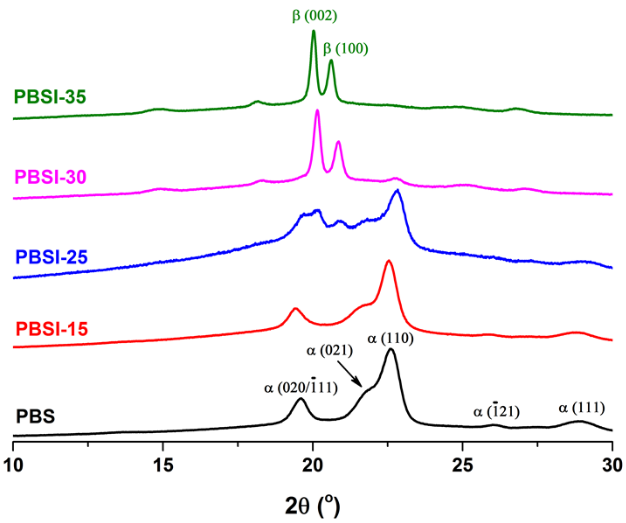

Figure S3. WAXD spectra of poly(butylene succinate) (PBS) and poly(butylene succinate-*co*-itaconate) (PBSI). The number 15/25/30/35 indicates the approximate molar percentage of itaconate in the co-polyesters.

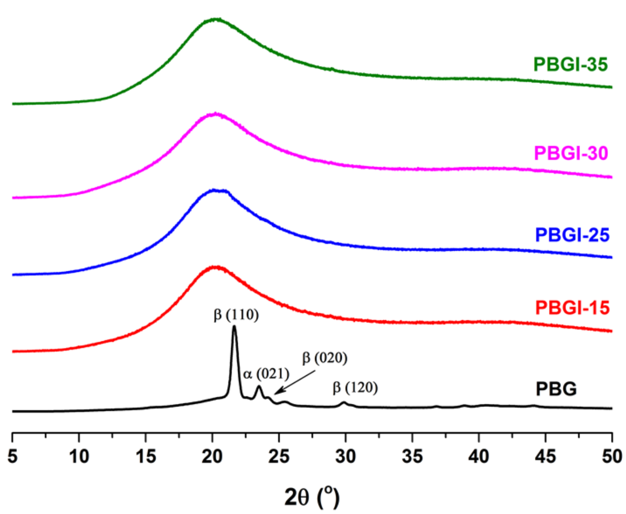

Figure S4. WAXD spectra of poly(butylene glutarate) (PBG) and poly(butylene glutarate-*co*-itaconate) (PBGI). The number 15/25/30/35 indicates the approximate molar percentage of itaconate in the co-polyesters.

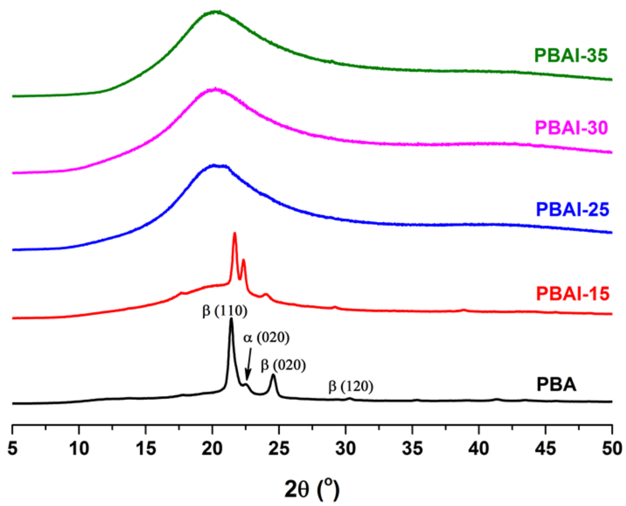

Figure S5. WAXD spectra of poly(butylene adipate) (PBA) and poly(butylene adipate-*co*-itaconate) (PBAI). The number 15/25/30/35 indicates the approximate molar percentage of itaconate in the co-polyesters.

