

Chiral-to-Chiral Communication in Polymers: A Unique Approach to Control both Helical Sense and Chirality at the Periphery

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Materials and Methods

CD measurements were done in a Jasco-720. The amount of polymer used for CD measurements was 0.3 mg/mL in THF. The concentration of perchlorate salts used in these studies was 10 mg/mL in THF.

UV spectra were registered in a Jasco V-630. The amount of polymers used for CD measurements were 0.3 mg/mL in CHCl₃. The concentration of perchlorate salts used in these studies was 10 mg/mL in THF.

G_{abs} was calculated using the following equation $G_{\text{abs}} = \text{CD}/(\text{UV} \times 3300)$, where CD is the value of circular dichroism at a given wavelength and UV is the absorption at a given wavelength.

Raman spectra were carried out in a Renishaw confocal Raman spectrometer (Invia Reflex model), equipped with two laser (diode laser 785 nm and Ar laser 514 nm).

DSC traces were obtained in a DSC Q200 Tzero Technology (TA Instruments, New Castle, UK), equipped with a refrigerated cooling system RCS90 (TA Instruments, New Castle, UK), using a Tzero low-mass aluminium pan.

TGA traces were obtained in a TGA Q5000 (TA Instruments, New Castle, UK) using a platinum pan.

GPC studies were carried out in a Waters Alliance equipped with Phenomenex GPC columns. The amount of polymer used for GPC measurements was 0.3 mg/mL.

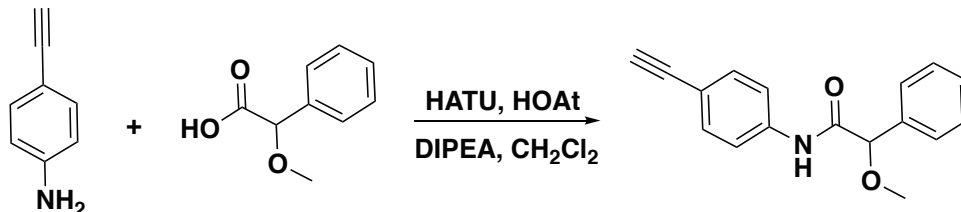
AFM measurements were performed in a MultiMode V Scanning Probe Microscope (Veeco Instruments) in air at rt with standard silicon cantilevers and super-sharp cantilevers in tapping mode using 12 μm and 1 μm scanners. Nanoscope processing software and WSxM 4.0 Beta 1.0 [4] (Nanotec Electronica, S.L.) were used for image analysis.

SEM measurements were performed on a LEO-435VP electron microscope equipped with an energy dispersive X-ray (EDX) spectrometer. A drop of a solution of different helical-polymer metal complexes (0.1 mg/mL in THF) was settled on a silicon wafer chip (Ted Pella, Inc.), and allowed to dry at rt for 12 h.

Synthesis of monomers

Monomers (*R*)-1, (*S*)-1, (*R*)-2, (*S*)-2 were prepared according Ref. S1.

Synthesis of monomers (*S*)-1 and (*R*)-1



(2-(7-Aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate) (HATU, 1.950 g, 1.2 equiv), 1-hydroxy-7-azabenzotriazole (HOAt, 700 mg, 1.2 equiv), (*R*)- or (*S*)-α-methoxy-α-phenylacetic acid (850 mg, 1.2 equiv) and diisopropyltriethylamine (DIEA, 895 μ L, 1.2 equiv) were dissolved in 45 mL of CH₂Cl₂, and the mixture was stirred for 10 min to activate the acid. Then, 4-ethynylaniline (500 mg, 1.0 equiv) was added and the reaction mixture was stirred for 1 day. Then, the organic solution was washed with HCl 1M, saturated solution of Na(HCO₃) and saturated solution of NaCl. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated at reduced pressure. The crude product was chromatographed on silica gel (70-230 mesh) with hexane/ethyl acetate (7/3) as eluent [934 mg (*S*)-1 and 900 mg (*R*)-1], (83% and 80% yield respectively of pure products).

Spectroscopic Data:

(*S*)-*N*-(4-ethynylphenyl)-2-methoxy-2-phenylacetamide (1):

$[\alpha]_D^{24} = +15$ ($c = 1.0$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.39 (s, 1H), 3.40 (s, 3H), 4.75 (s, 1H), 7.34-7.46 (m, 7H), 7.65-7.67 (m, 2H), 9.01 (broad s, 1H).

¹³C NMR (70 MHz, CDCl₃) δ (ppm): 57.7, 78.3, 83.9, 84.6, 128.1, 129.3, 129.4, 133.4, 138.3, 139.5, 170.1.

HRMS (ESI) m/z calcd for C₁₈H₁₆NO₃ [M + H]: 265.3065, found: 265.3043.

(*R*)-*N*-(4-ethynylphenyl)-2-methoxy-2-phenylacetamide (2):

$[\alpha]_D^{24} = -15$ ($c = 1.1$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.39 (s, 1H), 3.40 (s, 3H), 4.75 (s, 1H), 7.34-7.46 (m, 7H), 7.65-7.67 (m, 2H), 9.01 (broad s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ (ppm): 57.7, 78.3, 83.9, 84.6, 128.1, 129.3, 129.4, 133.4, 138.3, 139.5, 170.1.

HRM¹S (ESI) m/z calcd for C₁₈H₁₆NO₃ [M + H]: 265.3065, found: 265.2948.

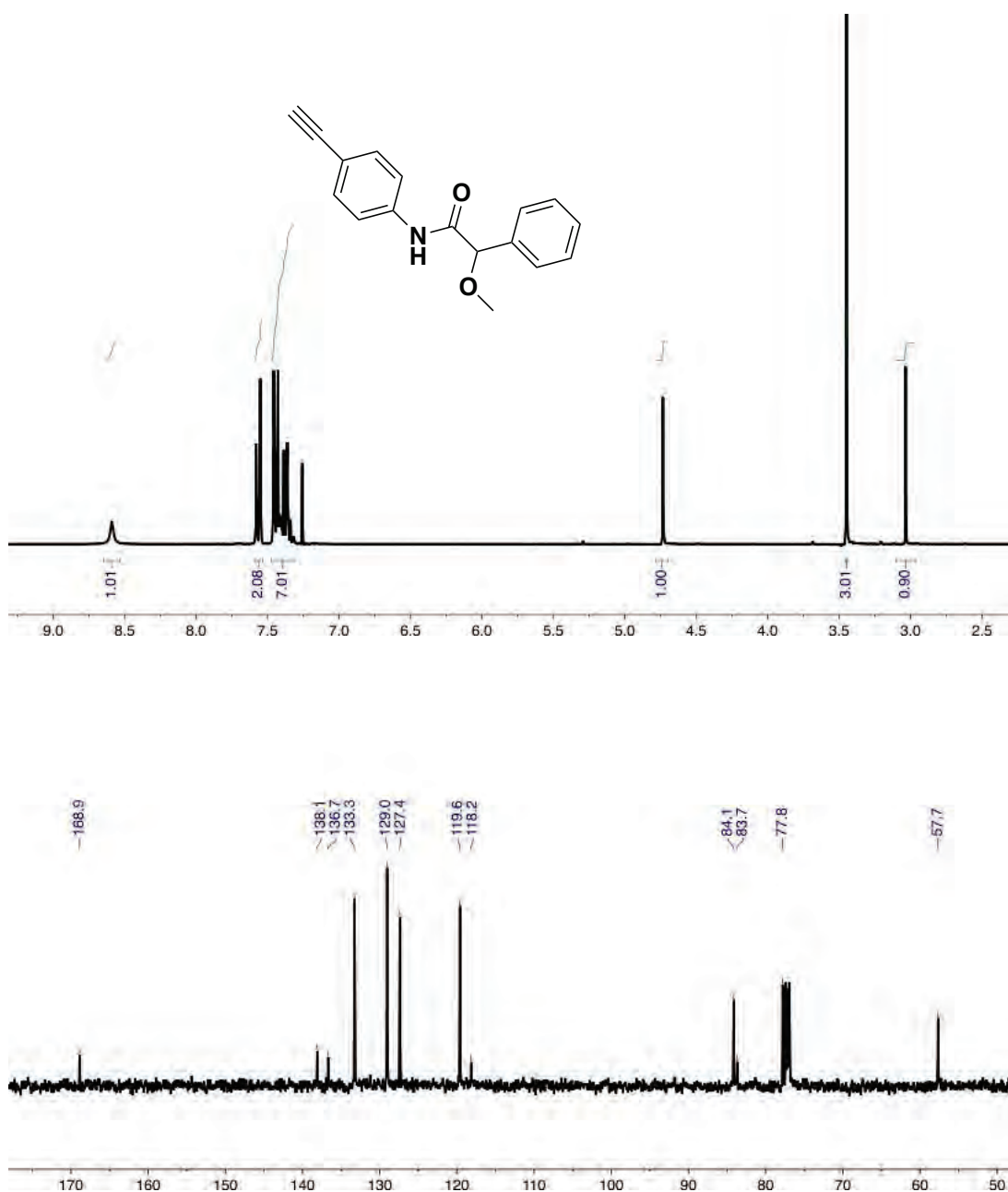
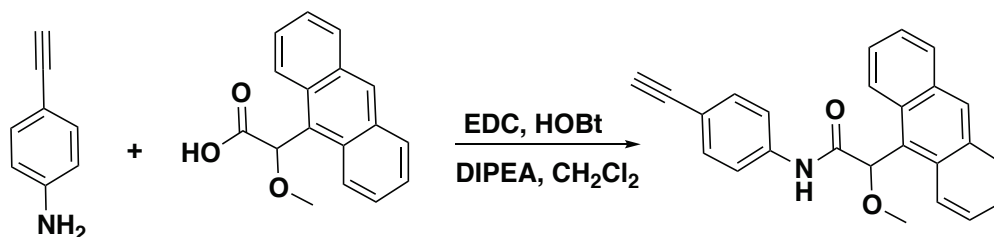


Figure S1: ¹H and ¹³C spectra of monomers (*S*)-1 and (*R*)-1 (CDCl₃, 300 MHz)

Synthesis of monomers (*S*)-2 y (*R*)-2



(1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide) (EDC, 140 g, 1.2 equiv), 1-hydroxy-7-azabenzotriazole (HOBT, 122 mg, 1.2 equiv), (*R*)- or (*S*)- α -methoxy-9-anthrylacetic acid (200 mg, 1.2 equiv) and diisopropyltriethylamine (DIEA, 157 μ L, 1.2 equiv) were dissolved in 45 mL of CH₂Cl₂, and the mixture was stirred for 15 min to activate the acid. Then, 4-ethynylaniline (106 mg, 1.0 equiv) was added and the reaction mixture was stirred for 1 day. Then, the organic solution was washed with HCl 1M, saturated solution of Na(HCO₃) and saturated solution of NaCl. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and the solvent was evaporated at reduced pressure. The crude product was precipitated in hexane and then it was chromatographed on silica gel (70-230 mesh) with CH₂Cl₂ as eluent [210 mg (*S*)-1 and 192 mg (*R*)-1], (76% and 70% yield respectively of pure products).

Spectroscopic Data:

(*S*)-2-(anthracen-9-yl)-*N*-(4-ethynylphenyl)-2-methoxy-2-ethanamide (3):

$[\alpha]_D^{23} = +151.65$ ($c = 2.0$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.04 (s, 1H), 3.33 (s, 3H), 6.36 (s, 1H), 7.55-7.42 (m, 6H), 7.67-7.61 (m, 2H), 8.05 (dd, 2H), 8.40 (dd, 2H), 8.53 (s, 1H), 9.06 (broad s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ (ppm): 57, 78.01, 83.4, 119.3, 123.7, 124.9, 128.7, 129, 131.5, 133, 138, 169.

HRMS (ESI) m/z calcd for C₂₅H₁₉NNaO₂ [$M + Na^+$]: 388.1308, found: 388.1316

(*R*)-2-(anthracen-9-yl)-*N*-(4-ethynylphenyl)-2-methoxy-2-ethanamide (4):

$[\alpha]_D^{23} = -152.35$ ($c = 2.0$, CHCl₃).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.04 (s, 1H), 3.33 (s, 3H), 6.36 (s, 1H), 7.55-7.42 (m, 6H), 7.67-7.61 (m, 2H), 8.05 (dd, 2H), 8.40 (dd, 2H), 8.53 (s, 1H), 9.06 (broad s, 1H).

¹³C NMR (75 MHz, CDCl₃) δ (ppm): 57.1, 83.4, 119.3, 123.7, 124.9, 126.7, 129.4, 131.5, 133.0, 137.9, 169.1.

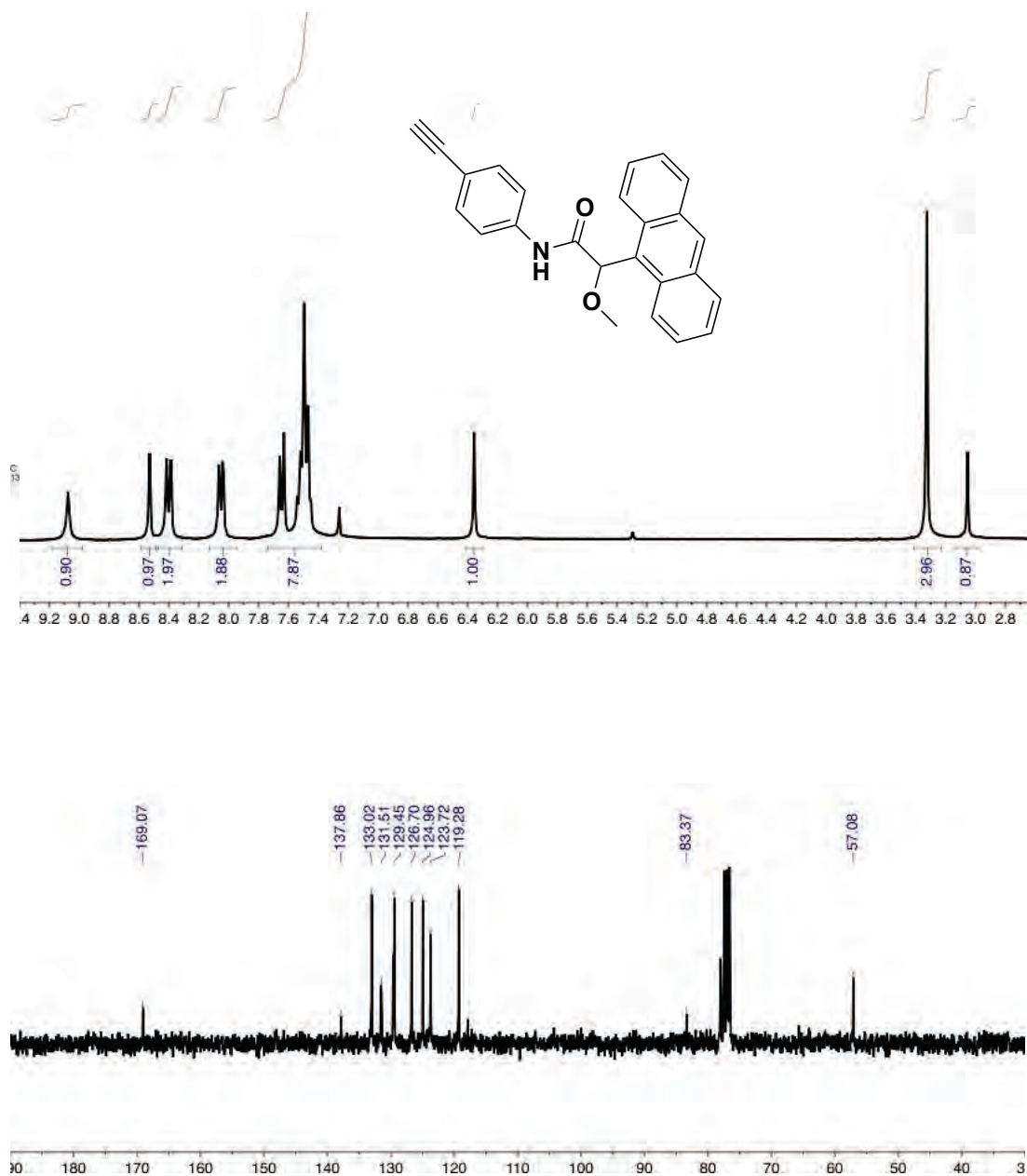


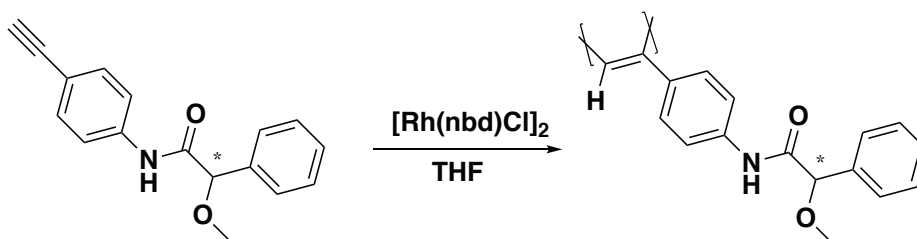
Figure S2: ¹H spectra of monomers (*S*)-2 and (*R*)-2 (CDCl₃, 300 MHz)

