



Supporting Information

for

Angew. Chem. Int. Ed. Z53738

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69451 Weinheim, Germany

Supramolecular Control of Stereochemistry of Diene Polymers

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Di(naphthylmethylammonium) (*E,Z*)-muconate (EZ-1): powder (methanol); m.p. 140 °C decomp.; ¹H NMR (400 MHz, CD₃OD) δ 8.05–8.12 (m, Ar, 2H and *trans*-CH=CHCO₂, 1H), 7.94 (t, *J* = 8.0 Hz, Ar, 4H) 7.50–7.65 (m, Ar, 8H), 6.36 (t, *J* = 11.2 Hz, *cis*-CH=CHCO₂, 1H), 5.95–6.03 (dd, *J* = 11.2 and 17.6 Hz, CH=CHCO₂, 2H), 4.56 (s, CH₂, 4H); IR (KBr) 1601 (ν_{C=C}), 1556 (ν_{C=O}) cm⁻¹; UV (CH₃OH) λ_{max} 261 nm (ε 27,000).

Di(4-methoxybenzyl) (*E,Z*)-muconate (EZ-2): platelets (chloroform); m.p. 84 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.43 (dd, *J* = 15.6 and 11.6 Hz, *trans*-CH=CHCO₂, 1H), 7.20–7.35 (m, Ar, 4H), 6.87–6.91 (m, Ar, 4H), 6.62 (t, *J* = 11.6 Hz, *cis*-CH=CHCO₂, 1H), 6.11 (d, *J* = 15.6 Hz, *trans*-CH=CHCO₂, 1H), 5.96 (d, *J* = 11.6 Hz, *cis*-CH=CHCO₂, 1H), 5.16 (s, OCH₂, 2H), 5.14 (s, OCH₂, 2H), 3.81 (s, OCH₃, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 165.91 and 165.07 (C=O), 159.67 (Ar), 140.78 and 138.82 (CH=), 130.28, 130.19, 128.97, 127.97, 127.75, and 124.54 (Ar), 114.00 and 113.96 (CH=), 63.34 and 66.26 (CH₂), 55.30 (CH₃); IR (KBr) 1711 (ν_{C=O}), 1595 (ν_{C=C}) cm⁻¹; UV (acetonitrile) λ_{max} 266 nm (ε 27,100).

Synthetic procedures and spectral data for **ZZ-1**, **EE-1**, **ZZ-2**, and **EE-2** are described in previous papers (refs. 15a and 16).

Poly(EZ-2): ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, *J* = 8.4 Hz, Ar), 6.78 (d, *J* = 8.4 Hz, Ar), 5.55 (s, CH=), 4.92 (s, CH₂), 3.71 (s, OCH₃), 3.30 (s, CH); ¹³C NMR (100 MHz, CDCl₃) δ 170.13 (C=O), 159.52, 130.00, 127.52, and 113.87 (Ar), 129.82 (CH=), 66.65 (CH₂), 55.12 (OCH₃), 51.58 (CH).

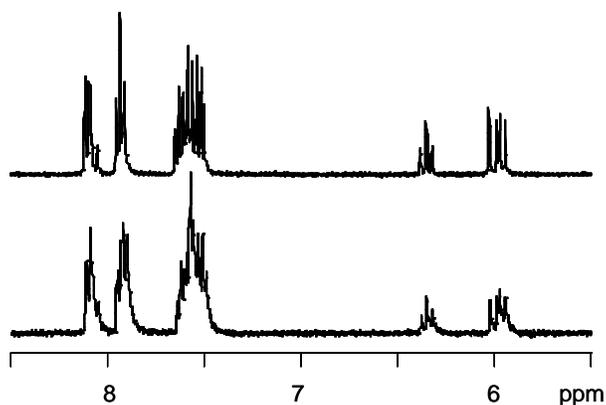


Figure S1. ^1H NMR spectra of (a) **EZ-1** monomer and (b) the recovered monomer after γ -radiation. Measurement solvent, CDCl_3 .

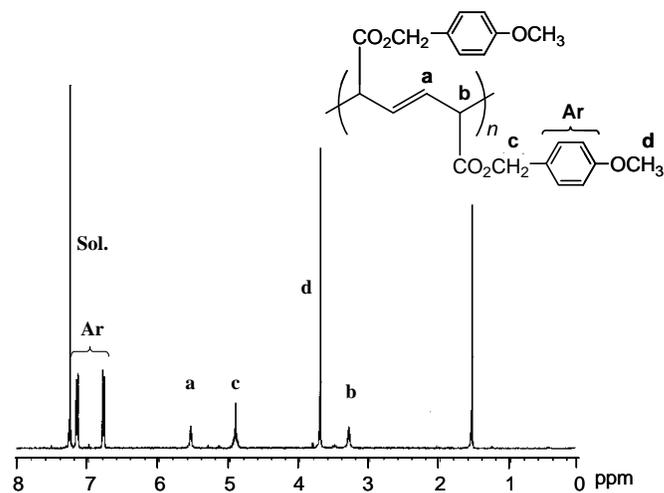


Figure S2. ^1H NMR spectrum of (a) **EZ-2**. Measurement solvent, CDCl_3 .

Poly(muconic acid) derived from poly(EZ-1): IR (KBr) $1705 (\nu_{\text{C=O}}) \text{ cm}^{-1}$.

Poly(triethylammonium muconate) derived from poly(EZ-1): ^{13}C NMR (100 MHz, CD_3OD) δ 178.64 (C=O), 131.26 (C=C), 56.08 (CH), 46.99 (CH_2), 10.51 (CH_3).

