Supporting Information

Synthesis of Alkyne Functionalized Helical Polycarbodiimides and their Ligation to Small Molecules using 'Click' and Sonogashira Reactions

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Supporting Informations

Contents

Synthesis of (R) and (S) – BINOL-titanium (IV) – diisopropoxide Catalyst. The catalyst was synthesized according to reported procedure in the literature. [5,11]

Click reaction with 6-azidohexanoic acid (Poly-1b). The azido compound, 6-azidohexanoic acid, was synthesized from 6-bromohexanoic acid and sodium azide according to the published literature.[27] To the stirring solution of polymer in tetrahydrofuran, 6-azidohexanoic acid and DBU (1.3:6.0 mol equiv per alkyne unit in the polymer) followed by the catalyst CuI (10 mol %) were added. A white solid precipitated out within 15 minutes. The reaction mixture was stirred overnight. The reaction can be monitored by disappereance of strong terminal alkyne C-H absorption band at 3305 cm^{-1} in the Infrared spectroscopy. Once completed, the polymer solid was separated by filtration. The solid was transferred to a vial containing chloroform and 1M HCl solution and stirred 6 hours at room temperature to remove any unreacted azido compound and the catalyst. The polymer solid was then separated by filtration; washed and dried overnight to get slightly yellow polymer; **Poly-1b** (Scheme 2).

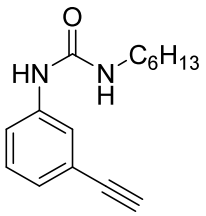
Click reaction with 3-azido-N-Boc-propylamine (Poly-1c). The same protocol as above was followed except for purification method. Once the reaction was complete, the polymer was precipitated in diethyl ether, separated by filtration and dried. For further purification, the solid polymer was dissolved in chloroform, reprecipitated in diethylether, filtered out and dried under high vacuum to get **Poly-1c** as a white solid.

Amino acid coupling to the carboxylic acid side chain (Poly-1b-ala). To the stirring solution of **Poly-1b** in dimethylformamide (DMF) at 0°C, N-hydroxysuccinimide and EDCI (1.0:1.2:1.2 mol equiv per alkyne unit in the polymer) were added. The reaction mixture was allowed to warm up to room temperature and stirred overnight under nitrogen atmosphere. A premixed solution of L-Alanine methylester hydrochloride (2.0 mol equiv per alkyne unit in the polymer) in triethyl amine (3.0 mL) was added to the reaction mixture. The reaction mixture was stirred overnight. The solvent was removed; polymer was dissolved in methanol and precipitated in ether, and washed several times with water to remove excess of amino acid-L-Alanine methylester hydrochloride. The polymer was then separated by filtration, and dried under vacuum to get **Poly-1b-ala** (Scheme 3).

Biotin azide coupling to the polymer side chain (Poly-2b-BT). Biotin azide was prepared according to the literature procedure[26] and used without further purification. The general click protocol as described above was applied. The resulting polymer was acidified with dilute HCl, washed with water several times until free from acid, filtered and dried under reduced pressure.

Compound characterization

Compound S1: 1-(3-ethynylphenyl)-3-hexylurea



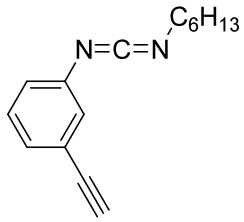
1-(3-ethynylphenyl)-3-hexylurea

White needle shaped crystal, Yield: 88%

^{1}H NMR, 300 MHz ($CDCl_3$, δ ppm, Reference TMS = 0 ppm): 7.39 (t, *J* = 1.8 Hz, 1H, Ar-H), 7.34 (dt, *J* = 3.9 Hz, 1.8 Hz, 1H, Ar-H), 7.21 (t, , *J* = 7.8 Hz, 1H, Ar-H), 7.15 (dt, *J* = 3.6 Hz, 1.5 Hz, 1H, Ar-H), 7.02 (s, br, 1H, CONH), 5.88 (t, *J* = 5.4 Hz, 1H, CONH), 3.16- 3.09 (m, 2H), 2.99 (s,1H, sp C-H), 1.48-1.32 (m, 2H), 1.30-1.14 (m, 6H), 0.84 (t, *J* = 6.9, 3H, -CH_3)

^{13}CNMR (100 MHz, $CDCl_3$, δ ppm Reference $CDCl_3$= 77.23 ppm): δ = 156.71, 139.29, 129.05, 126.66, 123.42, 122.83, 120.65, 83.49, 77.46, 40.42, 31.64, 30.20, 26.72, 22.67, 14.12.