Synthesis of homopolymers

General procedure for polymerization:

The reaction flask (sealed ampoule) was dried under vacuum and argon flushed for three times before the corresponding monomer (100 mg) was added as a solid. Then, the flask was evacuated on a vacuum line and flushed with dry argon (three times). Dry THF was added with a syringe and then triethylamine dropwise. A solution of rhodium norbornadiene chloride dimer, $[\text{Rh}(\text{nbd})\text{Cl}]_2$, in THF was added at 30° C. The reaction mixture was stirred at 30°C for 6 h. Then, the resulting polymer was diluted in CH_2Cl_2 and precipitated in a large amount of methanol, centrifuged (2 times) and reprecipitated in hexane and centrifuged again (see Ref. S3).

Synthesis of polymers poly-(*S*)-1 and poly-(*R*)-1



Following the general procedure, M-(*S*)-1 and M-(*R*)-1 (100 mg, 0.377 mmol), Et_3N (5 μL , 3.77×10^{-2} mmol) and $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (0.87 mg, 1.89×10^{-3} mmol) in THF (750 μL) yielded, after centrifugation, 90 mg (90%) of poly-1.

^1H NMR (300 MHz, CDCl_3 , 298 K) δ (ppm): 3.20 (s, 3H), 4.64 (s, 1H), 5.71 (s, 1H), 6.55 (s, 1H), 7.04 (s, 1H), 7.1-7.5 (m, 7H), 8.41 (s, 1H).

SEC: $M_n = 39607$, $M_w = 61195$, $M_z = 89611$, PDI = 1.55.

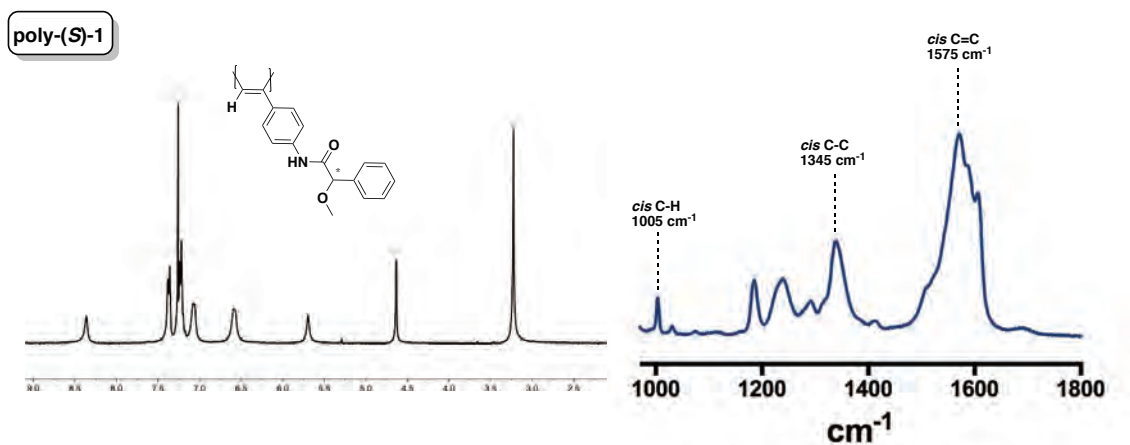
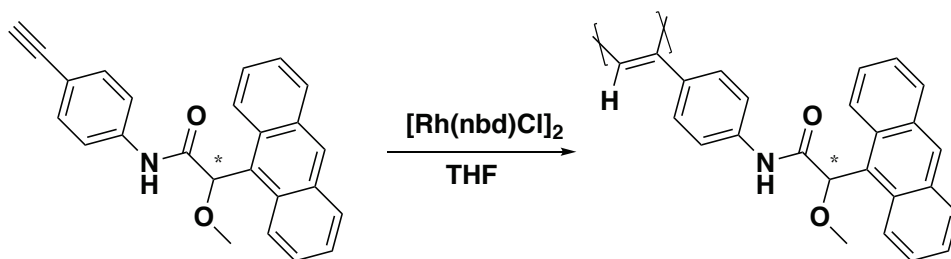


Figure S3: ^1H and Raman spectra of poly-(*S*)-1 (CDCl_3 , 300 MHz)

Synthesis of polymers poly-(*S*)-2 and poly-(*R*)-2



Following the general procedure, reaction of M-(*S*)-2 and M-(*R*)-2 (40 mg, 0.109 mmol), Et_3N (1.5 μL , 1.1×10^{-2} mmol) and $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (1.02 mg, 2.18×10^{-3} mmol) in THF (400 μL) yielded, after centrifugation, 38.5 mg (95%) of poly-(*S*)-2 and poly-(*R*)-2 36 mg (90%).

^1H NMR (300 MHz, CDCl_3 , 323 K) δ (ppm): 2.51 (s broad, 3H), 5.7-6.3 (d broad, 2H), 6.8-8.8 (m, 14H),

SEC: $M_n = 29367$, $M_w = 48802$, $M_z = 67385$, PDI = 1.66.

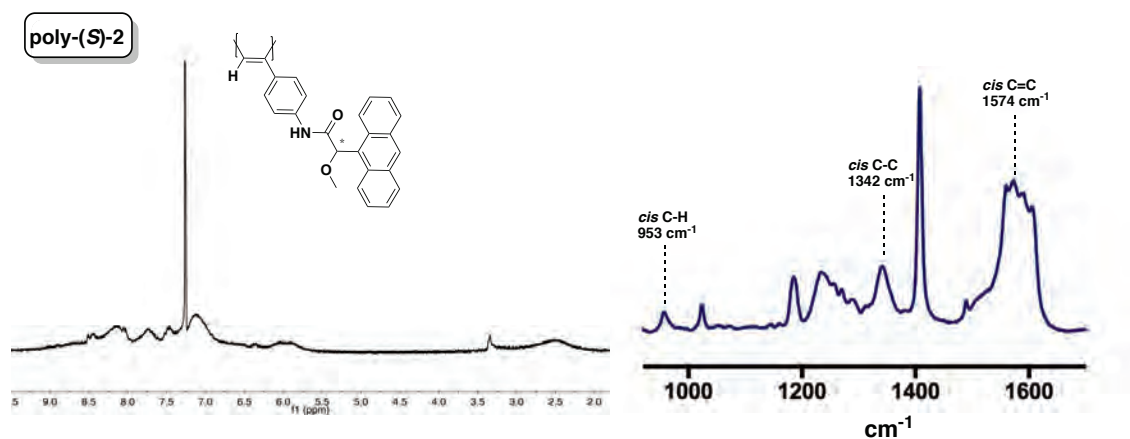
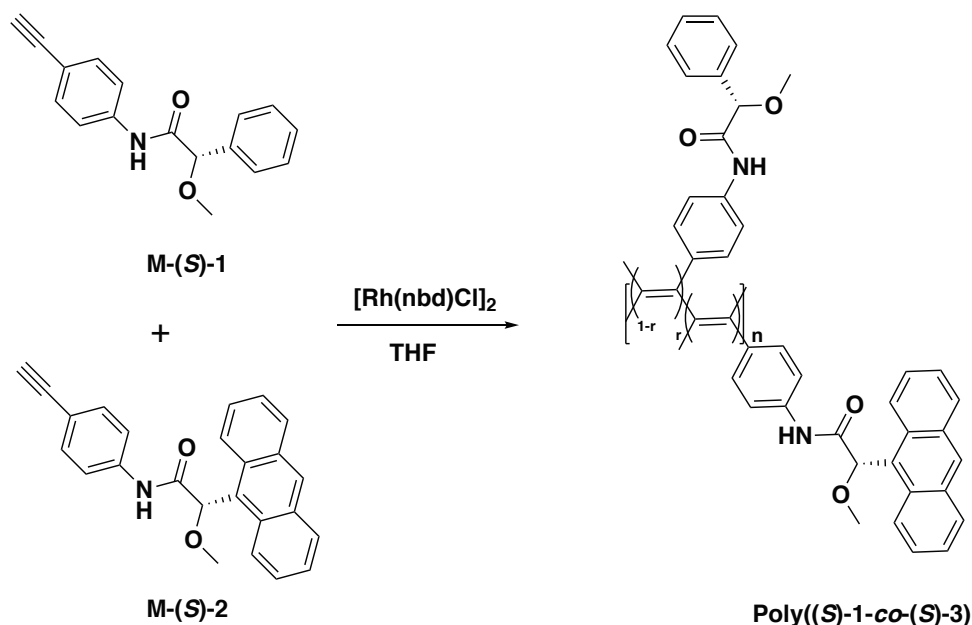


Figure S4: ^1H and Raman spectra of poly-(*S*)-2 (CDCl_3 , 300 MHz)

Synthesis of copolymers poly-(*S*)1-*co*-(*S*)-2) and poly-(*rac*)-1-*co*-(*S*)-2

Synthesis of copolymer poly-(*S*)1-*co*-(*S*)-2)



Following the general procedure, poly-(*S*)1-*co*-(*S*)-2 series was synthesized according to the amounts of different reagents (M-(*S*)-1, M-(*S*)-2, Et₃N, [Rh(nbd)Cl]₂ and THF) reported in Table S1.

Copolymer	M-(<i>S</i>)-1 (mg)	M-(<i>S</i>)-1 (mmol)	M-(<i>S</i>)-2 (mg)	M-(<i>S</i>)-2 (mmol)	Et ₃ N (μL)	[Rh(nbd)Cl] ₂ (mg)	THF (mL)	Yield (%)
poly((<i>S</i>)-1 _{0.9} - <i>co</i> -(<i>S</i>)-2 _{0.1})	26.9	0.1017	4.1	0.0113	1.57	1.0	0.25	93
poly((<i>S</i>)-1 _{0.8} - <i>co</i> -(<i>S</i>)-2 _{0.2})	24.0	0.0904	8.3	0.0226	1.57	1.0	0.25	95
poly((<i>S</i>)-1 _{0.7} - <i>co</i> -(<i>S</i>)-2 _{0.3})	21.0	0.0791	12.4	0.0339	1.57	1.0	0.25	95
poly((<i>S</i>)-1 _{0.67} - <i>co</i> -(<i>S</i>)-2 _{0.33})	20.1	0.0757	13.6	0.0373	1.57	1.0	0.25	92
poly((<i>S</i>)-1 _{0.65} - <i>co</i> -(<i>S</i>)-2 _{0.35})	19.5	0.0734	14.4	0.0395	1.57	1.0	0.25	93
poly((<i>S</i>)-1 _{0.63} - <i>co</i> -(<i>S</i>)-2 _{0.37})	18.9	0.0712	15.3	0.0418	1.57	1.0	0.25	95
poly((<i>S</i>)-1 _{0.6} - <i>co</i> -(<i>S</i>)-2 _{0.4})	18.0	0.0678	16.5	0.0452	1.57	1.0	0.25	96
poly((<i>S</i>)-1 _{0.5} - <i>co</i> -(<i>S</i>)-2 _{0.5})	15.0	0.0565	20.6	0.0565	1.57	1.0	0.25	93
poly((<i>S</i>)-1 _{0.4} - <i>co</i> -(<i>S</i>)-2 _{0.6})	12.0	0.0452	24.8	0.0678	1.57	1.0	0.25	92
poly((<i>S</i>)-1 _{0.3} - <i>co</i> -(<i>S</i>)-2 _{0.7})	9.0	0.0339	28.9	0.0791	1.57	1.0	0.40	95
poly((<i>S</i>)-1 _{0.2} - <i>co</i> -(<i>S</i>)-2 _{0.8})	6.0	0.0904	33.0	0.0226	1.57	1.0	0.40	97
poly((<i>S</i>)-1 _{0.1} - <i>co</i> -(<i>S</i>)-2 _{0.9})	3.0	0.0113	37.1	0.1017	1.57	1.0	0.40	95

Table S1. Quantities of **M-(S)-1**, **M-(S)-2**, base, catalyst and solvent.

Copolymer	M _n	M _w	M _z	PDI
poly((S)- 1 _{0.9} -co-(S)- 2 _{0.1})	8558	10300	12347	1.20
poly((S)- 1 _{0.8} -co-(S)- 2 _{0.2})	11797	29493	39027	2.50
poly((S)- 1 _{0.7} -co-(S)- 2 _{0.3})	10098	22810	29967	2.26
poly((S)- 1 _{0.67} -co-(S)- 2 _{0.33})	11792	20180	31292	2.32
poly((S)- 1 _{0.65} -co-(S)- 2 _{0.35})	16093	23802	34272	1.56
poly((S)- 1 _{0.63} -co-(S)- 2 _{0.37})	16872	22578	32689	1.87
poly((S)- 1 _{0.6} -co-(S)- 2 _{0.4})	17442	28221	35464	1.61
poly((S)- 1 _{0.5} -co-(S)- 2 _{0.5})	16855	25336	35464	1.50
poly((S)- 1 _{0.4} -co-(S)- 2 _{0.6})	19121	27963	34596	1.46
poly((S)- 1 _{0.3} -co-(S)- 2 _{0.7})	23272	37109	48007	1.59
poly((S)- 1 _{0.2} -co-(S)- 2 _{0.8})	29367	48802	67385	1.66
poly((S)- 1 _{0.1} -co-(S)- 2 _{0.9})	26319	42955	57696	1.62

Table S2. Poly((S)-**1**-co-(S)-**2**) SEC data.

