## Supporting Information

# Controlled cyclopolymerisation of 1,7-octadiyne derivatives using Grubbs catalyst

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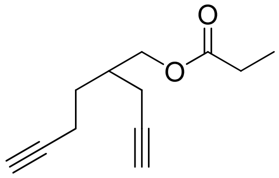
## General experimental

All reagents which are commercially available were used without further purification. Solvents for monomer synthesis were also commercially obtained: dichloromethane (DCM) was anhydrous (≥ 99.8%) grade and tetrahydrofuran (THF) was anhydrous (≥ 99.9%) grade from Sigma-Aldrich®. For polymerisation, THF was distilled from sodium and benzophenone. THF was degassed 10 minutes before using on polymerisation. Thin-layer chromatography (TLC) was carried out on MERCK TLC silica gel 60 F254 and flash column chromatography was performed using MERCK silica gel 60 (0.040~0.063 mm). $^{1}$H NMR and $^{13}$C NMR were recorded by Varian/Oxford As-500 (500 MHz for $^{1}$H and 125 MHz for $^{13}$C) and Bruker (300 MHz for $^{1}$H and 75 MHz for $^{13}$C) spectrometers. UV–vis spectra were measured by Jasco Inc. UV/vis-Spectrometer V-550. Gel permeation chromatography (GPC) for polymer molecular weight analysis was carried out with Waters system (1515 pump, 2414 refractive index detector) and Shodex GPC LF-804 column eluted with THF (GPC grade, Honeywell Burdick & Jackson®). Samples in 0.001-0.003 wt% THF were filtered with a 0.45-μm PTFE filter before injection. Flow rate was 1.0 mL/min and temperature of column was maintained at 35 °C. High resolution mass spectroscopy (HRMS) analyses were performed by the National Center for Inter-University Research Facility.

## Experimental procedure for monomer synthesis (M1-M4)

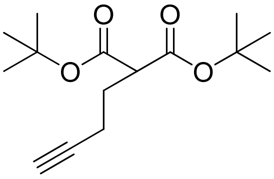
### 2-(prop-2-ynyl)hex-5-ynyl propionate (M1)



To a round bottom flask (RBF) charged with 2-(prop-2-ynyl)hex-5-yn-1-ol[1] 0.09 g, 0.66 mmol), triethylamine (0.12 mL, 1.98 mmol) and 4-dimethylaminopyridine (DMAP) (4.0 mg, 0.033 mmol) in dichloromethane (2 mL), propionic anhydride (0.12 mL, 0.99 mmol) was added. The reaction mixture was stirred for 3 hr at room temperature and was quenched by adding saturated $NaHCO_3$ aqueous solution. The mixture was washed with saturated $NH_4Cl$ solution and extracted by ethyl acetate (75 mL*2). The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 1:10) to afford compound **M1** as a colorless liquid

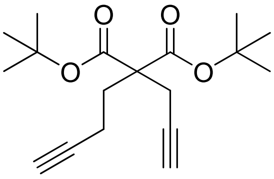
(0.12 g, 98%). $^1$H NMR (500 MHz, $CDCl_3$) : δ 1.15 (t, 3 H, $C(=O)CH_2\underline{CH_3}$), 1.70 (m, 2 H, $CH\underline{CH_2}CH_2$), 1.97 (s, 2 H, CH), 2.11 (s, 1 H, $OCH_2C\underline{H}$), 2.37-2.28 (m, 6 H, $\underline{CH_2}\underline{CH_2}CCH$ + $C(=O)\underline{CH_2}$), 4.11 (m, 2 H, $CH_2O$); $^{13}$C NMR (125 MHz, $CDCl_3$) : δ 9.34, 16.18, 20.22, 27.76, 29.06, 35.66, 65.62, 69.22, 70.45, 81.83, 83.62, 174.59; HRMS(CI+) : calcd. For $C_{12}H_{16}O_2$, 193.1229, found, 193.1233.

