Itaconic Acid as a Platform Chemical for Bio-Based Polymers: From Green Polymerization Strategies to Structure-Driven Applications

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Table S1 Calculation of the E-factor for the representative polymerization process.

Entry	Input Material	Input Weight (g)	Temperature Reaction Time	Output Material	Output Weight (g)	Conv. (%)/ Yield (%)	E-factor	Ref.
1	Di-*n*-butyl itaconate (DBI)	0.40	Polymerization of DBI segment 20 °C, 160 h Polymerization of PhII segment 50 °C, 19 h	PhII-*b*-DBI-*b*-PhII	0.32	Polymerization of DBI segment Conv.=58% Polymerization of PhII segment Conv.=58%	2.15	[1]
	N-phenylitaconimide (PhII)	0.148						
	V-70	0.001						
	RAFT agent	0.0097						
	AIBN	0.0005						
	1,4-Dioxane	0.45						
2	Di-*n*-methyl itaconate	42.3	20 °C, 20-60 h	Poly(di-*n*-alkyl itaconate-*co*-isoprene)	59.16	Yield=85%	4.83	[2]
	Di-*n*-ethyl itaconate	49.8			65.54		4.36	
	Di-*n*-propyl itaconate	57.3			71.91		3.99	
	Di-*n*-butyl itaconate	64.7			78.2		3.68	
	Di-*n*-pentyl itaconate	72.2			84.6		3.42	
	Di-*n*-hexyl itaconate	79.7			91.0		3.19	
	Di-*n*-heptyl itaconate	87.2			97.3		2.99	
	Di-*n*-octyl itaconate	94.7			103.7		2.82	
	Di-*n*-nonyl itaconate	102.2			110.1		2.67	
	Di-*n*-decyl itaconate	109.7			116.5		2.53	
	Isoprene	27.3						
	Deionized water	214.4						
	SDS/SDBS	46.0						

	K_3PO_3	2.0						
	KCl	5.0						
	SHS	2.0						
	Fe-EDTA	4.0						
	TBH	0.5						
	Hydroxylamine	0.4						
3	Styrene	0.558	50 °C, 4 h	Poly(styrene-*ran*-butadiene)	0.82	Yield=71%	27.8	[3]
	Butadiene	0.58						
	Titanium complex	0.008						
	MAO	0.72						
	Toluene	9.9						
	Ethanol	11.8						
	Antioxidant	0.06						
4	*β*-myrcene (MY)	33.2	70 °C, 20 h	Poly(MY-*co*-DBI)	93	Yield=93%	2.81	[4]
	Di-*n*-butyl itaconate	66.8						

	Deionized water	250						
	SDS	2.5						
	APS	0.35						
	$NaHCO_3$	1.5						
5	Di-*n*-butyl itaconate	240	6 °C, 5 h	Poly(dibutyl itaconate-*co*-butadiene-*co*-glycidyl methacrylate	391.4	Yield=95%	2.11	[5]
	Butadiene	160						
	Glycidyl methacrylate	12						
	Deionized water	785						
	Total emulsifier	14.4						
	Total activator	0.76						
	Potassium chloride	2.80						
	Tert-dodecyl mercaptan	0.48						
	Sodium hydrosulfite	0.25						
	Diisopropyl benzene	0.36						
6	Di-*n*-butyl itaconate	50	78 °C, 3.5 h	Poly(dibutyl itaconate-*co*-butyl acrylate-	97.48	Yield=96.3%	1.42	[6]

	Butyl acrylate (BA)	45		*co*-acrylic acid-*co*-glycidyl methacrylate)				
	Acrylic acid (AA)	2						
	Glycidyl methacrylate (GMA)	0.5						
	Ammonium persulfate	0.5						
	Deionized water	134						
	Ammonium allyloxynonylphenol polyoxyethylene (10) ether sulfate	2.25						
	Sodium dodecyl benzene sulfonate	0.75						
	Potassium chloride	0.3						
	Sodium bicarbonate	0.2						
	Aqueous ammonia	0.1						
7	Itaconic anhydride	0.560	100 ^{o}C, 1 h	Poly(itaconate-*co*-cyclohexene oxide)	Solution Polymerization 1.05	Solution polymerization Conv.=>99%	Solution polymerization 0.84	[7]
	Cyclohexene oxide	0.491						
	Toluene	0.862			Bulk polymerization 1.01	Bulk polymerization Conv.=96%	Bulk polymerization 0.02	
	Cr catalyst	0.0125						