This *cis*-stereoregularity was determined by ^1H NMR (vinyl proton resonance at 5.7-6.2 ppm) (Figure S5) and Raman Resonances (785 nm). The peak at 1576 cm^{-1} is assigned to C=C bond stretching in the *cis* polyacetylene overlapped with that of the phenyl ring. The peak at 1342 cm^{-1} is assigned to the *cis* C-C bond coupled with the single bond connecting the main chain and the phenyl ring. The peak at 1003 cm^{-1} is assigned to the C-H bond deformation of the *cis* form (see Figures S7)

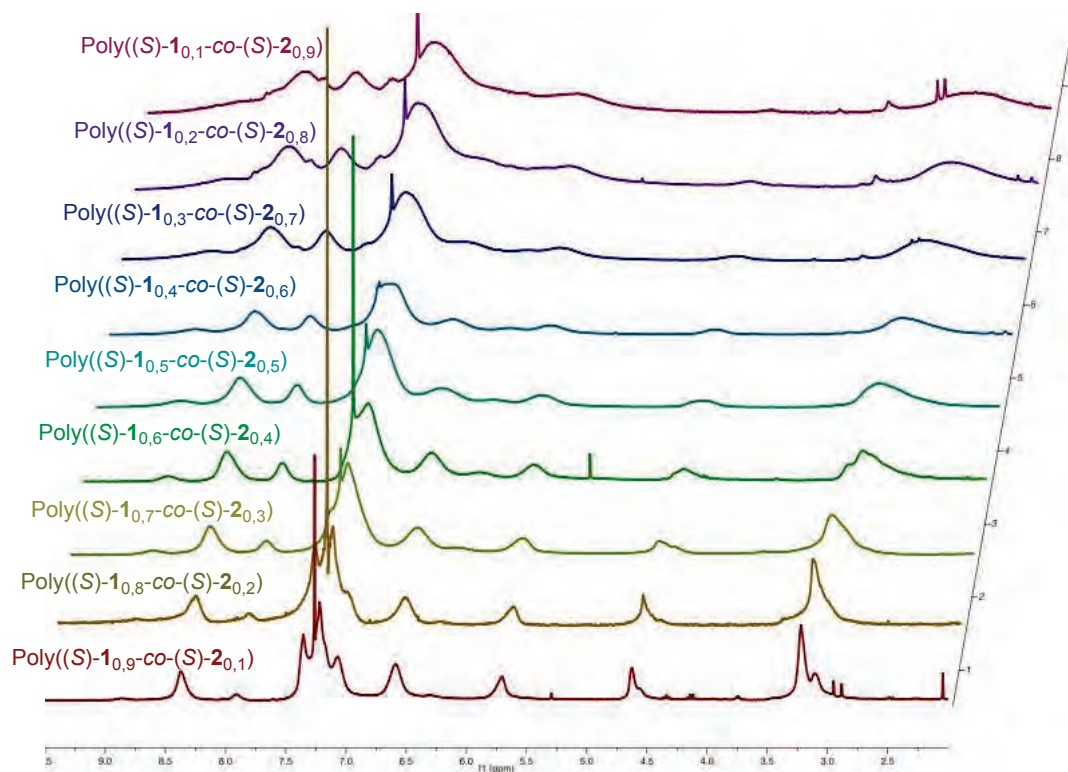


Figure S5. ^1H -NMR spectra of Poly((*S*)-1-*co*-(*S*)-2) series (CDCl_3 , 300 MHz).

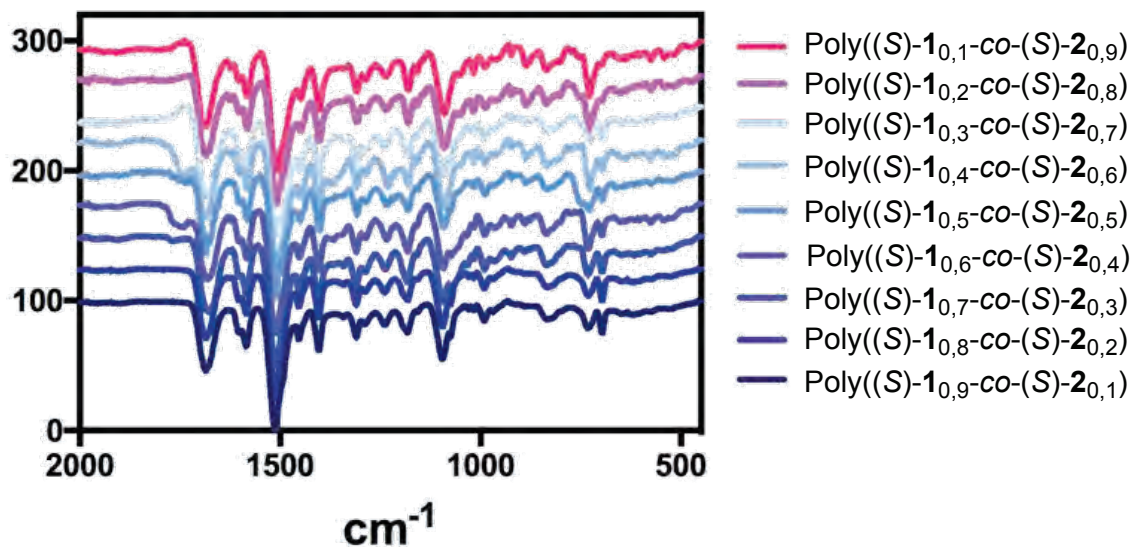


Figure S6. IR spectra of Poly((S)-1-co-(S)-2) series.

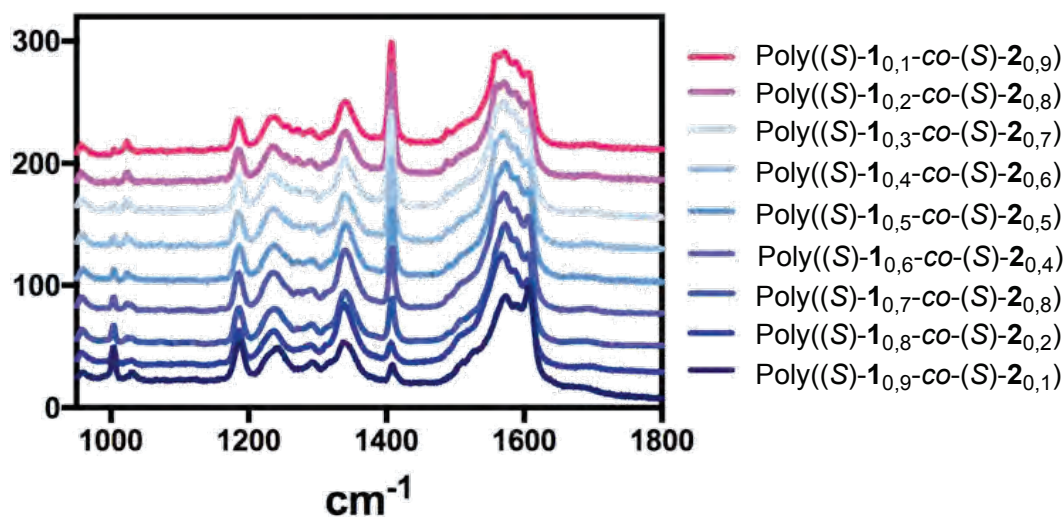
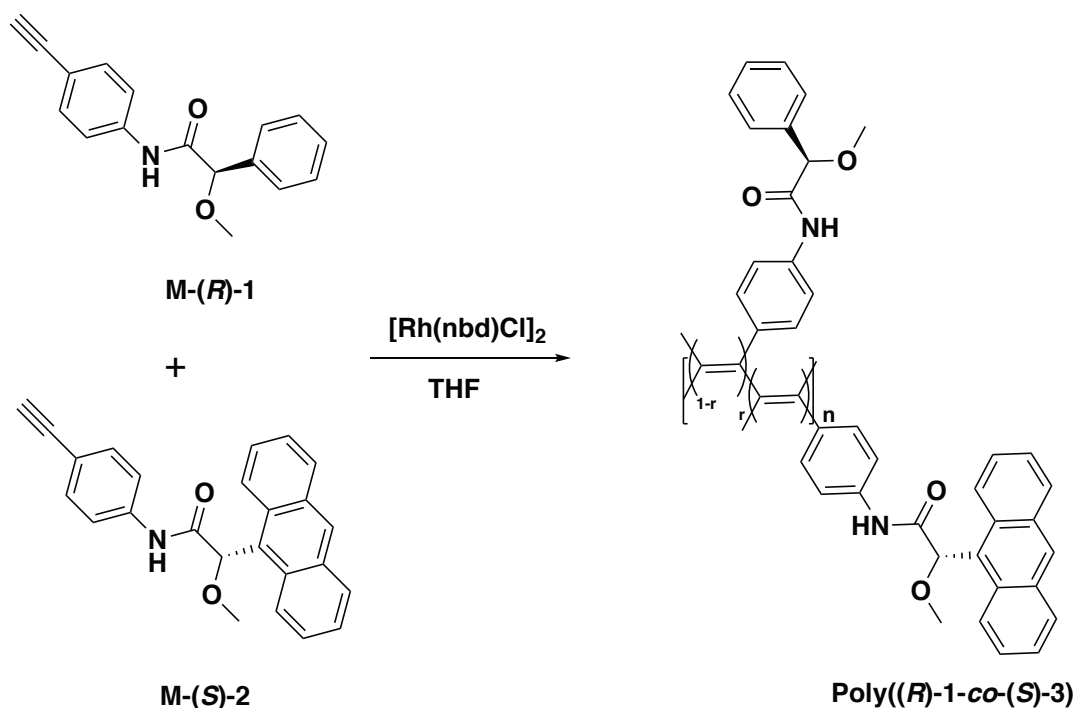


Figure S7. RAMAN spectra of Poly((S)-1-co-(S)-2) series.

copolymer	G_{abs} 20°C
Poly-(S)-2	0.004848
Poly((S)-1 _{0.9} -co-(S)-2 _{0.1})	0.001050
Poly((S)-1 _{0.8} -co-(S)-2 _{0.2})	0.002737
Poly((S)-1 _{0.7} -co-(S)-2 _{0.3})	0.004349
Poly((S)-1 _{0.67} -co-(S)-2 _{0.33})	0.004812
Poly((S)-1 _{0.65} -co-(S)-2 _{0.35})	0.004943
Poly((S)-1 _{0.63} -co-(S)-2 _{0.37})	0.005099
Poly((S)-1 _{0.6} -co-(S)-2 _{0.4})	0.005153
Poly((S)-1 _{0.5} -co-(S)-2 _{0.5})	0.005237
Poly((S)-1 _{0.4} -co-(S)-2 _{0.6})	0.005364
Poly((S)-1 _{0.3} -co-(S)-2 _{0.7})	0.005203
Poly((S)-1 _{0.2} -co-(S)-2 _{0.8})	0.005095
Poly((S)-1 _{0.1} -co-(S)-2 _{0.9})	0.005002
Poly(-S)-1	0.000000

Table **S3**. G_{abs} of Poly((S)-1_r-co-(S)-2_{1-r}) at 20°C.

Synthesis of copolymers Poly-*(R)*-1-*co*-(*S*)-2



Following the general procedure, poly-*(R)*-1-*co*-(*S*)-2 series was synthesized according to the amounts of different reagents (M-*(R)*-1, M-*(S)*-2, Et₃N, [Rh(nbd)Cl]₂ and THF) reported in Table S4.

Copolymer	M- <i>(R)</i> -1 (mg)	M- <i>(R)</i> -1 (mmol)	M- <i>(S)</i> -2 (mg)	M- <i>(S)</i> -2 (mmol)	Et ₃ N (μL)	[Rh(nbd)Cl] ₂ (mg)	THF (mL)	Yield (%)
poly((<i>R</i>)-1 _{0.9} - <i>co</i> -(<i>S</i>)-2 _{0.1})	26.9	0.1017	4.1	0.0113	1.57	1.0	0.25	95
poly((<i>R</i>)-1 _{0.8} - <i>co</i> -(<i>S</i>)-2 _{0.2})	24.0	0.0904	8.3	0.0226	1.57	1.0	0.25	92
poly((<i>R</i>)-1 _{0.7} - <i>co</i> -(<i>S</i>)-2 _{0.3})	21.0	0.0791	12.4	0.0339	1.57	1.0	0.25	90
poly((<i>R</i>)-1 _{0.67} - <i>co</i> -(<i>S</i>)-2 _{0.33})	20.1	0.0757	13.6	0.0373	1.57	1.0	0.25	87
poly((<i>R</i>)-1 _{0.65} - <i>co</i> -(<i>S</i>)-2 _{0.35})	19.5	0.0734	14.4	0.0395	1.57	1.0	0.25	94
poly((<i>R</i>)-1 _{0.63} - <i>co</i> -(<i>S</i>)-2 _{0.37})	18.9	0.0712	15.3	0.0418	1.57	1.0	0.25	80
poly((<i>R</i>)-1 _{0.6} - <i>co</i> -(<i>S</i>)-2 _{0.4})	18.0	0.0678	16.5	0.0452	1.57	1.0	0.25	95
poly((<i>R</i>)-1 _{0.5} - <i>co</i> -(<i>S</i>)-2 _{0.5})	15.0	0.0565	20.6	0.0565	1.57	1.0	0.25	92
poly((<i>R</i>)-1 _{0.4} - <i>co</i> -(<i>S</i>)-2 _{0.6})	12.0	0.0452	24.8	0.0678	1.57	1.0	0.25	94
poly((<i>R</i>)-1 _{0.3} - <i>co</i> -(<i>S</i>)-2 _{0.7})	9.0	0.0339	28.9	0.0791	1.57	1.0	0.40	89
poly((<i>R</i>)-1 _{0.2} - <i>co</i> -(<i>S</i>)-2 _{0.8})	6.0	0.0904	33.0	0.0226	1.57	1.0	0.40	87
poly((<i>R</i>)-1 _{0.1} - <i>co</i> -(<i>S</i>)-2 _{0.9})	3.0	0.0113	37.1	0.1017	1.57	1.0	0.40	91

Table S4. Quantities of M-*(R)*-1, M-*(S)*-2, base, catalyst and solvent.

Copolymer	M _n	M _w	M _z	PDI
poly((<i>R</i>)-1 _{0.9} -co-(<i>S</i>)-2 _{0.1})	8558	10300	12347	1.20
poly((<i>R</i>)-1 _{0.8} -co-(<i>S</i>)-2 _{0.2})	11797	29493	39027	2.50
poly((<i>R</i>)-1 _{0.7} -co-(<i>S</i>)-2 _{0.3})	10098	22810	29967	2.26
poly((<i>R</i>)-1 _{0.6} -co-(<i>S</i>)-2 _{0.4})	17442	28221	35464	1.61
poly((<i>R</i>)-1 _{0.5} -co-(<i>S</i>)-2 _{0.5})	16855	25336	35464	1.50
poly((<i>R</i>)-1 _{0.4} -co-(<i>S</i>)-2 _{0.6})	19121	27963	34596	1.46
poly((<i>R</i>)-1 _{0.3} -co-(<i>S</i>)-2 _{0.7})	23272	37109	48007	1.59
poly((<i>R</i>)-1 _{0.2} -co-(<i>S</i>)-2 _{0.8})	29367	48802	67385	1.66
poly((<i>R</i>)-1 _{0.1} -co-(<i>S</i>)-2 _{0.9})	26319	42955	57696	1.62

Table S5. poly((*R*)-1-co-(*S*)-2) series SEC data.