**Di-*tert*-butyl 2-(but-3-ynyl)malonate**



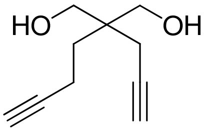
Sodium hydride (60%, dispersion in mineral oil) (100 mg, 2.6 mmol) in DMF (6 mL) was prepared at 0 °C in a RBF purged with argon. Di-*tert*-butyl malonate (0.45 mL, 2.0 mmol) was added by dropwise, and the temperature was raised to 25 °C. After 30 minutes, 4-bromobut-1-yne (0.28 mL, 3.0 mmol) was added and stirred for a day. The reaction was quenched by adding $NH_4Cl$ aqueous solution and extracted with diethyl ether. The oranic layer was dried with $MgSO_4$ and concentrated to give a yellow colored liquid. It was purified by column chromatography on silica gel (EtOAc:Hexane = 1:50) to afford di-*tert*-butyl 2-(but-3-ynyl)malonate as a colorless liquid (422.4 mg, 78%). $^1$H NMR (500 MHz, $CDCl_3$) : δ 1.45 (s, 18 H, $C(CH_3)_3$), 1.98 (s, 1 H, CH), 2.04 (q, 2 H, $\underline{CH_2}CCH$), 2.27 (t, 2 H, $CH\underline{CH_2}CH_2$), 3.36 (t, 1 H, $C(=O)CH$); $^{13}$C NMR (125 MHz, $CDCl_3$) : δ 16.54, 27.60, 28.13, 52.78, 69.54, 81.80, 83.04, 168.61; HRMS(CI+) : calcd. For $C_{15}H_{24}O_4$, 269.1753, found, 269.1764.

**Di-*tert*-butyl 2-(but-3-ynyl)-2-(prop-2-ynyl)malonate (M3)**



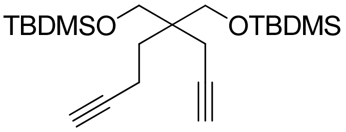
Sodium hydride (60%, dispersion in mineral oil) (54 mg, 1.35 mmol) in DMF (3 mL) was prepared at 0 °C in a RBF purged with argon. Di-*tert*-butyl 2-(but-3-ynyl)malonate (241.7 mg, 0.9 mmol) was added dropwisely, and the temperature was raised to 25 °C. After 30 minutes, propargyl bromide (80% in toluene) (0.13mL, 1.17 mmol) was added and stirred for a day. The reaction was quenched by adding $NH_4Cl$ aqueous solution and extracted with diethyl ether. The oranic layer was dried with $MgSO_4$ and concentrated to give a yellow coloered liquid. It was purified by column chromatography on silica gel (EtOAc:Hexane = 1:50) to afford **M3** as a white solid (267.1 mg, 96%). $^1H$ NMR (500 MHz, $CDCl_3$) : δ 1.46 (s, 18 H, $OC(CH_3)_3$), 1.97 (s, 1 H, CH), 2.01 (s, 1 H, CH), 2.17 (m, 2 H, $C\underline{CH_2}CH_2$), 2.25 (m, 2 H, $CCH_2\underline{CH_2}$), 2.73 (s, 2 H, $C\underline{CH_2}CCH$); $^{13}C$ NMR (125 MHz, $CDCl_3$) : δ 14.05, 23.00, 28.08, 31.09, 57.30, 68.96, 71.63, 79.12, 82.24, 83.55, 169.08; HRMS(CI+) : calcd. For $C_{18}H_{26}O_4$, 307.1909, found, 307. 1905.

**2-(But-3-ynyl)-2-(prop-2-ynyl)propane-1,3-diol**



Dimethyl 2-(but-3-ynyl)-2-(prop-2-ynl)malonate[2] (302.4 mg, 1.36 mmol) was dissolved in THF (4 mL) under argon. Lithium aluminum hydride (LAH) (100 mg, 2.72 mmol) was added at 0 °C and the mixture was allowed to warm to room temperature. After 3 hr, the mixture was cooled down to 0 °C, poured into ethyl acetate and water, and quenched with saturated $NH_4Cl$ aqueous solution. The organic layer was extracted by ethyl acetate. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated. It was purified by flash column chromatography on silica gel (EtOAc:Hexane = 3:1) to afford compound 2-(but-3-ynyl)-2-(prop-2-ynyl)propane-1,3-diol as a white solid (193.1 g, 85%). $^1H$ NMR (500 MHz, $CDCl_3$) : δ 1.72 (t, 2 H, $CH_2\underline{CH_2}CCH_2$), 2.04 (s, 1 H, CH), 2.00 (s, 1 H, CH), 2.12 (t, 2 H, $CH_2\underline{CH_2}CCH$), 2.29 (s, 2 H, $C\underline{CH_2}CCH$), 3.68 (s, 4 H, $\underline{CH_2}OH$); $^{13}C$ NMR (125 MHz, $CDCl_3$) : δ 13.14, 14.41, 21.68, 30.47, 42.01, 67.07, 68.80, 71.33, 80.62, 84.88.; HRMS(CI+) : calcd. For $C_{10}H_{14}O_2$, 167.1072, found, 167.1069.