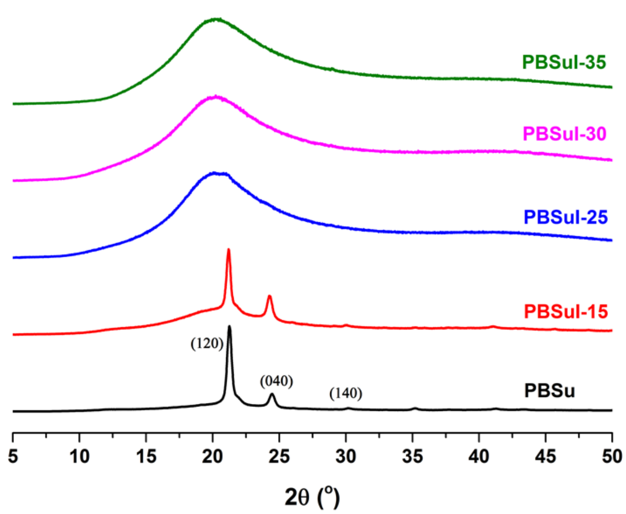

Figure S6. WAXD spectra of poly(butylene suberate) (PBSu) and poly(butylene suberate-*co*-itaconate) (PBSuI). The number 15/25/30/35 indicates the approximate molar percentage of itaconate in the co-polyesters.

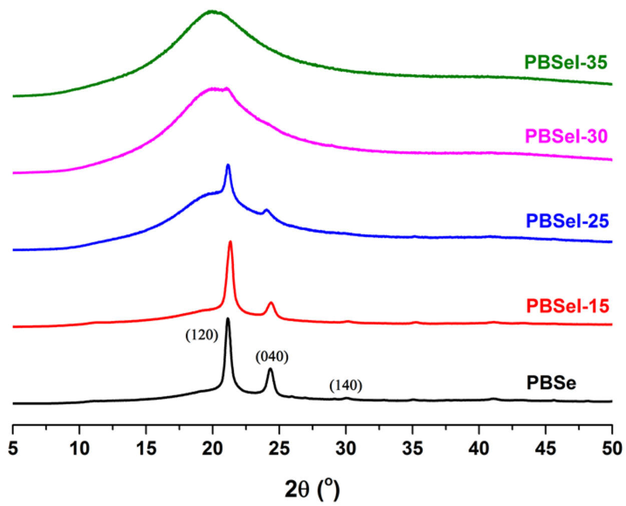

Figure S7. WAXD spectra of poly(butylene sebacate) (PBSe) and poly(butylene sebacate-*co*-itaconate) (PBSeI). The number 15/25/30/35 indicates the approximate molar percentage of itaconate in the co-polyesters.

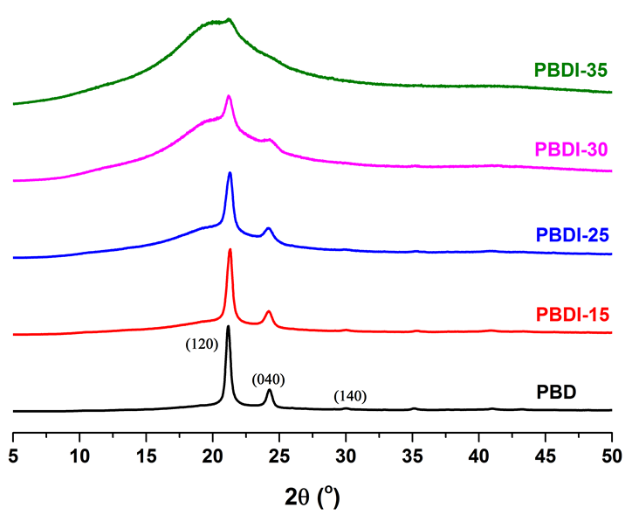

Figure S8. WAXD spectra of poly(butylene dodecanedioate) (PBD) and poly(butylene dodecanedioate-*co*-itaconate) (PBDI). The number 15/25/30/35 indicates the approximate molar percentage of itaconate in the co-polyesters.

Table S2. Thermal and crystalline properties of the obtained aliphatic polyesters.