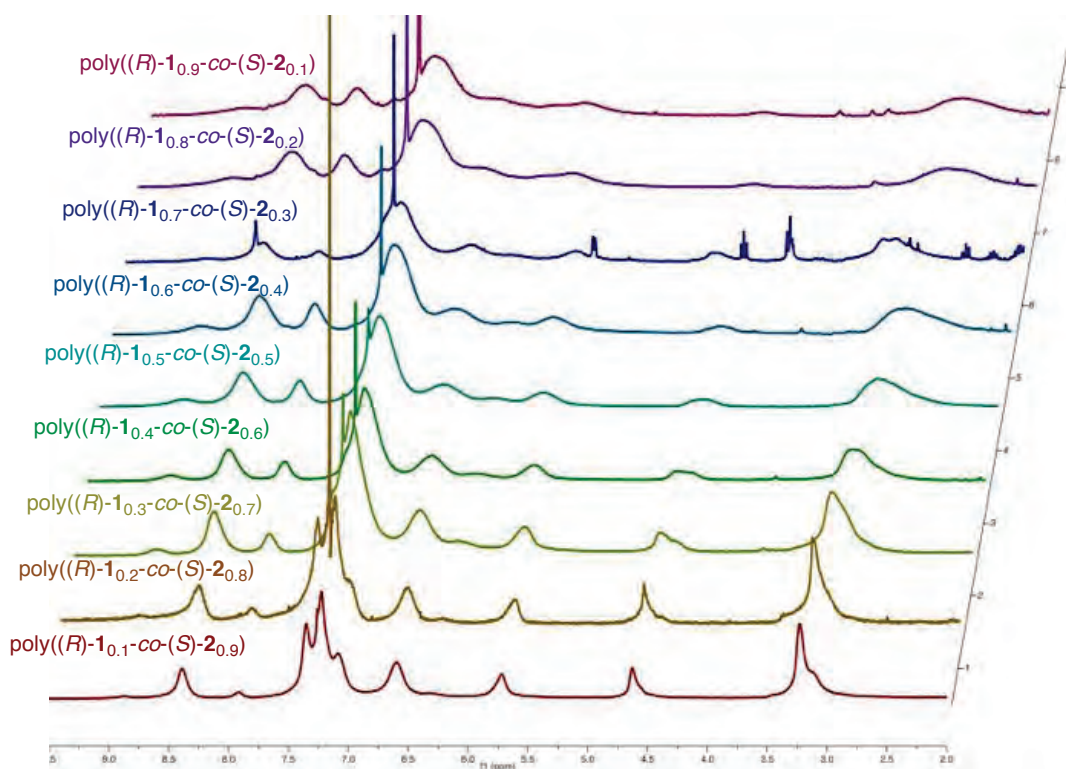


Figure S8. ¹H NMR spectra of poly((*R*)-1-co-(*S*)-2) series (CDCl₃, 300 MHz).

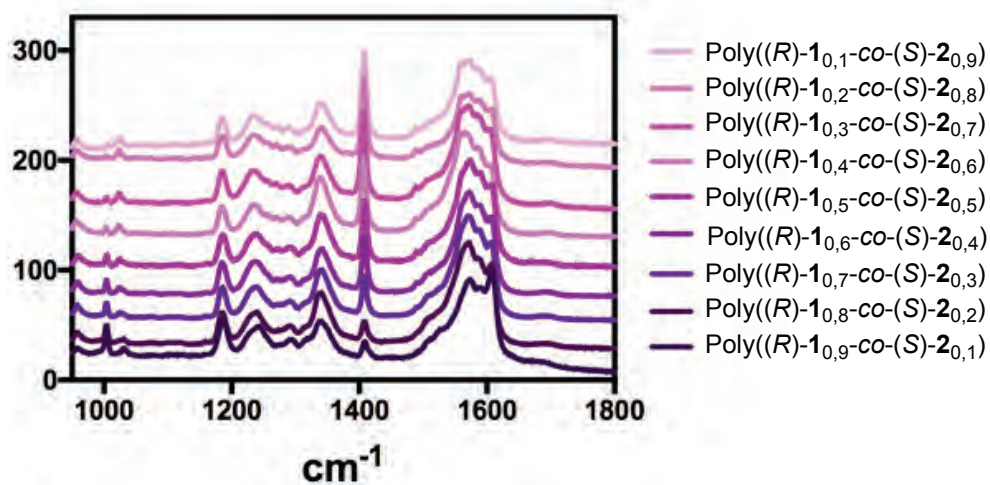


Figure S9. IR spectra of Poly((*R*)-1-*co*-(*S*)-2) series..

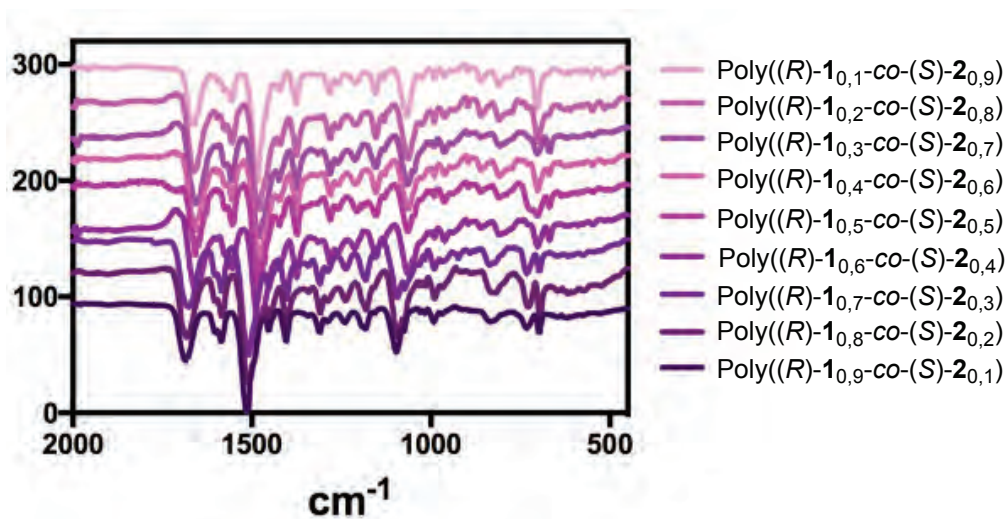
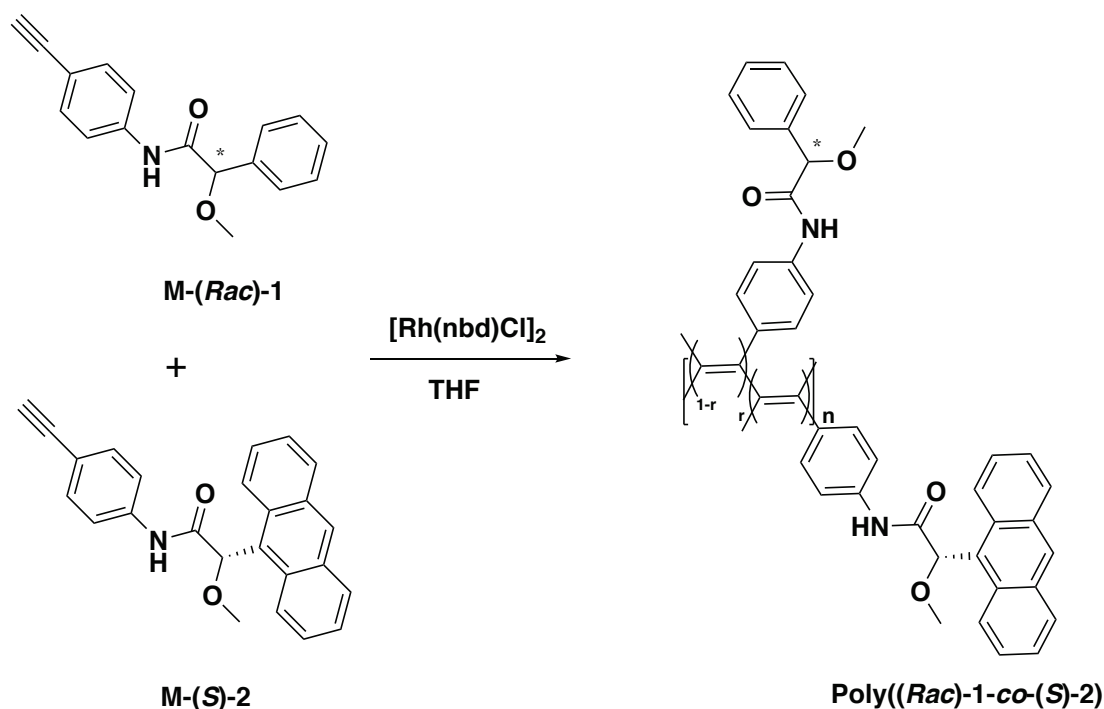


Figure S10. RAMAN spectra of Poly-((*R*)-1-*co*-(*S*)-2) series

copolymer	G_{abs} 20°C
Poly-(<i>S</i>)-2	0.004848
Poly((<i>R</i>)-1 _{0.9} - <i>co</i> -(<i>S</i>)-2 _{0.1})	0.000803
Poly((<i>R</i>)-1 _{0.8} - <i>co</i> -(<i>S</i>)-2 _{0.2})	0.001224
Poly((<i>R</i>)-1 _{0.7} - <i>co</i> -(<i>S</i>)-2 _{0.3})	0.002527
Poly((<i>R</i>)-1 _{0.67} - <i>co</i> -(<i>S</i>)-2 _{0.33})	0.004378
Poly((<i>R</i>)-1 _{0.65} - <i>co</i> -(<i>S</i>)-2 _{0.35})	0.004791
Poly((<i>R</i>)-1 _{0.63} - <i>co</i> -(<i>S</i>)-2 _{0.37})	0.004998
Poly((<i>R</i>)-1 _{0.6} - <i>co</i> -(<i>S</i>)-2 _{0.4})	0.004947
Poly((<i>R</i>)-1 _{0.5} - <i>co</i> -(<i>S</i>)-2 _{0.5})	0.005134
Poly((<i>R</i>)-1 _{0.4} - <i>co</i> -(<i>S</i>)-2 _{0.6})	0.005310
Poly((<i>R</i>)-1 _{0.3} - <i>co</i> -(<i>S</i>)-2 _{0.7})	0.005403
Poly((<i>R</i>)-1 _{0.2} - <i>co</i> -(<i>S</i>)-2 _{0.8})	0.005598
Poly((<i>R</i>)-1 _{0.1} - <i>co</i> -(<i>S</i>)-2 _{0.9})	0.005213
Poly-(<i>R</i>)-1	0.000000

Table S6. G_{abs} of Poly((*R*)-1_r-*co*-(*S*)-2_{1-r}) at 20°C.

Synthesis of copolymers Poly-((*rac*)-1-*co*-(*S*)-2)



Following the general procedure, poly-((*rac*)-1-*co*-(*S*)-2) series was synthesized according to the amounts of different reagents (M-(*rac*)-1, M-(*S*)-2, Et₃N, [Rh(nbd)Cl]₂ and THF) reported in Table S7.

Copolymer	M-(<i>Rac</i>)-1 (mg)	M-(<i>Rac</i>)-1 (mmol)	M-(<i>S</i>)-2 (mg)	M-(<i>S</i>)-2 (mmol)	Et ₃ N (μL)	[Rh(nbd)Cl] ₂ (mg)	THF (mL)	Yield (%)
poly((<i>rac</i>)-1 _{0.9} - <i>co</i> -(<i>S</i>)-2 _{0.1})	26.9	0.1017	4.1	0.0113	1.57	1.0	0.25	95
poly((<i>rac</i>)-1 _{0.8} - <i>co</i> -(<i>S</i>)-2 _{0.2})	24.0	0.0904	8.3	0.0226	1.57	1.0	0.25	92
poly((<i>rac</i>)-1 _{0.7} - <i>co</i> -(<i>S</i>)-2 _{0.3})	21.0	0.0791	12.4	0.0339	1.57	1.0	0.25	90
poly((<i>rac</i>)-1 _{0.67} - <i>co</i> -(<i>S</i>)-2 _{0.33})	20.1	0.0757	13.6	0.0373	1.57	1.0	0.25	90
poly((<i>rac</i>)-1 _{0.65} - <i>co</i> -(<i>S</i>)-2 _{0.35})	19.5	0.0734	14.4	0.0395	1.57	1.0	0.25	96
poly((<i>rac</i>)-1 _{0.63} - <i>co</i> -(<i>S</i>)-2 _{0.37})	18.9	0.0712	15.3	0.0418	1.57	1.0	0.25	97
poly((<i>rac</i>)-1 _{0.6} - <i>co</i> -(<i>S</i>)-2 _{0.4})	18.0	0.0678	16.5	0.0452	1.57	1.0	0.25	95
poly((<i>rac</i>)-1 _{0.5} - <i>co</i> -(<i>S</i>)-2 _{0.5})	15.0	0.0565	20.6	0.0565	1.57	1.0	0.25	92
poly((<i>rac</i>)-1 _{0.4} - <i>co</i> -(<i>S</i>)-2 _{0.6})	12.0	0.0452	24.8	0.0678	1.57	1.0	0.25	94
poly((<i>rac</i>)-1 _{0.3} - <i>co</i> -(<i>S</i>)-2 _{0.7})	9.0	0.0339	28.9	0.0791	1.57	1.0	0.40	89
poly((<i>rac</i>)-1 _{0.2} - <i>co</i> -(<i>S</i>)-2 _{0.8})	6.0	0.0904	33.0	0.0226	1.57	1.0	0.40	87
poly((<i>rac</i>)-1 _{0.1} - <i>co</i> -(<i>S</i>)-2 _{0.9})	3.0	0.0113	37.1	0.1017	1.57	1.0	0.40	91

Table S7. Quantities of M-(*rac*)-1, M-(*S*)-2, base, catalyst and solvent.