### 1,3-Di(*tert*-butyldimethylsilyloxy)-2-(but-3-ynyl)-2-(prop-2-ynyl)propane (M4)



*tert*-Butyldimethylsilyl chloride (300 mg, 2.00 mmol) was added to the mixture of 2-(but-3-ynyl)-2-(prop-2-ynyl)propane-1,3-diol (146.2 mg, 0.88 mmol), triethylamine (0.61 mL, 4.4 mmol), and DMAP (5.3 mg, 0.044 mmol) in dichloromethane (2 mL) at 0 °C. The mixture was stirred for 7 hr at room temperature then saturated $NaHCO_3$ aqueous solution was added. The mixture was washed with $NH_4Cl$ aqueous solution and extracted by ethyl acetate (75 mL*2). The organic layer was dried with $MgSO_4$ and concentrated. It was purified by flash column chromatography on silica gel (hexane only) to afford compound **M4** as a colorless liquid (239.7 mg, 69%). $^1$H NMR (500 MHz, $CDCl_3$) : δ 0.04 (s, 18 H, $C(CH_3)_3$), 0.89 (s, 12 H, $SiCH_3$), 1.64 (t, 2 H, $CH_2\underline{CH_2}CCH_2$), 1.94 (s, 2 H, CH), 2.05 (s, 2 H, $C\underline{CH_2}CCH$), 2.15 (t, 2 H, $CH_2\underline{CH_2}CCH$), 3.43 (q, 4 H, $CH_2O$); $^{13}$C NMR (125 MHz, $CDCl_3$) : δ -5.28, 13.29, 18.44, 21.31, 26.00, 30.92, 42.98, 64.11, 68.14, 70.48, 81.42, 85.32; HRMS(CI+) : calcd. For $C_{22}H_{42}O_2Si_2$, 395.2802, found, 395.2799.

## Experimental procedure for catalyst

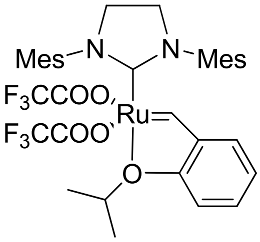
### Third-generation Grubbs catalyst (1)

Second-generation Grubbs catalyst (51.8 mg, 0.0610 mmol) and 3-chloropyridine (1 mL) were mixed in 20-ml sized vial for 5 minutes. Cold *n*-pentane was poured to the vial. After storage in freezer a few hours, the solid was filtered and washed by pentane. The green product (39.1 mg, 0.0491 mmol, 80.5%) was dried *in vacuo* and stored in desiccator.

### General polymerisation procedure (poly(M1) - poly(M4))

Monomer (0.100 mmol) was weighed in a 5-ml sized screw-cap vial with septum and purged with argon. Distilled and degassed solvent (0.4 mL) was added to the vial. The solution of initiator (0.1 mL) was added at once under vigorous stirring. After confirming the monomer conversion by TLC, the reaction was quenched by excess ethyl vinyl ether. The concentrated reaction mixture was precipitated by methanol, and the obtained dark-purple solid was dried *in vacuo*.

### Polymerisation of M3 using other catalyst



**1-b**

We tested the polymerisation of **M3** to confirm the reactivity of **1-b**[4], which was also known Ru catalyst for promoting the cyclopolymerisation of 1,6-hepadiyne derivatives. Catalyst efficiency was checked beforehand by the polymerisation of diethyl dipropargylmalonate over 90% of conversion. The polymerisation condition varied with the solvent (THF/DCM) and temperature (rt – 45 °C). The [M]/[I] was 50, reaction time was over 16 hr, and concentration was 0.4 M. Monomer conversion was confirmed by crude $^1$H NMR, recording roughly 30%. Yield could not be calculated because there was no precipitated polymer but only the suspension of the polymer mixed with remaining monomer. This suspension was analyzed by SEC after dry, resulting in small part of polymer ($M_n$~ 6-7000) and a large peak of unreacted monomer.