	DSC [b]														
	First Heating				Cooling		Second Heating				TMDSC [c]	TGA [d]			WAXD [e]
Polyester [a]	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_m (J/g)	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)	T_g (°C)	$T_{d\text{-}5\%}$ (°C)	$T_{d\text{-}10\%}$ (°C)	$T_{d\text{-}max}$ (°C)	χ_c (%)
PBS	-28	80	98, 113 [f]	91	68	71	-30	88	99, 111 [f]	83	-29	339	360	406	69
PBSI-15	-37	39	82	59	/	/	-36	40	80	16	-29	358	374	411	49
PBSI-25	-38	/	36, 60 [f]	30	/	/	-36	/	/	0	-37	327	365	406	31
PBSI-30	-39	/	42	35	/	/	-36	/	/	0	-37	274	342	398	57
PBSI-35	-43	/	39	38	/	/	-38	/	/	0	-38	279	344	399	63
PBG	-58	/	53	58	/	/	-59	-23	26, 38 [f]	38	-58	381	390	422	47
PBGI-15	-54	/	/	/	/	/	-52	/	/	0	-51	352	382	419	0
PBGI-25	-49	/	/	/	/	/	-45	/	/	0	-44	365	381	418	0
PBGI-30	-47	/	/	/	/	/	-43	/	/	0	-43	356	374	415	0
PBGI-35	-43	/	/	/	/	/	-36	/	/	0	-33	368	385	425	0
PBA	-55	/	61, 66 [f]	78	29	36	-59	/	54	33	-59	377	387	418	59
PBAI-15	-53	/	26	31	/	/	-53	-10	18	25	-54	366	385	423	16
PBAI-25	-51	/	/	/	/	/	-48	/	/	0	-48	363	385	430	0
PBAI-30	-48	/	/	/	/	/	-45	/	/	0	-43	363	380	422	0
PBAI-35	-45	/	/	/	/	/	-44	/	/	0	-40	357	379	419	0
PBSu	-56	/	59	102	36	74	-59	/	57	78	-62	384	393	420	63
PBSuI-15	-56	/	31, 40 [f]	42	/	/	-54	/	18	4	-57	369	391	421	31
PBSuI-25	-57	/	/	/	/	/	-55	/	/	0	-55	326	371	414	0
PBSuI-30	-53	/	/	/	/	/	-51	/	/	0	-51	361	381	422	0
PBSuI-35	-47	/	/	/	/	/	-46	/	/	0	-46	354	376	418	0
PBSe	-55	/	65	101	48	73	-55	/	67	81	-54	382	391	420	62
PBSeI-15	-55	/	48	60	20	46	-55	/	39	52	-52	384	394	426	46
PBSeI-25	-55	-43	23	32	/	/	-59	-36	7	21	-51	352	383	429	14
PBSeI-30	-54	-24	7	22	/	/	-55	-18	5	13	-54	351	380	428	5
PBSeI-35	-49	/	/	/	/	/	-52	/	/	0	-48	364	382	424	0
PBD	-44	/	59, 73 [f]	121	56	88	-46	/	56, 72 [f]	96	-46	384	394	421	75
PBDI-15	-48	/	54	78	31	50	-49	/	51	59	-47	384	396	429	60
PBDI-25	-48	/	45	65	16	33	-48	/	32, 39 [f]	40	-45	378	390	430	37
PBDI-30	-48	/	23, 45 [f]	26	5	29	-48	/	27, 36[f]	30	-46	365	382	426	14
PBDI-35	-49	0	15	18	-24	16	-50	-1	12	13	-45	366	385	428	5

[a] PBSI-25, PBSI-30 and PBSI-35 were prepared from the CALB-catalyzed azeotropic polymerization in the mixture of cyclohexane and toluene (see Y. Jiang, G. O. R. Alberda van Ekenstein, A. J. J. Woortman and K. Loos, *Macromol. Chem. Phys.*, 2014, **215**, 2185-2197). The other aliphatic polyesters were produced from the CALB-catalyzed two-stage polymerization in diphenyl ether; [b] T_g = glass transition temperature, T_{cc} = cold crystallization temperature upon heating, T_m = melting temperature, ΔH_m = enthalpy of transition, T_c = crystallization temperature, / = not detected at the tested time scale; [c] TMDSC = Temperature Modulated Differential Scanning Calorimetry; [d] $T_{d\text{-}5\%}$ = decomposition temperature at 5 % weight loss, $T_{d\text{-}10\%}$ = decomposition temperature at 10 % weight loss, $T_{d\text{-}max}$ = temperature at maximum rate of decomposition; [e] The degree of crystallinity (χ_c) was calculated from WAXD; [f] Multiple melting temperatures were observed.