Compound S2: *N*-(3-ethynylphenyl)-*N*'-hexylcarbodiimide



Clear colorless oil, Yield: 87 %

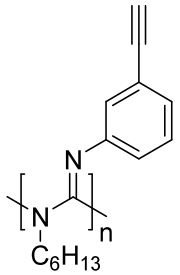
FTIR (cm^{-1}): 3295(terminal alkyne C-H), 2142 (N=C=N)

^{1}H NMR (300 MHz, $CDCl_3$, δ ppm, Reference TMS = 0 ppm): 7.23-7.20 (m, 3H, Ar-H), 7.07-7.03 (m,1H, Ar-H), 3.41(t, *J* = 6.9, 2H), 3.07 (s,1H, sp C-H), 1.72-1.64 (m, 2H), 1.46-1.25 (m, 6H), 0.88 (t, *J* = 6.9, 3H, -CH_3)

^{13}C NMR (75 MHz, $CDCl_3$, δ ppm, Reference $CDCl_3$= 77.23 ppm): δ = 141.31, 129.49, 128.37, 127.09, 124.28, 123.31, 83.20, 77.69, 46.95, 31.45, 31.44, 26.62, 22.71, and 14.17.

HRMS m/z $(M+H)^+$: 227.1543 (Calculated); 227.1538 (found)

Compound S3: Poly(*N*-(3-ethynylphenyl)-*N*'-hexyl)carbodiimide, Poly-1



Poly-1

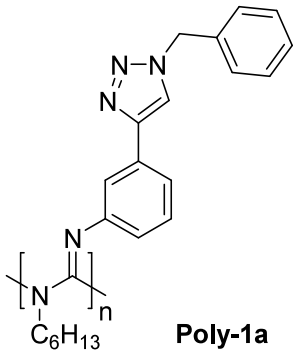
Pale Yellow solid, Monomer:Catalyst(molar ratio) 100:1, Yield: 86 %, 1.2 g

FTIR (cm^{-1}): 3305 (terminal alkyne C-H), 2107 (C□C), 1629 (imine),

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, Reference TMS = 0 ppm): 7.60-6.20 (br, Ar-H),), 4.0-2.2 (br), 3.0 (br, s, alkyne-H), 1.8-0 (br)

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm Reference $CDCl_3$= 77.23 ppm): δ = 149.10, 147.90, 128.34, 126.37, 123.0, 83.69, 77.31, 48.92, 31.84, 28.96, 26.51, 23.06, and 14.33.

Compound S4: Poly-1a



Poly-1a

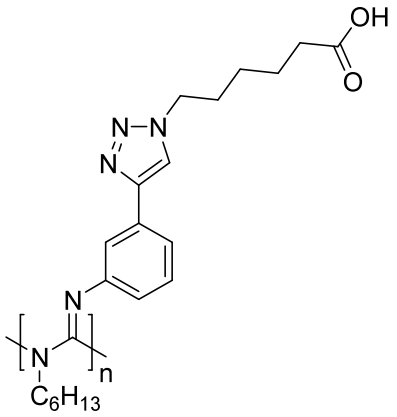
White solid, Yield: quantitative by NMR and IR

FTIR (cm^{-1}): 1631 (imine),

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, Reference TMS = 0 ppm): 7.80-6.0 (br, Ar-H), 5.37(br), 3.8-2.2 (br), 1.2-(-0.8) (br)

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm Reference $CDCl_3$= 77.23 ppm): δ = 148.09, 134.99, 130.81, 128.89, 127.50, 121.71, 119.81, 77.33, 53.68, 48.92, 31.55, 26.48, 22.70, and 14.03.