### Diblock copolymerisation procedure of poly[(M5)-*b*-(M4)]

2,2-Di(prop-2-ynyl)propane-1,3-diyl dipropionate (**M5**)[5] (0.01 g, 0.038 mmol) was weighed in a 5-ml sized screw-cap vial with septum and purged with argon. Distilled and degassed THF (0.05 mL) was added to the vial. The vial was placed in a cold bath. The solution of initiator (0.0012 g, 0.0015 mmol) in THF (0.05 mL) was added at once under vigorous stirring. After confirming the monomer conversion by TLC (15 minutes), **M4** (0.03 g, 0.076 mmol) in THF (0.2 mL) was added rapidly at room temperature. After 24 hr, the reaction mixture was quenched by excess ethyl vinyl ether. The concentrated reaction mixture was precipitated by methanol, and obtained red solid was dried *in vacuo*.

## $^1$H NMR (500 MHz, $CDCl_3$) characterisation of polymers

Poly(**M1**): δ 1.15 (br m, 3 H, $C(=O)CH_2\underline{CH_3}$), 1.70 (br m, 2 H, $CH\underline{CH_2}CH_2$), 2.03 (br m, 1 H, $OCH_2C\underline{H}$), 2.36 (br m, 6 H, $\underline{CH_2}\underline{CH_2}CCH + C(=O)\underline{CH_2}$), 4.07 (m, 2 H, $CH_2O$), 7.05 (br m, 2 H, $H_{olefin}$)

Poly(**M2**): δ 2.20-2.34 (br m, 4 H, $C\underline{CH_2}\underline{CH_2}$), 2.94 (br m, 2 H, $CCH_2$), 3.75 (br m, 6 H, $CH_3$), 7.05 (br m, 2 H, $H_{olefin}$)

Poly(**M3**): δ 1.45 (br m, 18 H, $C(CH_3)_3$), 2.14 (br m, 2 H, $C\underline{CH_2}CH_2$), 2.43 (br m, 2 H, $CCH_2\underline{CH_2}$), 2.75 (br m, 2 H, $C\underline{CH_2}CCH$), 7.05 (br m, 2 H, $H_{olefin}$)

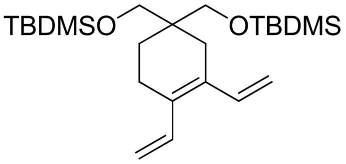
Poly(**M4**): δ 0.07 (br m, 12 H, $SiCH_3$), 0.88 (br m, 18 H, $SiC(CH_3)_3$), 1.61 (br m, 2 H, $CH_2\underline{CH_2}CCH_2$), 2.25, 2.17 (br d, 2 H, $C\underline{CH_2}CCH$), 2.40 (br m, 2 H, $CH_2\underline{CH_2}CCH$), 3,45 (br m, 4 H, $CH_2O$), 7.05 (br m, 2 H, $H_{olefin}$)

*Block copolymer* - poly[(**M5**)$_{25}$-*b*-(**M4**)$_{50}$]: δ 0.07 (br m, 12 H, $SiCH_3$), 0.88 (br m, 18 H, $SiC(CH_3)_3$), 1.17 (br s, 6 H, $CH_3$), 1.61 (br m, 2 H, $CH_2\underline{CH_2}CCH_2$), 2.53 (br s, 4 H, $C(=O)CH_2$), 2.43 (br s, 4 H, $CCH_2 + C\underline{CH_2}CCH + CH_2\underline{CH_2}CCH$), 3,45 (br m, 4 H, $CH_2O$), 4.11 (br s, 4 H, $CH_2O$), 6.63 (br s, 2 H, $H_{olefin\text{-}6membered\ ring}$), 7.05 (br m, 2 H, $H_{olefin\text{-}5membered\ ring}$).

*Random copolymer* of **M4** and **M5**: δ 0.07 (br m, 12 H, $SiCH_3$), 0.88 (br m, 18 H, $SiC(CH_3)_3$), 1.17 (br s, 6 H, $CH_3$), 1.61 (br m, 2 H, $CH_2\underline{CH_2}CCH_2$), 2.53 (br s, 4 H, $C(=O)CH_2$), 2.43 (br s, 4 H, $CCH_2 + C\underline{CH_2}CCH + CH_2\underline{CH_2}CCH$), 3,45 (br m, 4 H, $CH_2O$), 4.11 (br s, 4 H, $CH_2O$), 6.63 (br s, $H_{olefin\text{-}6membered\ ring}$), 6.85 (br s, $H_{olefin\text{-}mixture}$), 7.05 (br m, $H_{olefin\text{-}5membered\ ring}$).