Copolymer	M _n	M _w	M _z	PDI
poly((<i>rac</i>)- 1 _{0.9} - <i>co</i> -(<i>S</i>)- 2 _{0.1})	8558	10300	12347	1.20
poly((<i>rac</i>)- 1 _{0.8} - <i>co</i> -(<i>S</i>)- 2 _{0.2})	11797	29493	39027	2.50
poly((<i>rac</i>)- 1 _{0.7} - <i>co</i> -(<i>S</i>)- 2 _{0.3})	10098	22810	29967	2.26
poly((<i>rac</i>)- 1 _{0.6} - <i>co</i> -(<i>S</i>)- 2 _{0.4})	17442	28221	35464	1.61
poly((<i>rac</i>)- 1 _{0.5} - <i>co</i> -(<i>S</i>)- 2 _{0.5})	16855	25336	35464	1.50
poly((<i>rac</i>)- 1 _{0.4} - <i>co</i> -(<i>S</i>)- 2 _{0.6})	19121	27963	34596	1.46
poly((<i>rac</i>)- 1 _{0.3} - <i>co</i> -(<i>S</i>)- 2 _{0.7})	23272	37109	48007	1.59
poly((<i>rac</i>)- 1 _{0.2} - <i>co</i> -(<i>S</i>)- 2 _{0.8})	29367	48802	67385	1.66
poly((<i>rac</i>)- 1 _{0.1} - <i>co</i> -(<i>S</i>)- 2 _{0.9})	26319	42955	57696	1.62

Table S8. poly((*rac*)-**1**-*co*-(*S*)-**2**) SEC data.

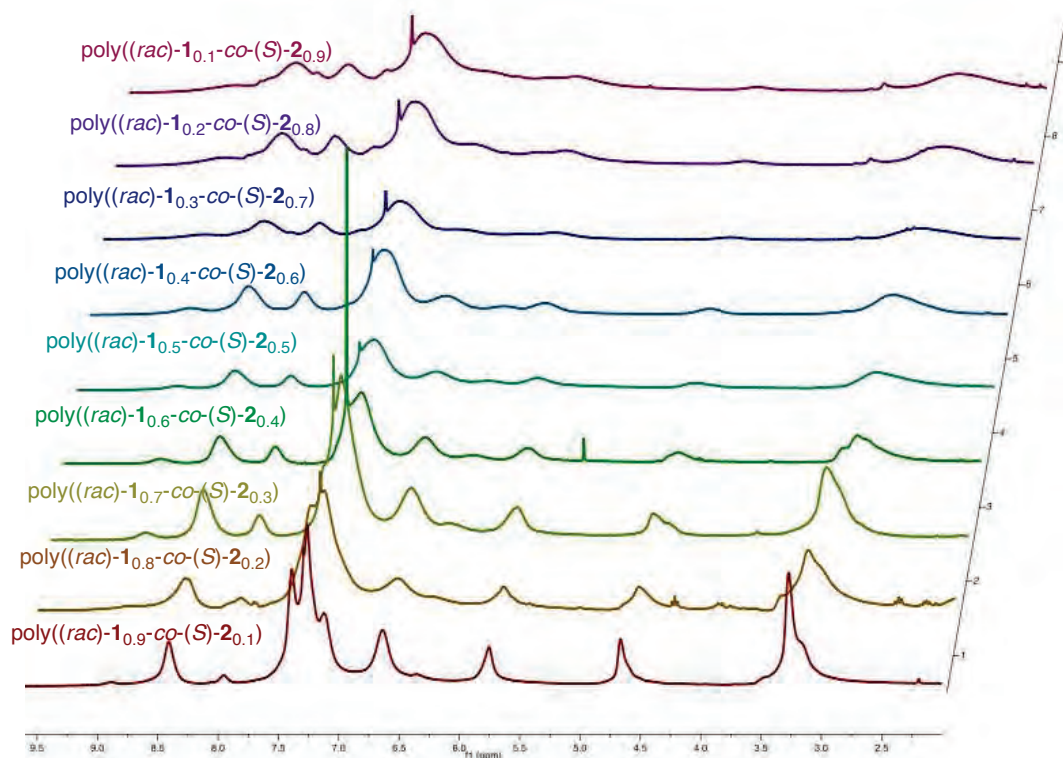


Figure S11. ¹H NMR spectra of poly((*rac*)-**1**-*co*-(*S*)-**2**) series (CDCl₃, 300 MHz).

copolymer	G _{abs} 20°C
Poly-(<i>S</i>)-2	0.00484
Poly((<i>rac</i>)-1 _{0.9} - <i>co</i> -(<i>S</i>)-2 _{0.1})	0.00080
Poly((<i>rac</i>)-1 _{0.8} - <i>co</i> -(<i>S</i>)-2 _{0.2})	0.00122
Poly((<i>rac</i>)-1 _{0.7} - <i>co</i> -(<i>S</i>)-2 _{0.3})	0.00252
Poly((<i>rac</i>)-1 _{0.67} - <i>co</i> -(<i>S</i>)-2 _{0.33})	0.00437
Poly((<i>rac</i>)-1 _{0.65} - <i>co</i> -(<i>S</i>)-2 _{0.35})	0.00479
Poly((<i>rac</i>)-1 _{0.63} - <i>co</i> -(<i>S</i>)-2 _{0.37})	0.00499
Poly((<i>rac</i>)-1 _{0.6} - <i>co</i> -(<i>S</i>)-2 _{0.4})	0.00494
Poly((<i>rac</i>)-1 _{0.5} - <i>co</i> -(<i>S</i>)-2 _{0.5})	0.00513
Poly((<i>rac</i>)-1 _{0.4} - <i>co</i> -(<i>S</i>)-2 _{0.6})	0.00531
Poly((<i>rac</i>)-1 _{0.3} - <i>co</i> -(<i>S</i>)-2 _{0.7})	0.00540
Poly((<i>rac</i>)-1 _{0.2} - <i>co</i> -(<i>S</i>)-2 _{0.8})	0.00559
Poly((<i>rac</i>)-1 _{0.1} - <i>co</i> -(<i>S</i>)-2 _{0.9})	0.00521
Poly-(<i>rac</i>)-1	0.00000

Table S9. G_{abs} of Poly(*rac*)-1_r-*co*-(*S*)-2_{1-r}) at 20°C.

Determination of the monomer reactivity ratios in copolymerizations

To estimate the monomer reactivity ratios in the copolymerizations of Poly((*S*)-1-*co*-(*S*)-2) [(*S*)-1 and (*S*)-2] and in Poly((*R*)-1-*co*-(*S*)-2) [(*R*)-1 and (*S*)-2], the copolymerizations of (*S*)-1 with (*S*)-2 and (*R*)-1 with (*S*)-2 at varying monomer feed ratios were carried out and were terminated at low conversions by adding, in both cases, MeOH (10 mL) 5 seconds after the catalyst addition. The resulting Poly((*S*)-1-*co*-(*S*)-2) and Poly((*R*)-1-*co*-(*S*)-2) were collected by centrifugation and dried in vacuum at room temperature overnight. The copolymer compositions were determined from their ¹H NMR spectra (Figure S12) and the results are summarized in table S7. The copolymer compositions are almost similar to the corresponding monomer feed ratios. For the determination of *r*₁ and *r*₂, and *r*₁ and *r*₃ the Kelen-Tüdös method was used (See Ref. S2). In this method, the following equation is employed:

$$\eta = \left(r_1 + \frac{r_2(r_3)}{\alpha} \right) \xi - \frac{r_2(r_3)}{\alpha}$$

Where η and ξ are expressed as $G/(\alpha + H)$ and $H/(\alpha + H)$, respectively, by using G and H are defined as $G = F(f-1)/f$ y F^2/f , respectively, with F and f representing

the molar ratios of monomers in the feed and the molar ratios in the copolymers. A is a parameter defined as $\alpha = (F_{min}^* F_{max})^{0.5}$, where F_{min} and F_{max} correspond to the lowest and highest values of F , respectively. A plot of η versus ξ affords a straight line (Figure S13), The intercept at $\xi = 0$ y $\xi = 1$ gives $-(S)-1$ (or $(R)-1$) and $(S)-2$, respectively. The estimated monomer reactivity ratios for $(S)-1 - (S)-2$ copolymer are $(S)-1 = 0,987$ and $(S)-2 = 0,9724$ and those for $(R)-1 = 0,9685$ $(S)-2 = 0,9901$. The products of the monomer reactivity ratios for the copolymerizations of $(S)-1$ with $(S)-2$ and $(R)-1$ with $(S)-2$ 0,9597 and 0,9589 respectively, suggesting that the monomer distributions in the copolymers are mostly random.

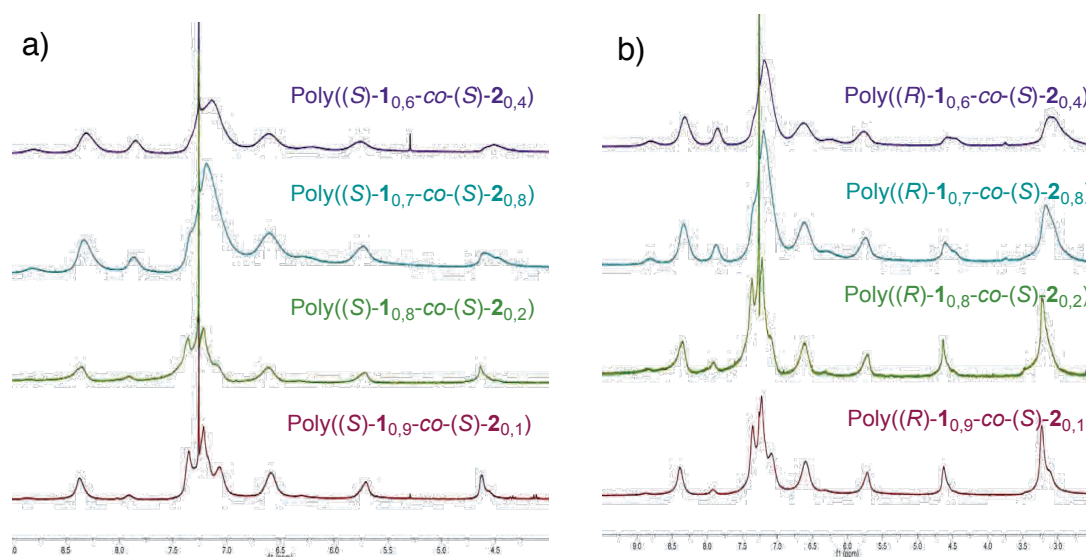


Figure S12. ^1H NMR spectra of copolymerizations at low conversion of Poly((S)- $1_{0.9}$ -co-(S)- $2_{0.1}$), Poly((S)- $1_{0.8}$ -co-(S)- $2_{0.2}$), Poly((S)- $1_{0.7}$ -co-(S)- $2_{0.3}$), and Poly((S)- $1_{0.6}$ -co-(S)- $2_{0.4}$).

Monomer		Polymer	
Run	F	yield(%) ^a	f
Poly((S)- $1_{0.9}$ -co-(S)- $2_{0.1}$)	0.9	43	0.9148
Poly((S)- $1_{0.8}$ -co-(S)- $2_{0.2}$)	0.8	37	0.8014
Poly((S)- $1_{0.7}$ -co-(S)- $2_{0.3}$)	0.7	35	0.7047
Poly((S)- $1_{0.6}$ -co-(S)- $2_{0.4}$)	0.6	51	0.6104
Poly((R)- $1_{0.9}$ -co-(S)- $2_{0.1}$)	0.9	37	0.9148
Poly((R)- $1_{0.8}$ -co-(S)- $2_{0.2}$)	0.8	42	0.8014
Poly((R)- $1_{0.7}$ -co-(S)- $2_{0.3}$)	0.7	38	0.7047
Poly((R)- $1_{0.6}$ -co-(S)- $2_{0.4}$)	0.6	49	0.6104

Table S10. F and f molar fractions and conversions of Poly((S)- 1_r -co-(S)- 2_{1-r}) and Poly((R)- 1_r -co-(S)- 2_{1-r})

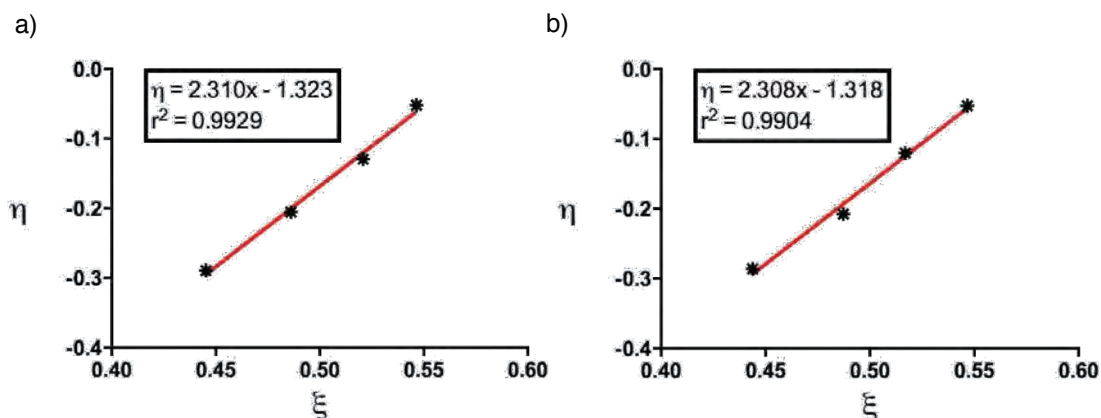


Figure S13. Kelen-Tüdös plots for the copolymerization of Poly((*S*)-1_{*r*}-co-(*S*)-2_{1-*r*}) and Poly((*R*)-1_{*r*}-co-(*S*)-2₁)

Thermal Studies

In order to determinate the geometry of the helical polyene backbone DSC studies of a pristine copolymer sample were performed. In order to study the thermal stability of the copolymer series TGA studies were carried out. For detailed information of DSC and TGA experimental procedures and thermal studies of the parent polymers [poly-(*S*)-1, poly(*R*)-1], (see Ref. S4)

DSC Studies

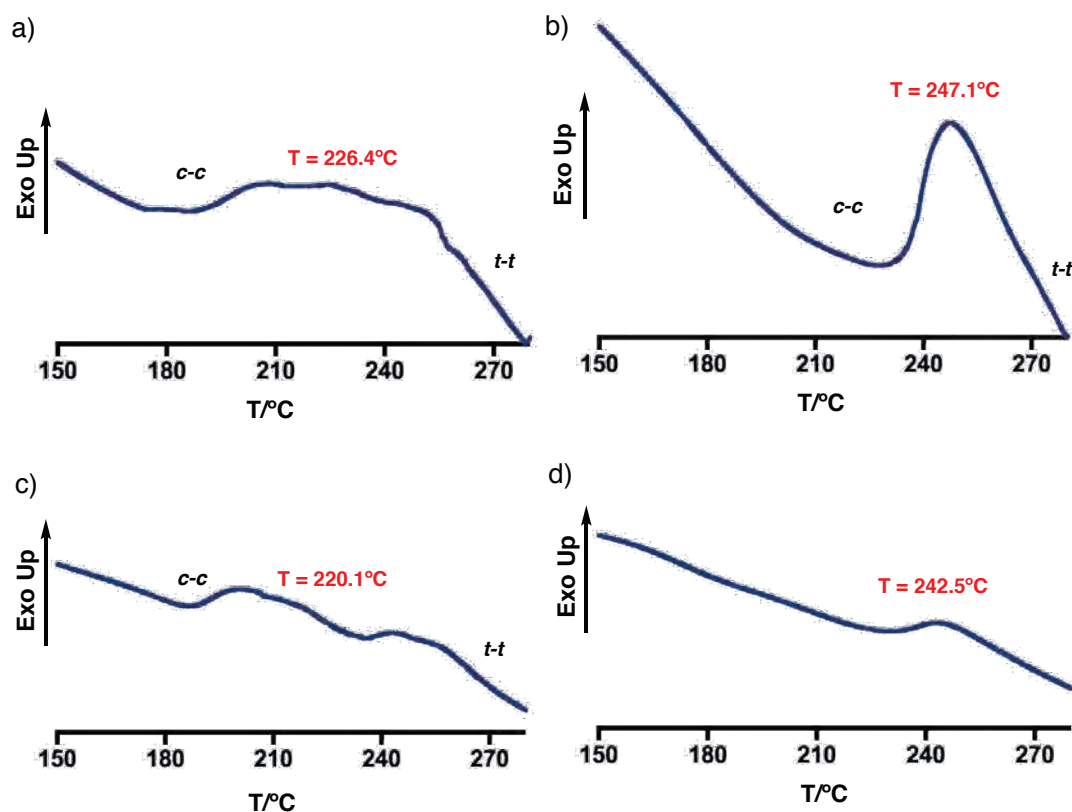


Figure S14. DSC of a) Poly[(*S*)-1_{0.80}-co-(*S*)-2_{0.20}], b) Poly[(*S*)-1_{0.20}-co-(*S*)-2_{0.80}], c) Poly[(*R*)-1_{0.80}-co-(*S*)-2_{0.20}] and Poly[(*R*)-1_{0.20}-co-(*S*)-2_{0.80}]