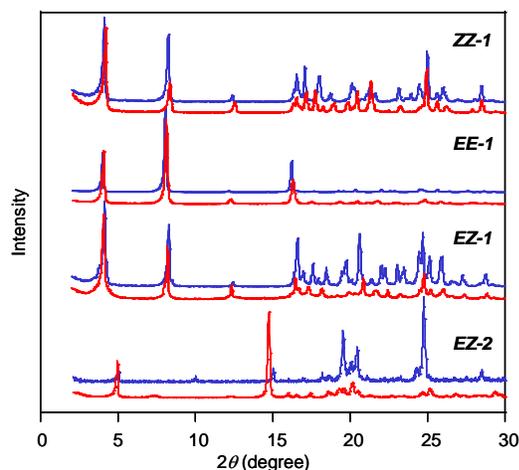


Figure S3. Powder X-ray diffraction profiles of three kinds of 1-naphthylmethylammonium muconates (**ZZ-1**, **EE-1**, and **EZ-1**) and 4-methoxybenzyl (*E,Z*)-muconate (**EZ-2**). Blue and red indicate results for the monomers and polymers, respectively. Polymer was prepared by γ -radiation polymerization (200 kGy) and purified by removing the unreacted monomers with methanol.

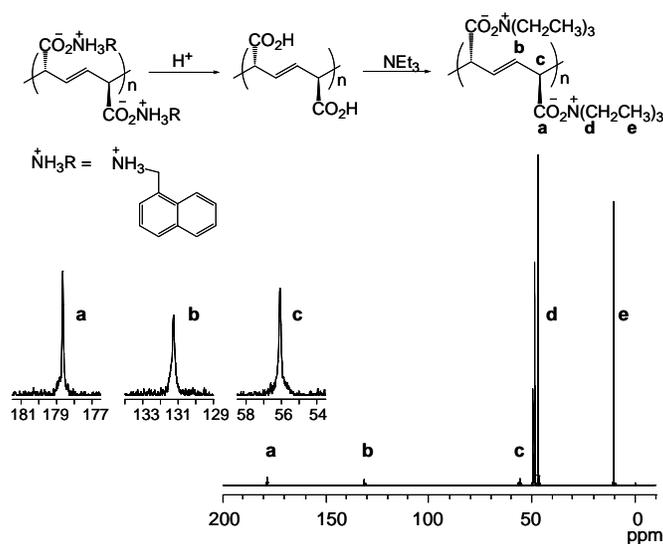


Figure S4. ^1H NMR spectrum of poly(triethylammonium muconate) derived from poly(**EZ-1**). Measurement solvent, CDCl_3 .

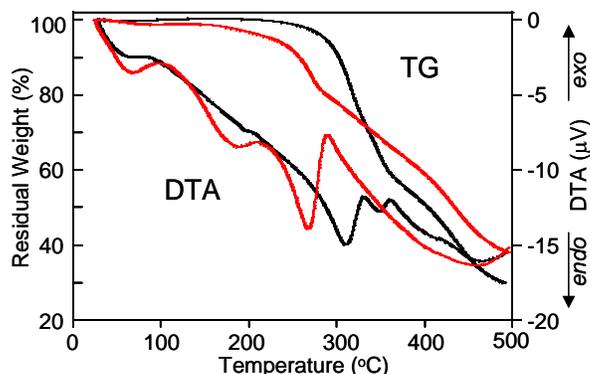


Figure S5. TG and DTA curves of poly(muconic acid)s derived from poly(**EZ-1**) (red) and poly(**ZZ-1**) (black). Analysis done in a nitrogen stream at a heating rate of 10 °C/min.

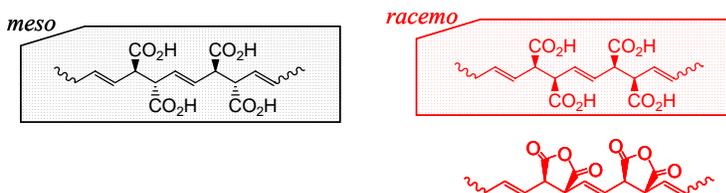


Table S1. ^{13}C NMR chemical shift of stereoregular poly(benzyl muconate)s

Polymer	Tacticity	Chemical shift (ppm)		
		C=O	CH=CH	C-H
Poly(ZZ-2)	<i>racemo</i> -disyndiotactic	170.95	129.31	50.74
Poly(EE-2)	<i>racemo</i> -disyndiotactic	170.94	129.38	50.71
Poly(EE-3MeO)	<i>meso</i> -diisotactic	170.20	129.71	51.74
Poly(ZZ-4BuO)	<i>meso</i> -diisotactic	170.28	129.74	51.27
Poly(EMU)	<i>meso</i> -diisotactic	170.48	129.59	52.04
Poly(EZ-2)	<i>meso</i> -disyndiotactic	170.16	129.85	51.61

Chemical shifts were determined in CDCl_3 at room temperature with tetramethylsilane as the internal standard using a 100-MHz ^{13}C NMR spectrometer. The polymer was isolated as an amorphous solid upon heating in 1,2-dichlorobenzene at 100 °C, and the subsequent reprecipitation with methanol. **ZZ-2**: di(4-methoxybenzyl) (*Z,Z*)-muconate, **EE-2**: di(4-methoxybenzyl) (*E,E*)-muconate, **EE-3MeO**: di(3-methoxybenzyl) (*E,E*)-muconate, **ZZ-4BuO**: di(4-*n*-butoxybenzyl) (*Z,Z*)-muconate, **EMU**: diethyl (*Z,Z*)-muconate, **EZ-2**: di(4-methoxybenzyl) (*E,Z*)-muconate. **EE-3MeO**, **ZZ-4BuO**, and **EMU** provide *meso*-diisotactic polymers by translational molecular stacking in the monomer crystals.