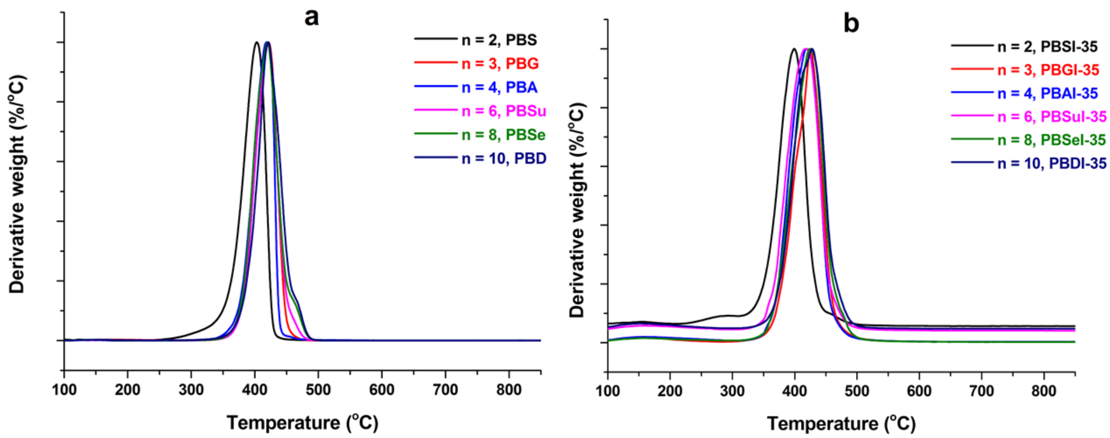

Figure S9. Representative TGA traces of the obtained aliphatic polyesters: (a) saturated aliphatic polyesters; and (b) unsaturated aliphatic polyesters containing around 35 % itaconate.

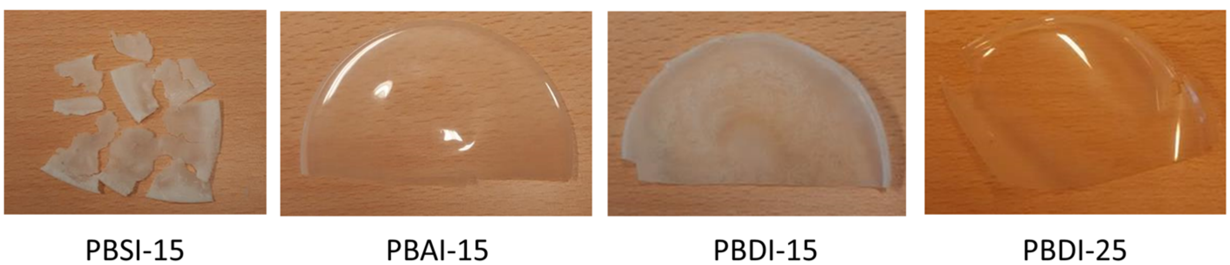

Figure S10. Representative UV-cured unsaturated aliphatic polyester films: poly(butylene succinate-*co*-itaconate) containing around 15 % itaconate (PBSI-15), poly(butylene adipate-*co*-itaconate) containing around 15 % itaconate (PBAI-15), poly(butylene dodecanedioate-*co*-itaconate) containing around 15 % (PBDI-15) and poly(butylene dodecanedioate-*co*-itaconate) containing around 25 % itaconate (PBDI-25).

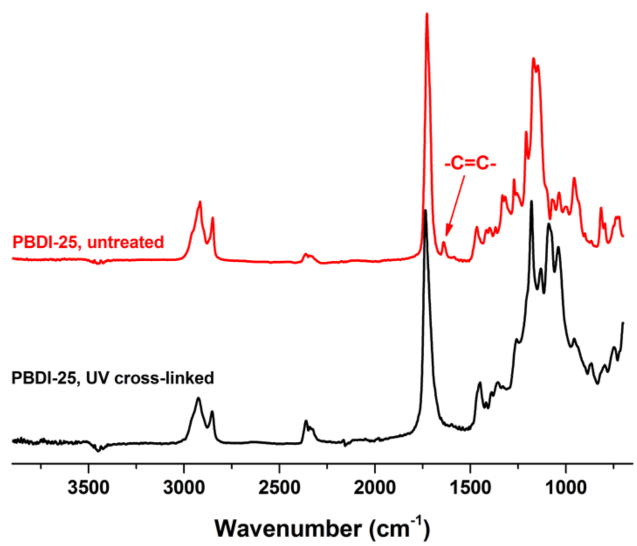

Figure S11. Representative ATR-FTIR spectra of poly(butylene dodecanedioate-*co*-itaconate) containing around 25 % itaconate (PBDI-25) before and after UV cross-linking.