Compound S5: Poly 1b



Poly-1b

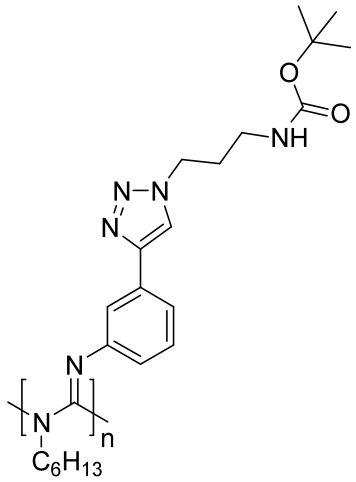
Pale yellow solid, Yield: quantitative (as determined by NMR data)

FTIR (cm^{-1}): 3388(br) and 1714(-COOH), 1633 (imine)

^{1}H NMR (400 MHz, CD_3OD, δ ppm, Reference solvent peak =3.31ppm): 8.8-8.0(br Ar-H), 7.80-6.4 (br, Ar-H), 4.6-4.0(br), 2.23 (br), 1.87-1.30(br, overlapping), 0.8-(-0.6) (br).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm Reference $CDCl_3$= 77.23 ppm): δ = 177.29, 77.33, 53.68, 46.40, 34.75, 32.74, 31.41, 28.09, 27.21, 25.54, 23.58, and 14.70. (Aromatic protons have poor resolution)

Compound S6: Poly-1c



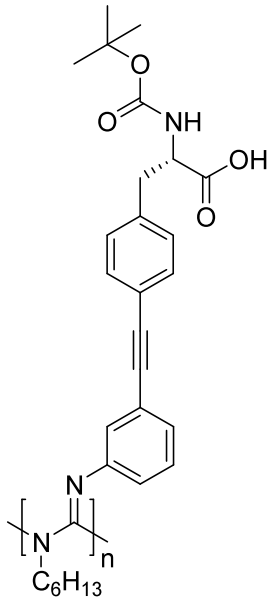
Poly-1c

FTIR (cm^{-1}): 3328(br) and 1699(-CO), 1629(imine)

^{1}H NMR (400 MHz, CD_3OD, δ ppm, Reference solvent peak =3.31ppm): 8.8-8.0(br Ar-H), 7.80-6.4 (br, Ar-H), 4.6-4.0(br), 2.23 (br), 1.87-1.30(br, overlapping), 0.8-0.6) (br).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm Reference $CDCl_3$= 77.23 ppm): δ = 177.29, 77.33, 53.68, 46.40, 34.75, 32.74, 31.41, 28.09, 27.21, 25.54, 23.58, and 14.70. (Aromatic protons have poor resolution)

Compound S7: Poly-1-phe

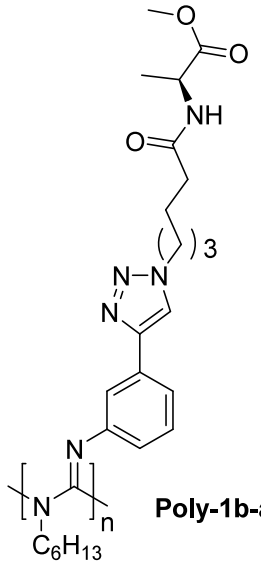


Poly-1-phe

FTIR (cm^{-1}): 3430, 3303, 1716(-CO), 1627 (imine)

^{1}H NMR (400 MHz, Pyridine-D_5, δ ppm, Reference TMS = 0 ppm): 7.8-6.6 (br Ar-H), 5.02 (s,-NH), 3.95(br, s), 3.58 (br), 3.39 (br), 2.759, br, s), 1.8-0.6 (br, overlapping)

Compound S8: Poly-1b-ala

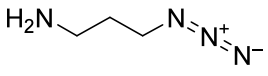


Poly-1b-ala

FTIR (cm^{-1}): 3307, 1745(-CO_2Me), 1637 approx (br, imine & amide overlap)

^{1}H NMR (400 MHz, CD_3OD, δ ppm, Reference solvent = 4.78 ppm): 8.2-6.6 (br Ar-H), 4.23 (s,br-CH_2), 3.50 (br, -OCH_3), 2.07 (br), 1.78 (br), 1.48, 1.20 (br), 0.16 (br).