TGA Studies

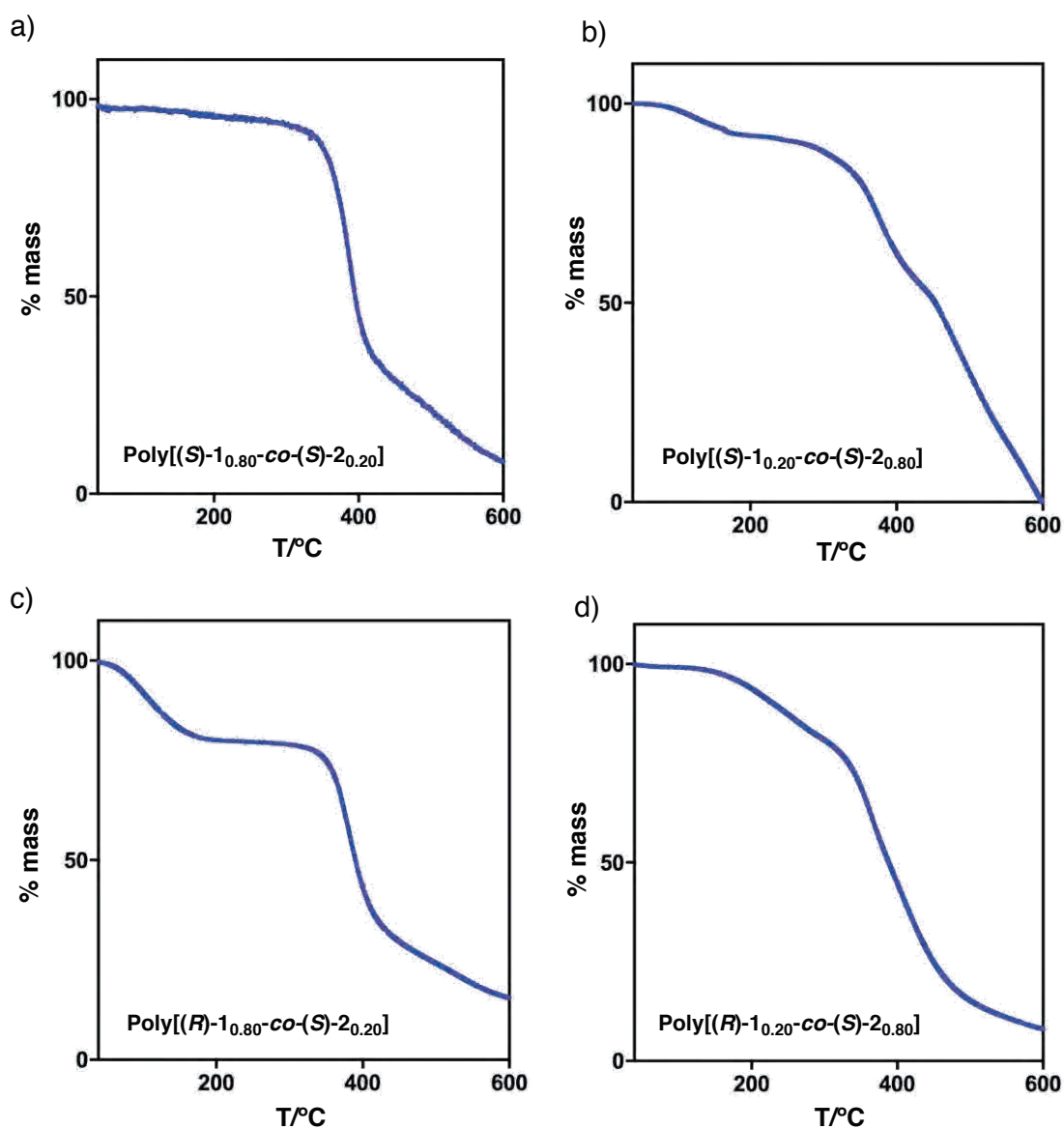


Figure S15. TGA of a) Poly[(S)-1_{0.80}-co-(S)-2_{0.20}], b) Poly[(S)-1_{0.20}-co-(S)-2_{0.80}], c) Poly[(R)-1_{0.80}-co-(S)-2_{0.20}] and Poly[(R)-1_{0.20}-co-(S)-2_{0.80}]

AFM Studies

In order to elucidate the secondary structure of the different copolymer series, well-ordered 2D-crystals were prepared. For this purpose 0.01 mg/ml solutions of the corresponding copolymer were by spin-coated onto freshly cleaved HOPG. Subsequent AFM analysis in tapping mode afforded high-resolution AFM images providing the main helical parameters (helical sense, helical pitch and packing angle).

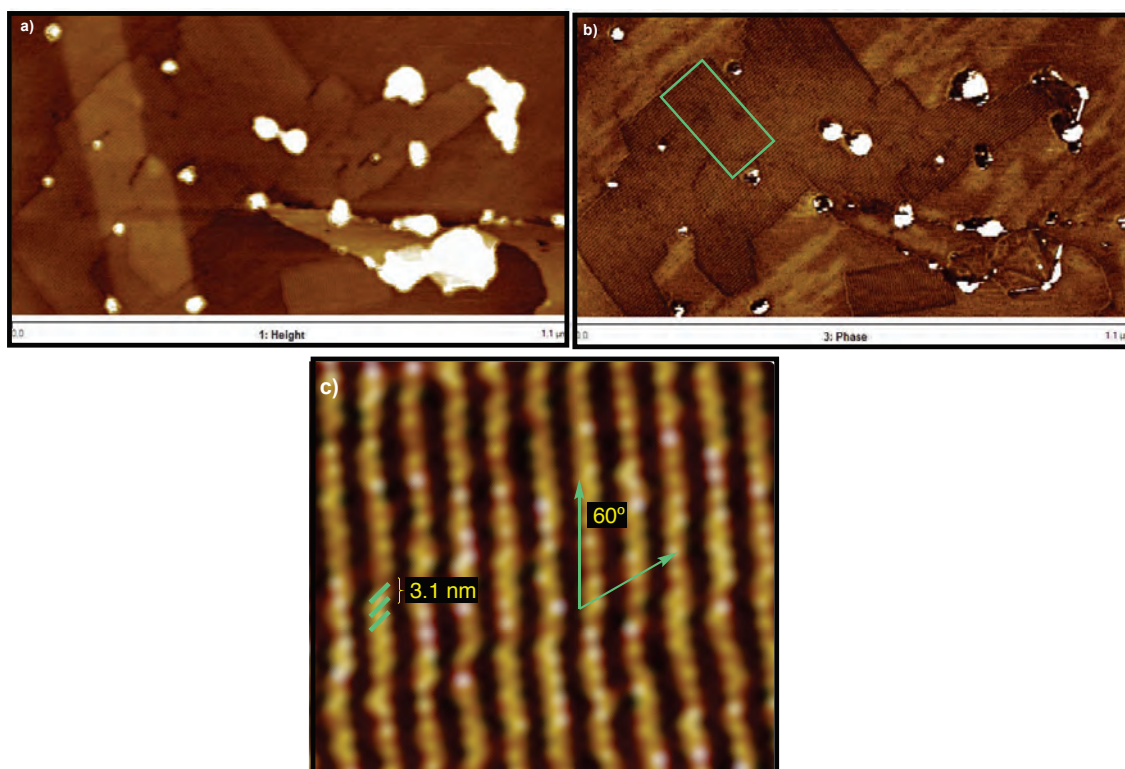


Figure S16. a) and b) large area of well ordered 2D-crystals of poly-(*S*)-2 height and phase images respectively. c) Magnification of the highlighted green area in image b) showing right-handed polymer chains.

Nanostructuration of Copolymers

We previously reported the ability of poly-*(R)*-1 to form nanostructures when complexed with different metal cations (see Ref. S5), so we decided to test the ability of this copolymer series to form nanostructures when complexed with divalent metal ions (e.g., Ba²⁺) and monovalent metal ions (e.g., Na⁺). DLS, SEM studies showed the formation of nanospheres once the polymer undergoes complexation with metal cations.

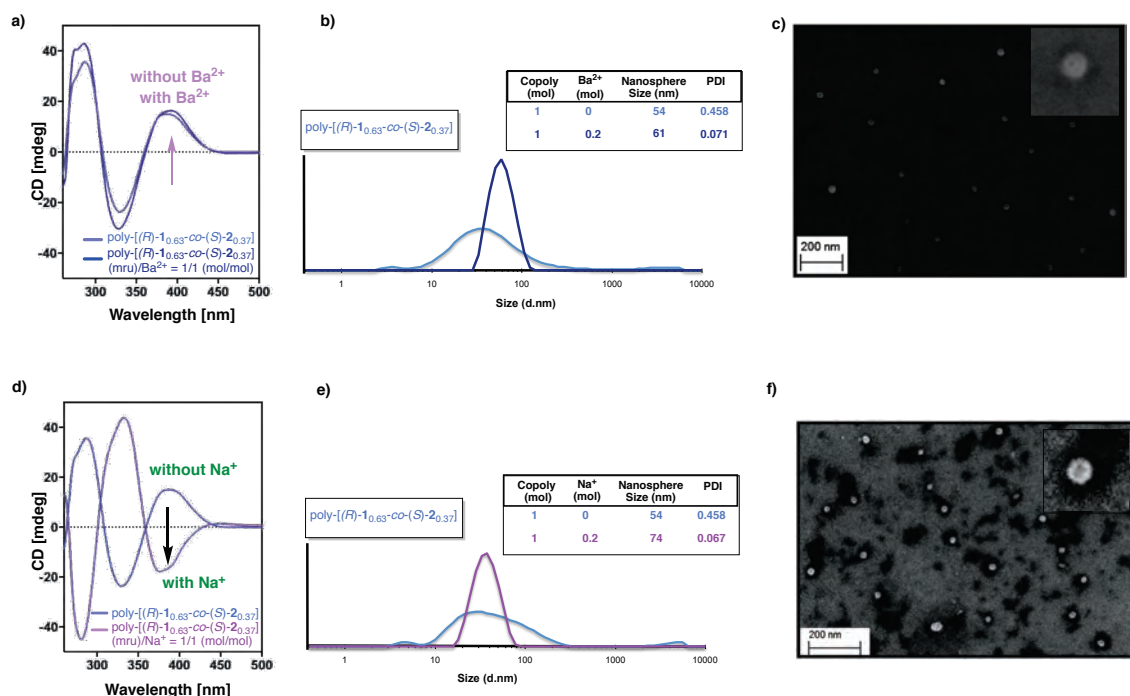


Figure S17. a) CD of Poly-[(*R*)-1_{0.63}-co-(*S*)-2_{0.37}] showing the chirality of polymer remains after addition of Ba(ClO₄)₂ b) DLS trace of Poly-[(*R*)-1_{0.63}-co-(*S*)-2_{0.37}] before and after the addition of Ba(ClO₄)₂ showing the formation of larger nanostructures in solution. c) Representative SEM image of the nanospheres formed after the complexation of the copolymers with divalent metal ions (e.g. Ba²⁺). d) CD of Poly-[(*R*)-1_{0.63}-co-(*S*)-2_{0.37}] showing the chirality of polymer remains after addition of NaClO₄. e) DLS trace of Poly-[(*R*)-1_{0.63}-co-(*S*)-2_{0.37}] before and after the addition of NaClO₄ showing the formation of larger nanostructures in solution. f) Representative SEM image of the nanospheres formed after the complexation of the copolymers with divalent metal ions (e.g. Na⁺)

Interactions between aromatic systems in the pendants

The distances between aromatic systems measured from the models suggest that "pi-stacking" interactions between anthryl and phenyls ring ("sandwich or parallel-displaced" type) are possible (See Ref. S6). See Figures S18-19.

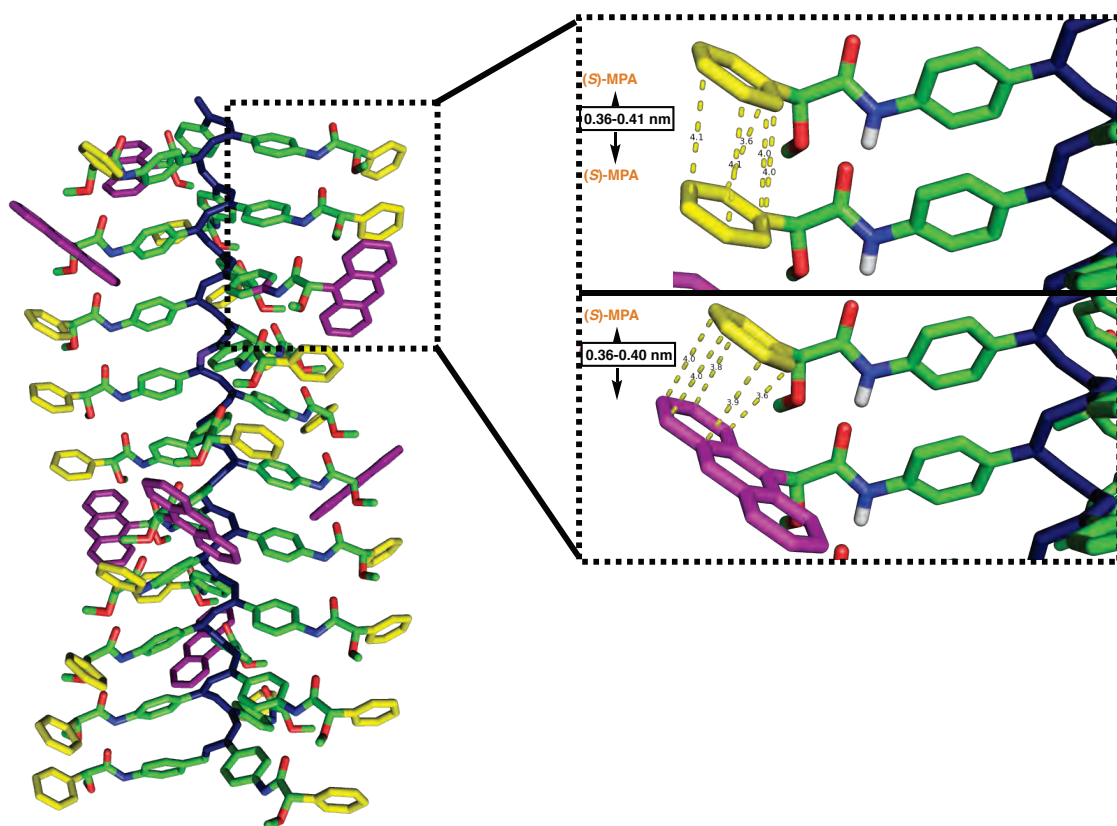


Figure S18. Side view of copolymers Poly-[(S)-1-*co*-(S)-2-*r*] and magnification of the highlighted area shows the virtually identical distances between (S)-MPA-(S)-MPA units and (S)-MPA-(S)-9-AMA units. (S)-MPA in yellow and (S)-9-AMA in purple.