	PPNCl	0.0115						
8	Di(10-undecenyl) itaconate (DUI) Grubbs catalyst (Ru-G1) CH_2Cl_2	0.8693 0.0082 0.665	40 °C, 10 h	Poly(DUI)	0.748	Yield=86%	1.06	[8]
9	DMI-derived bis(pyrrolidone) diesters 1,8-Octanediol CALB	2.72 0.88 0.36	1) 85 °C, 6 h 1 bar 2) 85 °C, 18 h 15 mbar	PE128	3.528	Yield=98%	0.12	[9]
10	Diethyl adipate Dimethyl itaconate 1,4-Butanediol Diphenyl ether CALB	1.12 1.11 1.00 4.845 0.323	1) 80 °C, 2 h 760 mmHg 2) 80 °C, 94 h 2 mmHg	PBAI-25	2.778	Yield=86%	2.02	[10]
11	Di-*n*-butyl itaconate 1,12-Dodecanediol Dibutyltin dilaurate	1.00 0.83 0.052	1) 160 °C, 12 h 760 mmHg 2) 165 °C, 3 h <1 Torr	Poly(dodecyl itaconate)	1.41	Yield=77%	0.34	[11]

	Quinol	0.00114						
12	Itaconic acid Deionized water NaOH *Tert*-butyl hydroperoxide	200 151.1 2.40 3.5	100 °C, 1 h	Poly(itaconic acid)	120	Yield=60%	1.98	[12]
13	Itaconic acid PEGDA600 BPO N,N-dimethylaniline DMSO	0.392 1.83 0.022 0.011 8.80	1) 160 °C, 12 h 760 mmHg 2) 165 °C, 3 h <1 Torr	Poly(itaconic acid-*co*-PEGDA600)	2.222	Yield>99%	3.98	[13]
14	Itaconic anhydride Toluene AIBN	2.0 1.73 0.0145	70 °C, 24 h	Poly(itaconic anhydride)	1.73	Yield=87%	1.16	[14]
15	Itaconic anhydride *n*-Butyl methacrylate (BMA)	0.50 1.9	70 °C, 24 h	P(IAH-*ran*-BMA)	2.1	Yield=87%	2.61	[14]

	1,4-Dioxane	5.15						
	AIBN	0.03						
16	P(IAH-*ran*-BMA)	1.0	90 °C, 24 h	P(IAH-*ran*-BMA)-*g*-PLA	0.73	Yield=40%	8.93	[14]
	PLA	2.41						
	$Sn(Oct)_2$	0.03						
	1,4-Dioxane	3.81						
17	PLA	1	190 °C, 6 min	PLA-*g*-IAH	1.004	Yield>99%	0.02	[15]
	Itaconic anhydride	0.005						
	L101	0.02						
18	IABDO-diol	7.00	1) 70 °C, 40 min 2) 80 °C, 70 min	ICH-PU	14	Yield=100%	3.93	[16]
	HMDI	4.31						
	N,N-Dimethylformamide	55						
	DBTDL	0.08						
	CCTG	2.69						
19	Itaconic acid	130.1	1) 25 °C, 30 min 2) 230 °C, 7 h	IA-derived polyamide	220.4	Yield=89.5%	1.91	[17]

	Hexamethylenediamine	116.2						
	EtOH	394.5						
	NaH_2PO_4	0.23						
20	Itaconic acid	5.84	1) 150 °C, 1 h 2) 180 °C, 2 h	EP thermoset	21.84	Yield>99%	0.72	[18]
	Epoxidized vegetable oil	16						
	Ethanol	15.78						
21	DCHU	0.00224	100 °C, 18 h	EP thermoset	2.17	Yield=61%	0.62	[19]
	PPNCl	0.0057						
	Itaconic anhydride	1.12						
	Epoxidized vegetable oil	2.39						
22	Itaconic acid	50	1) 105 °C, 0.5 h 2) 50 °C, 3 h	EIA	64.4	Yield=15.9%	6.56	[20]
	Epichlorohydrin	355.5						
	Tetrabutylammonium bromide	1.5						
	50 wt% Sodium hydroxide solution	80						

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