Compound S9: 3-azidopropan-1-amine

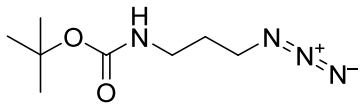


FTIR (cm^{-1}): 3365 (br) (N-H), 2102 (azide)

^{1}HNMR (300 MHz, $CDCl_3$, δ ppm, Reference TMS = 0 ppm): δ = 3.38 (t, *J* = 6.9 Hz, 2H), 2.80 (t, *J* = 6.9 Hz, 2H), 1.78-1.69 (m, 2H), 1.16 (s, 2H, NH_2).

^{13}CNMR (75 MHz, $CDCl_3$, δ ppm, Reference $CDCl_3$= 77.23 ppm): δ = 49.25, 39.45, and 32.57.

Compound S10: *tert*-butyl 3-azidopropylcarbamate

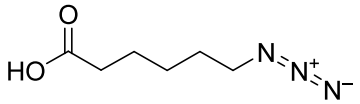


FTIR (cm^{-1}): 3351 (N-H), 2098 (azide), 1693 (C=O, carbamate)

^{1}HNMR (400 MHz, $CDCl_3$, δ ppm, Reference: TMS = 0.00 ppm): δ = 4.77(s, 2H, NH_2), 3.36 (t, *J* = 6.8 Hz, 2H), 3.21 (t, *J* = 6.4 Hz, 2H), 1.80-1.74 (m, 2H), 1.44(br, s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, Reference $CDCl_3$= 77.23 ppm): δ = 156.12, 85.32, 79.49, 49.27, 38.15, 29.42, 28.51, and 27.54.

Compound S11: 6-azidohexanoic acid

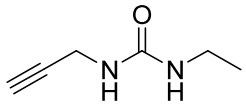


FTIR (cm^{-1}): 2098 (azide)

^{1}HNMR (300 MHz, $CDCl_3$, δ ppm): 11.64 (s, 1H, -COOH), 3.29 (t, *J* = 6.9, 2H), 2.38 (t, *J* = 7.5, 2H), 1.72-1.58 (m, 4H), 1.49-1.40 (m, 2H).

^{13}CNMR (75 MHz, $CDCl_3$, δ ppm, Reference $CDCl_3$= 77.23 ppm): δ = 179.75, 51.31, 33.99, 28.65, 26.27, and 24.29.

Compound S12: 1-ethyl-3-(prop-2-ynyl)urea

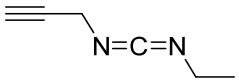


Yield: 100%, white crystalline solid (needle shape)

^{1}HNMR (400 MHz, $CDCl_3$, δ ppm); Reference: TMS = 0.00 ppm, δ = 5.82(br s,1H, NH), 5.58 (br s, 1H, NH), 3.96 (2H), 3.22 (2H), 2.20 (t, *J* = 2.8 Hz, 1H), and 1.13 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$ = 77.23 ppm, δ = 158.99, 81.59, 71.14, 35.61, 30.36, and 15.95.

Compound S13: *N*-hexyl-*N*□-prop-2-yn-1-ylcarbodiimide (Mono-2a)



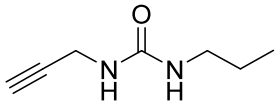
Yield: 70%, (1.0 g), colorless clear oily liquid

FTIR (KBr thin film, neat, cm^{-1}): 3311 (spC-H), s, 2134(N=C=N, carbodiimide)

^{1}HNMR (400 MHz, $CDCl_3$, δ ppm); Reference: TMS = 0.00 ppm, δ = 3.89(d, *J* = 2.4 Hz, 2H), 3.31 (q, *J* = 7.2 Hz, 2H), 2.41 (t, *J* = 2.4 Hz, 1H), and 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$ = 77.23 ppm, δ = 142.10, 79.79, 73.16, 41.69, 35.98, and 17.09.