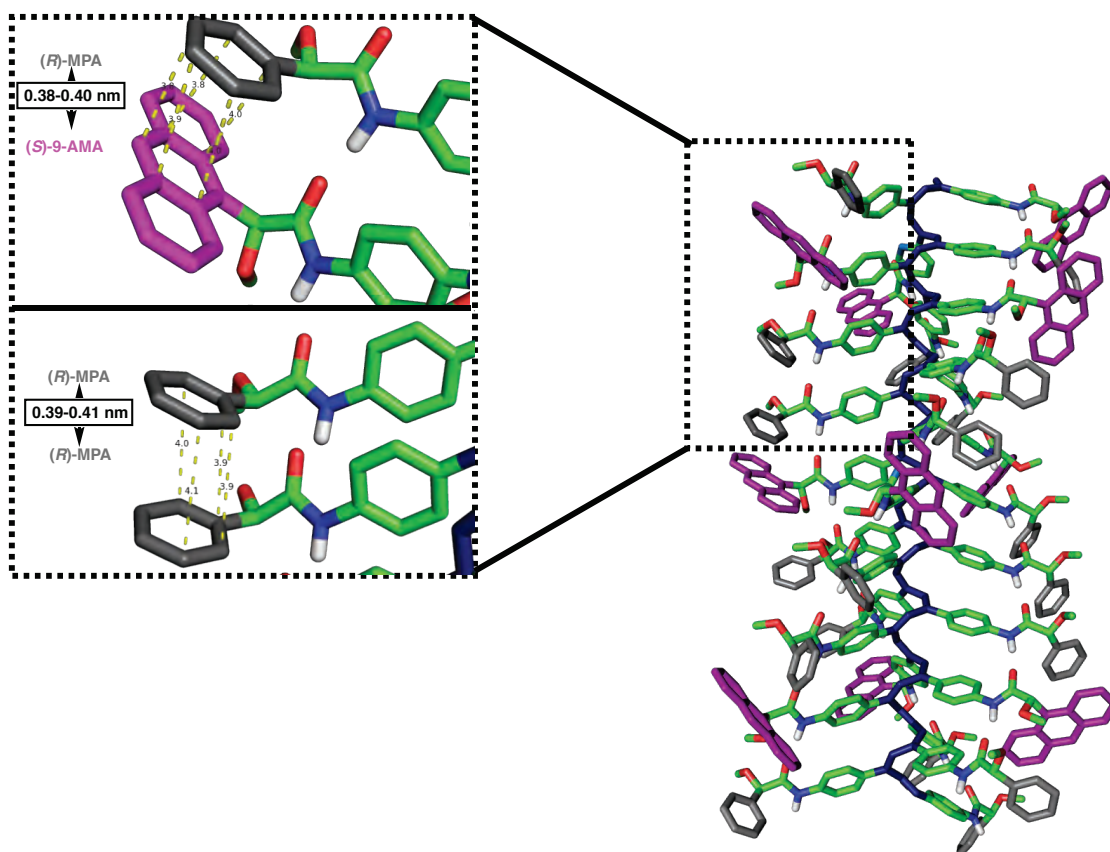


Figure S19. Side view of copolymers Poly-[(*R*)-1_r-co-(*S*)-2_{1-r}] and magnification of the highlighted area shows the virtually identical distances between (*R*)-MPA-(*R*)-MPA units and (*R*)-MPA-(*S*)-9-AMA units. (*R*)-MPA in grey and (*S*)-9-AMA in purple.

Circular dichroism studies

CD and UV spectra of M-(*S*)-2 and poly-(*S*)-2

CD spectrum of M-(*S*)-2 shows an CD band around 280 nm which corresponds to the interaction between the carbonyl and the anthryl group (See Ref. S7).

CD spectrum of a helical structure adopted by poly-(*S*)-2.

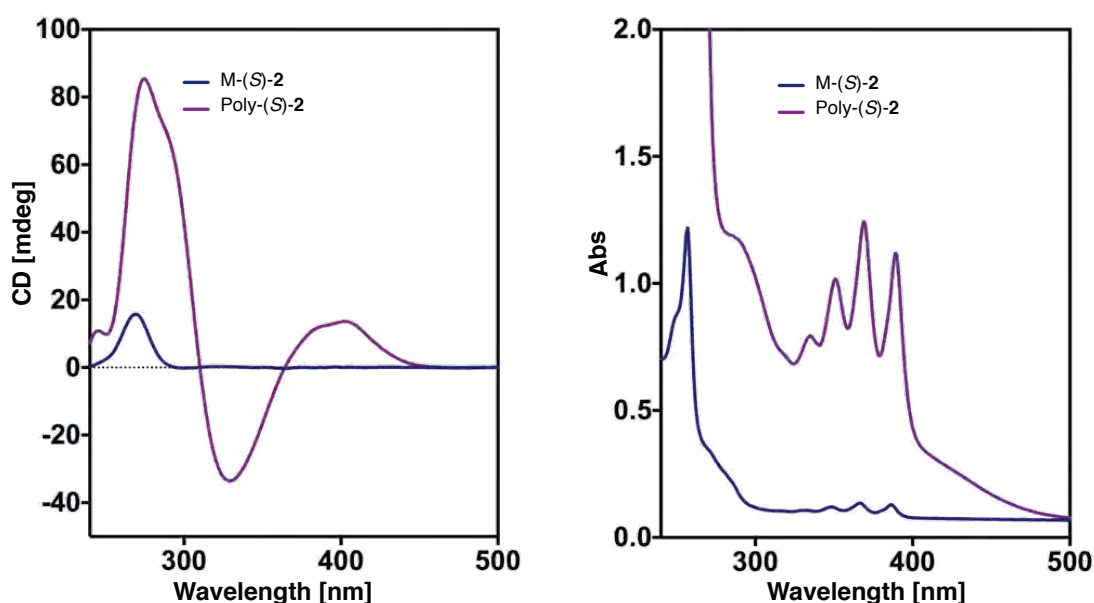


Figure S20. CD and UV spectra of M-(*S*)-2 (CHCl_3 , 0.1 mg/mL) and poly-(*S*)-2 (CHCl_3 , 0.3 mg/mL).

CD studies of copolymers measured in solvents with different polarity

First, the copolymers were measured in solvents of low polarity due to the good solubility observed. DCM, CHCl_3 and THF are among these low-polar solvents, being THF the most used since it shows higher *r*-values than the others.

In more polar non-protic solvents such as DMF and DMSO, 9-Ama loses the helicity, so the study in those solvents becomes unfeasible. Finally, the study of these polymers in protic polar solvents cannot be done since their solubility is very low.

Studies in a variety of solvents, in addition to those shown in the main article (in THF), follow.

Copolymers S-S series

1) Low polar solvents: CHCl_3 , DCM

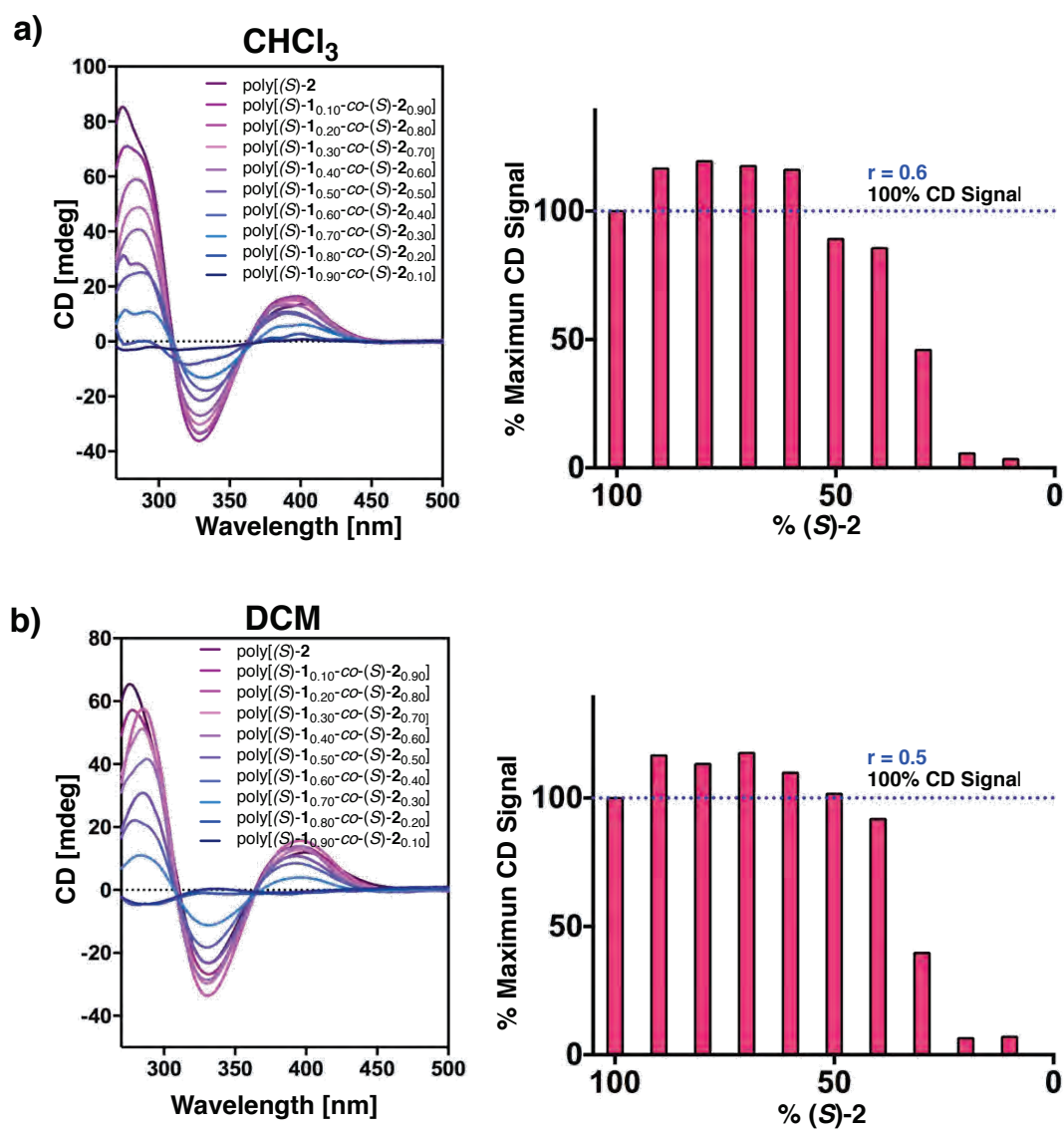


Figure S21. CD spectra and r values of the different copolymers of serie poly-[(S)-1- r -co-(S)-2_(1-r)] in non-polar solvents: (a) CHCl_3 , (b) DCM

2) Polar non-protic solvents: DMF, DMSO

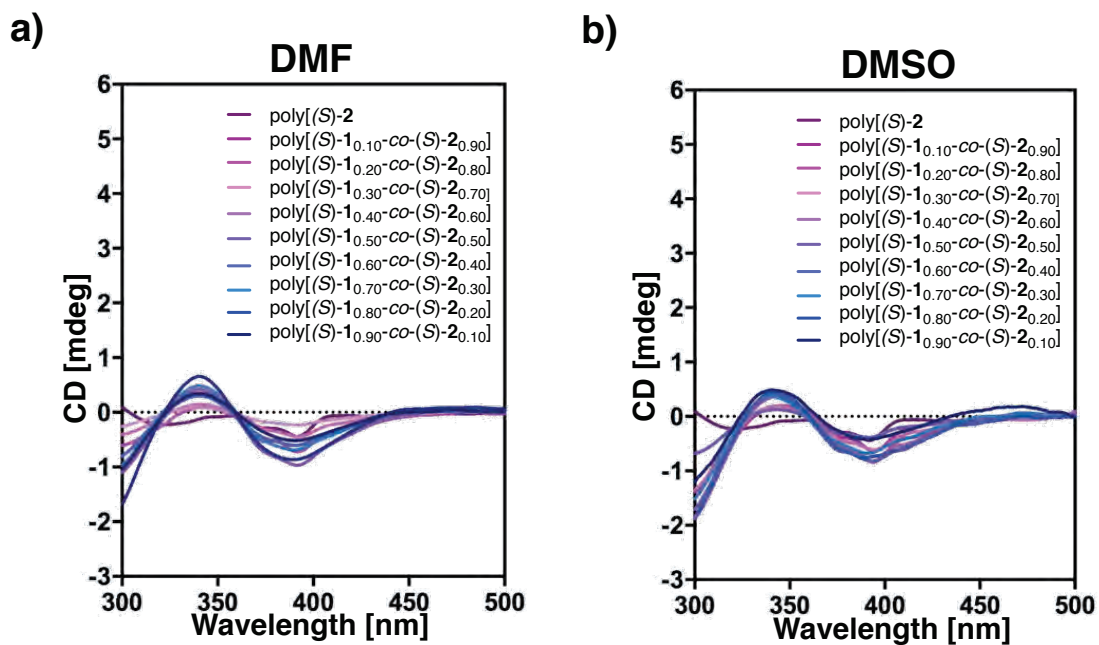


Figure S22. CD spectra of the different copolymers of serie poly-[(S)-1-*r*-co-(S)-2]_(1-r) in polar non-protic solvents: (a) DMF, (b) DMSO