Compound S14: 1-(prop-2-ynyl)-3-propylurea



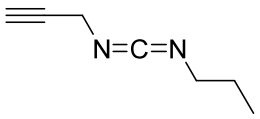
Yield: 100%, white crystalline solid (needle shape)

FTIR (KBr disc, cm^{-1}): 3338, 3282 (N-H),s, 2954, 2917, 2846 (C-Hs),s, 1621, 1590

^{1}HNMR (300 MHz, $CDCl_3$, δ ppm); Reference: TMS = 0.00 ppm, δ = 6.08(br s,1H, NH), 5.25 (br s, 1H, NH), 3.98 (d, *J* = 2.7 Hz, 2H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.20 (t, J = 2.7 Hz, 1H), 1.58-1.45 (m, 2H), and 0.92 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$= 77.23 ppm, δ = 158.41, 81.13, 71.07, 42.41, 30.21, 23.59 and 11.59.

Compound S15: *N*-propyl-*N*□-prop-2-yn-1-ylcarbodiimide (Mono-2b)



Yield: 85 %,(1.0 g), colorless clear oily liquid

FTIR (KBr thin film, neat, cm^{-1}): 3298 (terminal alkyne C-H), s, 2964, 2877 (C-H), s, 2132(N=C=N, carbodiimide)

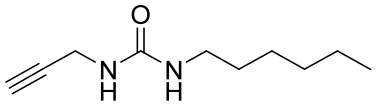
^{1}HNMR (300 MHz, $CDCl_3$, δ ppm); Reference: TMS = 0.00 ppm, δ = 3.89 (2H), 3.24 (2H), 2.40 (1H), 1.66-1.61 (m, 2H), and 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$ = 77.23 ppm, δ = 141.49, 79.85, 73.10, 48.53, 35.94, 24.84, and 11.60.

HRMS m/z $(M+H)^+$: 123.0919; (found), 123.0917 Calculated for $C_7H_{10}N_2$

(note: The corresponding polymer from Mono-2 is insoluble in most of the common organic solvents)

Compound S16: 1-hexyl-3-(prop-2-ynyl)urea



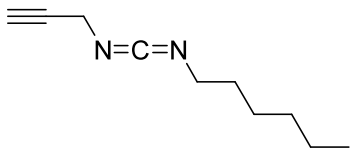
Yield: 95 %, white crystalline solid (needle shape)

FTIR (cm^{-1}): 3315 (N-H),s, 2954, 2921, 2854 (C-Hs),s, 1623(C=O, urea)

^{1}HNMR (300 MHz, $CDCl_3$, δ ppm); Reference: TMS = 0.00 ppm, δ = 5.74(br s, 1H, NH), 5.53 (br s, 1H, NH), 3.96 (s, 2H), 3.16 (t, *J* = 6.9 Hz, 2H), 2.19 (t, *J* = 2.5 Hz, 1H), 1.51-1.43 (m, 2H), 1.36-1.25(m, 6H) and 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$ = 77.23 ppm, δ = 158.67, 81.26, 70.87, 40.65, 31.76, 30.39, 30.11, 26.81, 22.77, and 14.21.

Compound S17: *N*-hexyl-*N*□-prop-2-yn-1-ylcarbodiimide (Mono-2c)



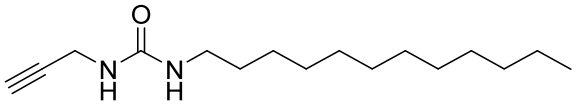
Yield: 83%, (1.5 g), colorless clear oily liquid

FTIR (cm^{-1}): 3297 (terminal alkyne C-H), s, 2929, 2857 (C-H), s, 2132(N=C=N, carbodiimide)

^{1}HNMR (400 MHz, $CDCl_3$, δ ppm); Reference: TMS = 0.00 ppm, δ = 3.86 (d, *J* = 2.8 Hz, 2H), 3.27 (t, *J* = 6.8 Hz, 2H), 2.40 (t, *J* = 2.8 Hz, 1H), 1.51-1.43 (m, 2H), 1.36-1.25(m, 6H) and 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$ = 77.23 ppm, δ = 141.50, 79.87, 73.09, 46.79, 35.96, 31.56, 31.56, 31.51, 26.65, 22.76, and 14.23.

Compound S18: 1-dodecyl-3-(prop-2-ynyl)urea



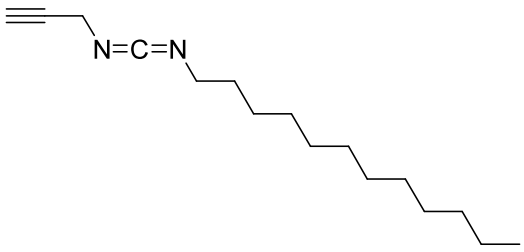
Yield: 98 %, white crystalline solid (needle shape)

FTIR (KBr disc, cm^{-1}): 3338, 3282 (N-H),s, 2954, 2917, 2846 (C-Hs),s, 1621, 1590 (C=O, urea)

^{1}HNMR (400 MHz, DMSO-d_6, δ ppm); Reference: DMSO = 2.50 ppm, δ = 6.08(t, *J* = 5.8 Hz, 1H, NH), 5.93 (t, *J* = 5.6 Hz, 1H, NH), 3.76-3.74 (m, 2H), 3.03 (t, *J* = 2.4 Hz, 1H), 2.97-2.93 (m, 2H), 1.35-1.23 (m, 20H), and 0.85 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): Reference DMSO-d_6 = 39.51 ppm, δ = 157.45, 82.62, 72.44, 31.31, 29.94, 29.06, 29.03, 28.18, 28.77, 28.73, 26.38, 22.11 and 13.97.

Compound S19: *N*-dodecyl-*N*□-prop-2-yn-1-ylcarbodiimide (Mono-2d)



Yield: 95%, colorless clear oily liquid

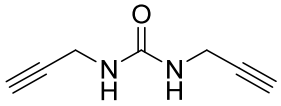
FTIR (KBr thin film, neat, cm^{-1}): 3311 (terminal alkyne C-H), s, 2925, 2854 (C-H), s, 2134(N=C=N, carbodiimide)

^{1}HNMR (300 MHz, $CDCl_3$, δ ppm); Reference: TMS = 0.00 ppm, δ = 3.89(d, *J* = 2.4 Hz, 2H), 3.26 (t, *J* = 6.9 Hz, 2H), 2.39 (t, *J* = 2.4 Hz, 1H), 1.65-1.56 (m, 2H), 1.39-1.26(m, 20H) and 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$ = 77.23 ppm, δ = 141.50, 79.89, 73.09, 46.80, 35.97, 32.12, 31.56, 29.86, 29.84, 29.80, 29.75, 29.56, 29.39, 26.98, 22.90, and 14.33.

HRMS m/z (M+H)$^+$: 249.2324 (found); 249.2325(calculated) for $C_{16}H_{29}N_2$

Compound S20: 1, 3-diprop-2-yn-1-ylurea



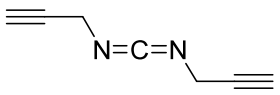
Yield: 75%, (0.7 g) white crystalline solid (fine crystals)

FTIR (KBr disc, cm^{-1}): 3324, 3295, 3276, 3147, 3008, 2921, 2830, 1608

^{1}HNMR (400 MHz, DMSO-d_6, δ ppm); Reference: DMSO-d_6 = 2.50 ppm, δ = 6.33(t, *J* = 5.6 Hz, 2H, NHs), 3.77 (dd, *J* = 2.8 Hz, 5.6 Hz, 4H), 3.05 (t, *J* = 2.8 Hz, 2H).

^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): Reference DMSO-d_6 = 39.51 ppm, δ = 157.02, 82.41, 72.67, and 28.88.

Compound S21: *N,N*□-diprop-2-yn-1-ylcarbodiimide (Mono-3)



Yield: 65%, 0.43g, colorless clear oily liquid, purified by column chromatography on silica gel using diethyl ether as solvent.

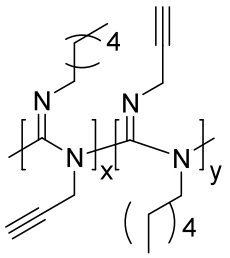
FTIR (KBr thin film, neat, cm^{-1}): 3292 (terminal alkyne C-H), s, 2925 (C-H), s, 2134(N=C=N, carbodiimide)

^{1}HNMR (400 MHz, $CDCl_3$, δ ppm); Reference: TMS = 0.00 ppm, δ = 3.96(d, *J* = 2.0 Hz, 4H), 2.43 (t, *J* = 2.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference TMS = 0.00 ppm, δ = 148.05, 79.04, 73.34, and, 35.71.