Copolymers R-S series

1) Low polar solvents: CHCl₃, DCM

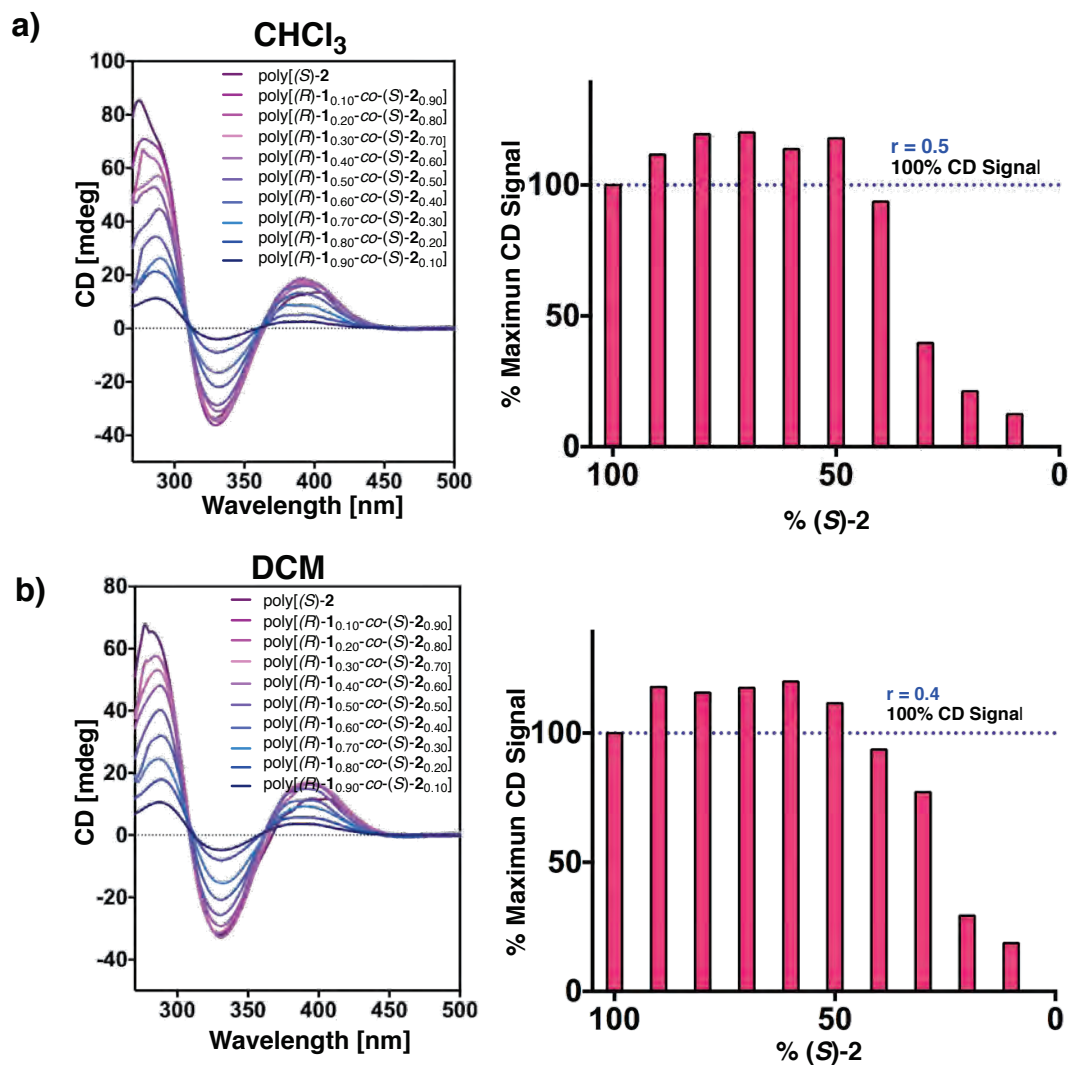


Figure S23. CD spectra and r values of the different copolymers of serie poly-[(R)-1 _{r} -co-(S)-2_(1-r)] in non-polar solvents: (a) CHCl₃, (b) DCM

2) Polar non-protic solvents: DMF, DMSO

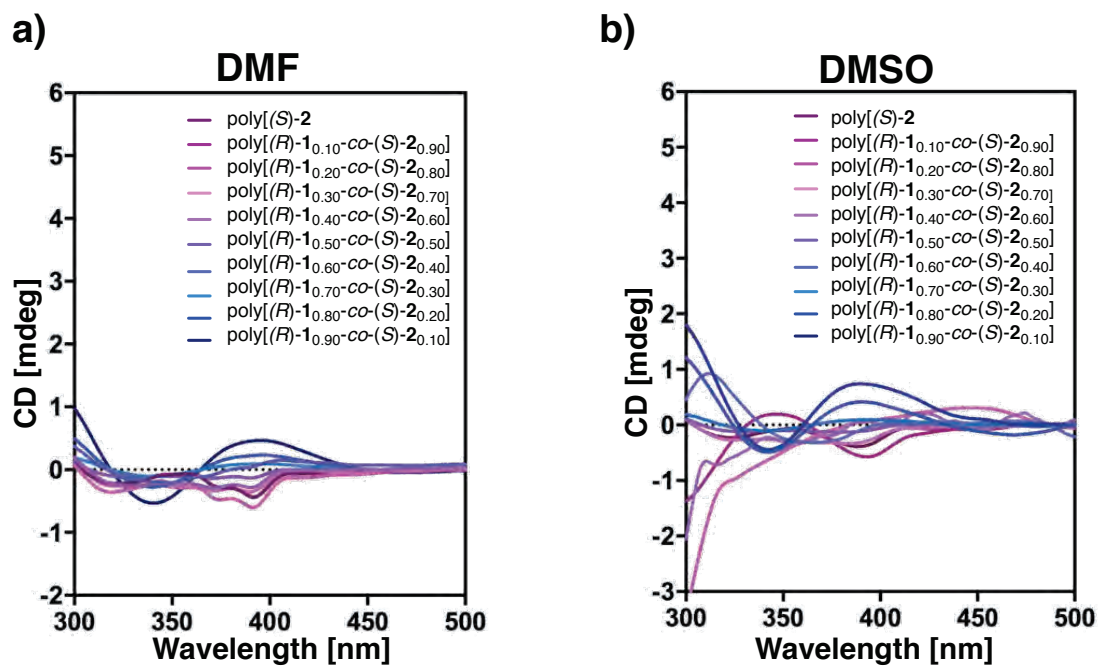


Figure S24. CD spectra of the different copolymers of serie poly-[(R)-1-co-(S)-2]_(1-r) in polar non-protic solvents: (a) DMF, (b) DMSO

Copolymers racemic series

1) Low polar solvents: DCM, CHCl_3

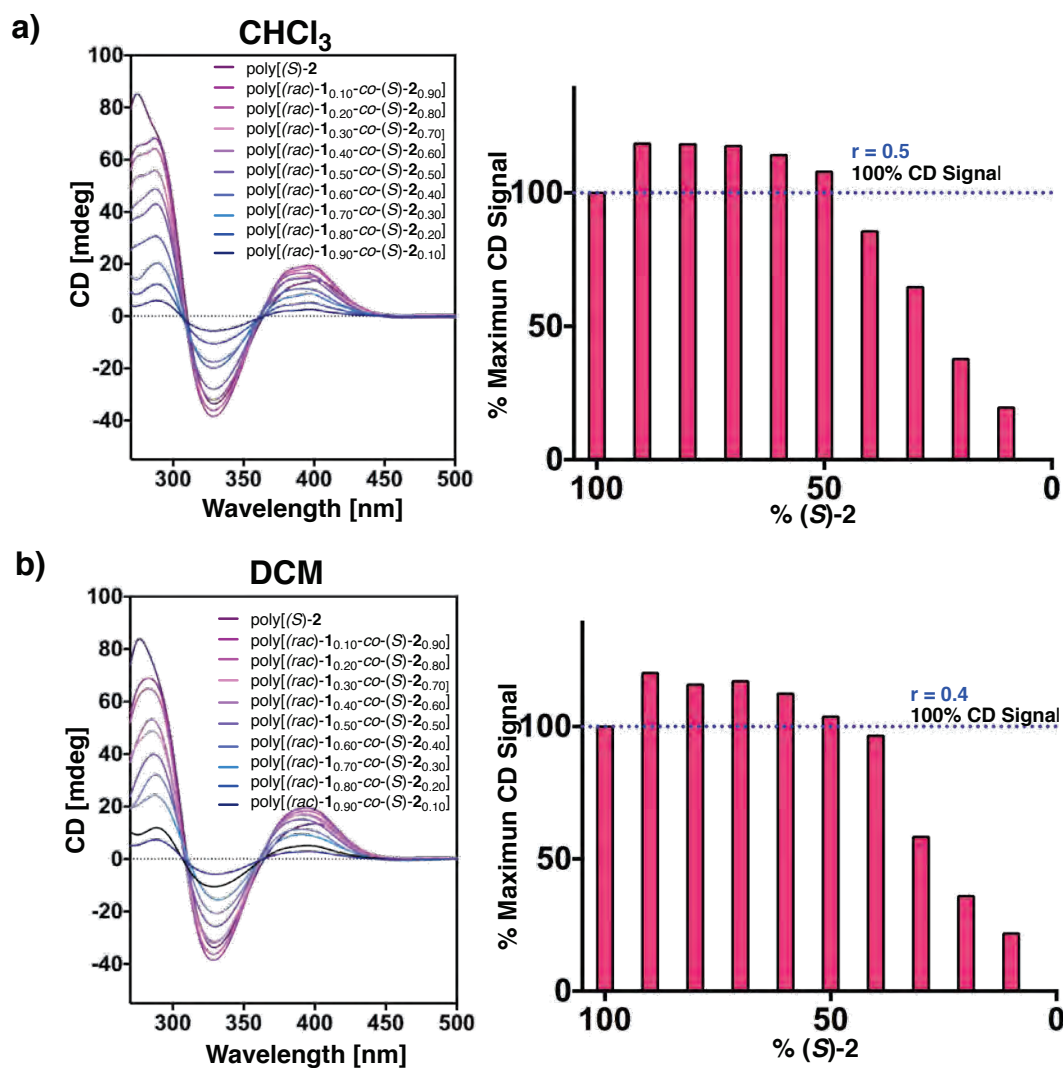


Figure S25. CD spectra and r values of the different copolymers of serie poly-[(*rac*)-1- r -co-(*S*)-2_(1- r)] in non-polar solvents: (a) CHCl_3 , (b) DCM

2) Polar non-protic solvents: DMF, DMSO

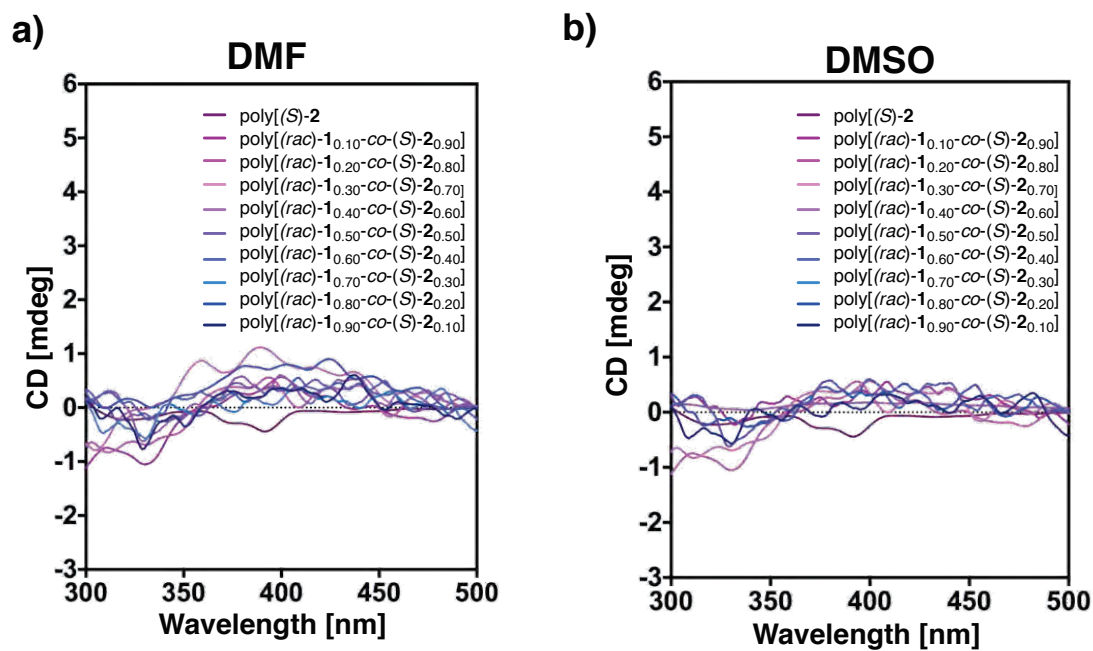


Figure S26. CD spectra of the different copolymers of serie poly-[(rac)-1_r-co-(S)-2_(1-r)] in polar non-protic solvents: (a) DMF, (b) DMSO

Studies of poly-[(*rac*)-1_r-co-(*S*)-2_(1-r)] with metal cations

Because MPA is racemic, the amplification originated by a MPA unit by adding a metal cation cancels the amplification of its enantiomer. However, the 9-AMA response can be seen amplified (with Li⁺) or inverted (with Ba²⁺). (See Ref S1)

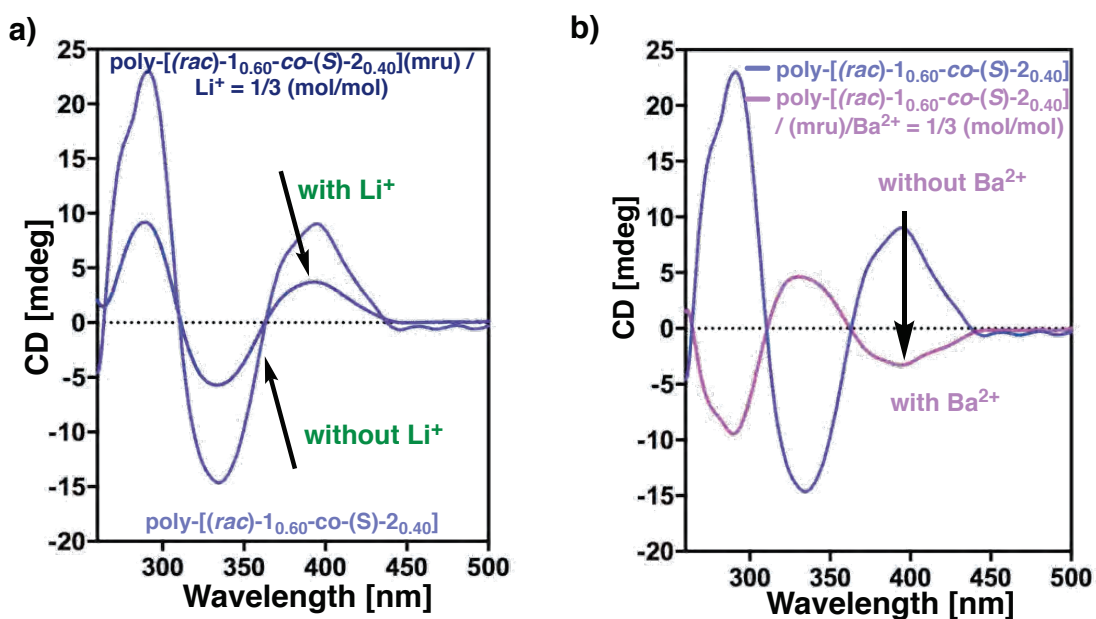


Figure S27. Studies of poly-[(*rac*)-1_r-co-(*S*)-2_(1-r)] with (a) monovalent and (b) divalent metal cations.

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