HRMS m/z (M+H)$^+$: 119.0590 (found); 119.0604 (calculated) for $C_7H_7N_2$

Compound S22: poly(*N*-hexyl-*N*□-prop-2-yn-1-yl)carbodiimide Poly(2c)



Monomer:Catalyst (molar ratio) 100:1, Yield: 83%

FTIR (cm^{-1}): 3313 (alkyne C-H), 2121 (C□C), 1650 (imine)

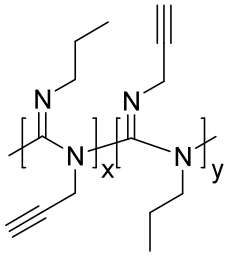
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): Reference TMS = 0.00 ppm, δ = 4.12 (br), 3.82(br), 2.06 (br), 1.60-1.25 (br), 0.88 (br).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$= 77.23 ppm

δ = 146.15, 71.71, 48.96, 32.18, 27.75, 23.00, 14.37.

$[\alpha]_{589}^{25}$ = +16.0 (c = 0.22 in $CHCl_3$, l = 0.5 dm)

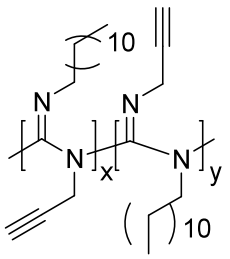
Compound S23: *N*-propyl-*N*□-prop-2-yn-1-ylcarbodiimide (Poly-2b)



Monomer:Catalyst (molar ratio) 100:1, Yield: 70 %, 0.52 g

FTIR (cm^{-1}): 3309 (alkyne C-H), 2121 (C□C), 1654 (imine),

Compound S24: *N*-dodecyl-*N*□-prop-2-yn-1-ylcarbodiimide (Poly-2d)



Monomer:Catalyst (molar ratio) 100:1, Yield: 90 %, 0.9 g

FTIR (cm^{-1}): 3313(terminal alkyne C-H), 1648 (imine)

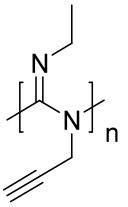
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): Reference TMS = 0.00 ppm, δ = 4.13 (br), 3.36(br), 2.17- 2.0 (br), 1.60-1.25 (br), 0.88 (br).

^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): Reference $CDCl_3$= 77.23 ppm

δ = 150.65, 146.27, 83.94, 80.41, 73.31, 69.00, 49.10, 37.96, 32.19, 30.03, 29.67, 28.20, 22.93, 14.34.

$[\alpha]_{589}^{25}$ = +10.0 (c = 0.22 in $CHCl_3$, l = 0.5 dm)

Compound S25: *N*-ethyl-*N*□-prop-2-yn-1-ylcarbodiimide (Poly-2a)

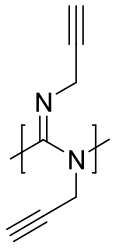


Poly-2a

Monomer:Catalyst (molar ratio) 100:1, Yield: 90 %, 0.76 g

FTIR (cm^{-1}): 3307(terminal alkyne C-H), 2966, 2923, 2865, 2119 (C□C), 1654 (imine)

Compound S26: poly(*N*, *N*□-diprop-2-yn-1-yl)carbodiimide (Poly-3)



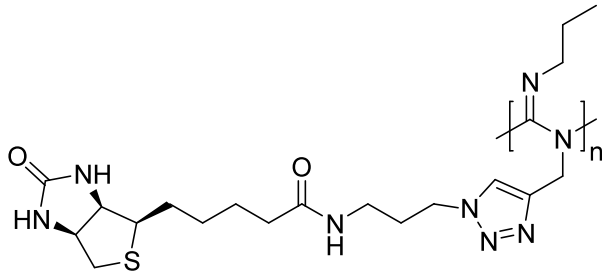
Yield: 87%, (0.078 g), pale yellow solid

FTIR (cm^{-1}): 3294 (terminal alkyne C-H), 2121 (C□C), 1654, 1641 (imine from guanidine backbone)

^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): Reference DMSO = 2.50 ppm, δ = 4.20 (br), 4.03 (br), 3.39 (br), 2.92-2.85 (br).

^{13}C NMR (100 MHz, DMSO-d_6, δ ppm): Reference DMSO = 39.51 ppm, δ = 146.91, 82.28, 78.76, 76.52, 72.63, 37.89, 36.35.

Compound S27: poly-2b-BT



Poly-2b-BT

^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): Reference DMSO = 2.50 ppm, δ = 8.00 (br), 4.30 (br), 4.20 (br), 3.10 (br), 2.80 (br), 2.60 (br), 2.3, 2.2, 2.1, 1.9, 1.6, 1.4, 1.3, 0.90. (The peaks have poor resolution)

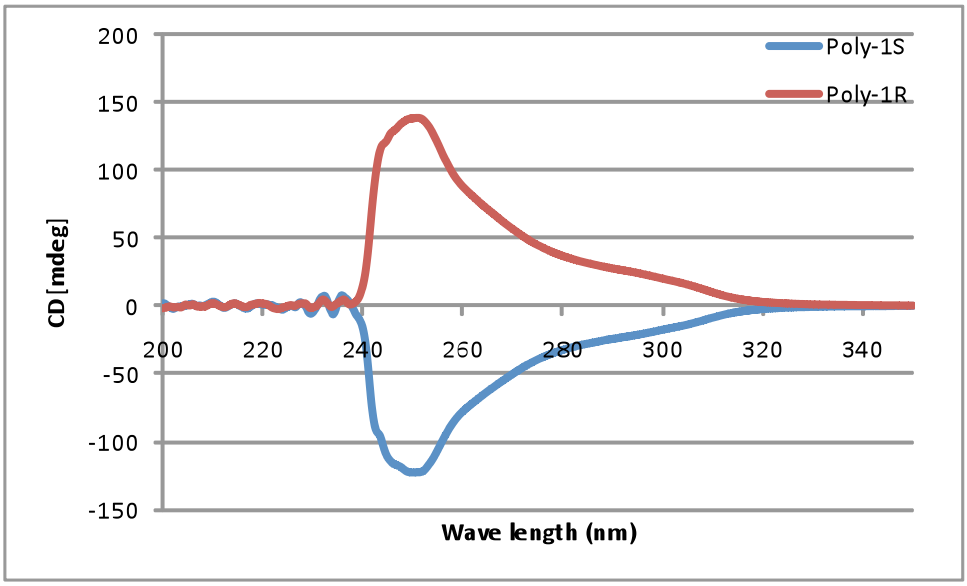


Figure S1: CD spectra of two polymers prepared from enantiomer catalysts under similar conditions. **Poly-1S** was prepared using S-BINOL-Ti catalyst whereas **Poly-1R** was prepared using R-BINOL-Ti catalyst. The concentrations of the samples used were 44 μg/mL in chloroform.

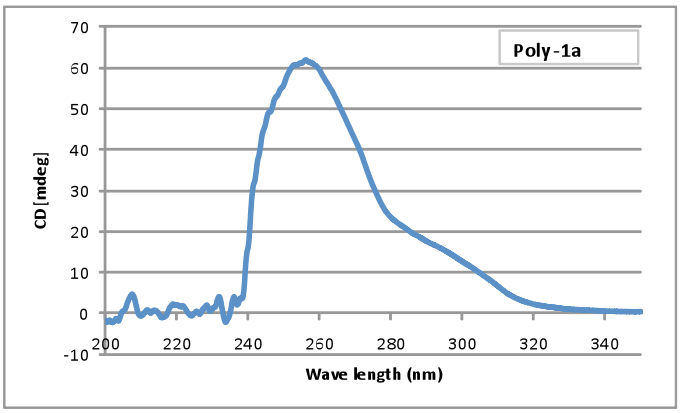


Figure S2: CD spectra of **Poly-1a** prepared from **Poly-1R** after click reaction. The concentrations of the samples used were 44 μg/mL in chloroform.