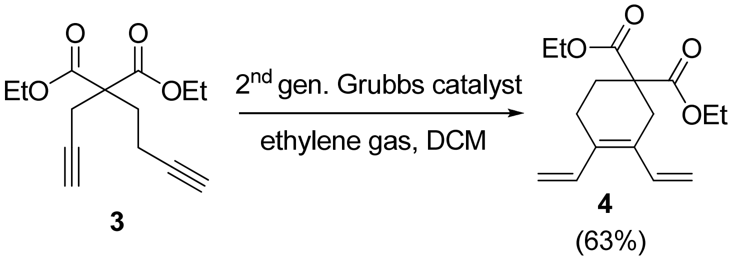
## Ene-yne reaction procedure

### 3,4-Divinylcyclohex-3-ene-1,1-diyl)bis(methylene)bis(oxy)bis(*tert*-butyldimethylsilane (2)



**M4** (39.7 mg, 0.1 mmol) was weighed in a 25-ml sized RBF with septum and air was exchanged to ethylene gas. Distilled and degassed DCM (9.5 mL) was added to the flask. Hoveyda-Grubbs second-generation catalyst (5 mol%) in DCM (0.5 mL) was added at once under vigorous stirring. This catalyst addition was done at every 24 hr after reaction, making total catalyst addition to 15 mol%. After 72 hr, the reaction was quenched by excess ethyl vinyl ether. The concentrated reaction mixture was purified by flash column chromatography on silica gel (Hexane) to afford compound **2** as a colorless liquid (19.5 mg, 43 %). $^1$H NMR (500 MHz, $CDCl_3$) : δ 0.01 (s, 12 H, $SiCH_3$), 0.74 (s, 18 H, $SiC(CH_3)_3$), 1.49 (s, 2 H, $CH_2CCH_2CH_2$), 2.05 (s, 2 H, $CCH_2CCH$), 2.24 (s, 2 H, $CCH_2CH_2CCH$), 3.40 (dd, 4 H, $OCH_2$), 5.05 (st, 1 H, $H_{olefin}$), 5.19 (sd, 1 H, $H_{olefin}$), 7.04 (t, 1 H, $H_{olefin}$); $^{13}$C NMR (125 MHz, $CDCl_3$) : δ -5.27, 18.50, 22.35, 25.03, 26.13, 30.29, 38.83, 65.36, 112.82, 112.94, 131.55, 132.42, 133.79, 134.16; HRMS(CI+) : calcd. For $C_{24}H_{46}O_2Si_2$, 422.3036, found, 422.3037.

### Diethyl 3,4-divinylcyclohex-3-ene-1,1-dicarboxylate (4)



Diethyl 2-(but-3-ynyl)-2-(prop-2-ynyl)malonate (**3**)[6] (25 mg, 0.1 mmol) was weighed in a 25-ml sized round bottom flask with septum and air was exchanged to ethylene gas. Distilled and degassed DCM (9.5 mL) was added to the flask. Hoveyda-Grubbs second-generation catalyst (6 mol%) in DCM (0.5 mL) was added at once under vigorous stirring. After 24 hr, the reaction was quenched by excess ethyl vinyl ether. The concentrated reaction mixture was purified by flash column chromatography on silica gel (Ethyl Acetate : Hexane = 1 : 10) to afford compound **4** as a colorless liquid (19.5 mg, 63%). $^1$H NMR (500 MHz, $CDCl_3$) : δ 1.24 (t, 6 H, $CH_3$), 2.18 (s, 2 H, $CH_2C\underline{CH_2}CH_2$), 2.35 (s, 2 H, $C\underline{CH_2}CCH$), 2.85 (s, 2 H, $CCH_2\underline{CH_2}CCH$), 4.19 (q, 4 H, $O\underline{CH_2}CH_3$), 5.09 (d, 1 H, $H_{olefin}$), 5.13 (d, 1 H, $H_{olefin}$), 5.19 (d, 1 H, $H_{olefin}$), 5.29 (d, 1 H, $H_{olefin}$), 6.99 (t, 1 H, $H_{olefin}$), 7.02 (t, 1 H, $H_{olefin}$); $^{13}$C NMR (75 MHz, $CDCl_3$) : δ 14.04, 22.79, 27.10, 31.05, 53.05, 61.41, 113.52, 113.54, 129.96, 131.25, 133.09, 171.40; HRMS(EI+) : calcd. For $C_{16}H_{22}O_4$, 278.1518, found, 278.1515.

## $^{13}$C NMR analyses for six-membered ring unit of poly(M4)

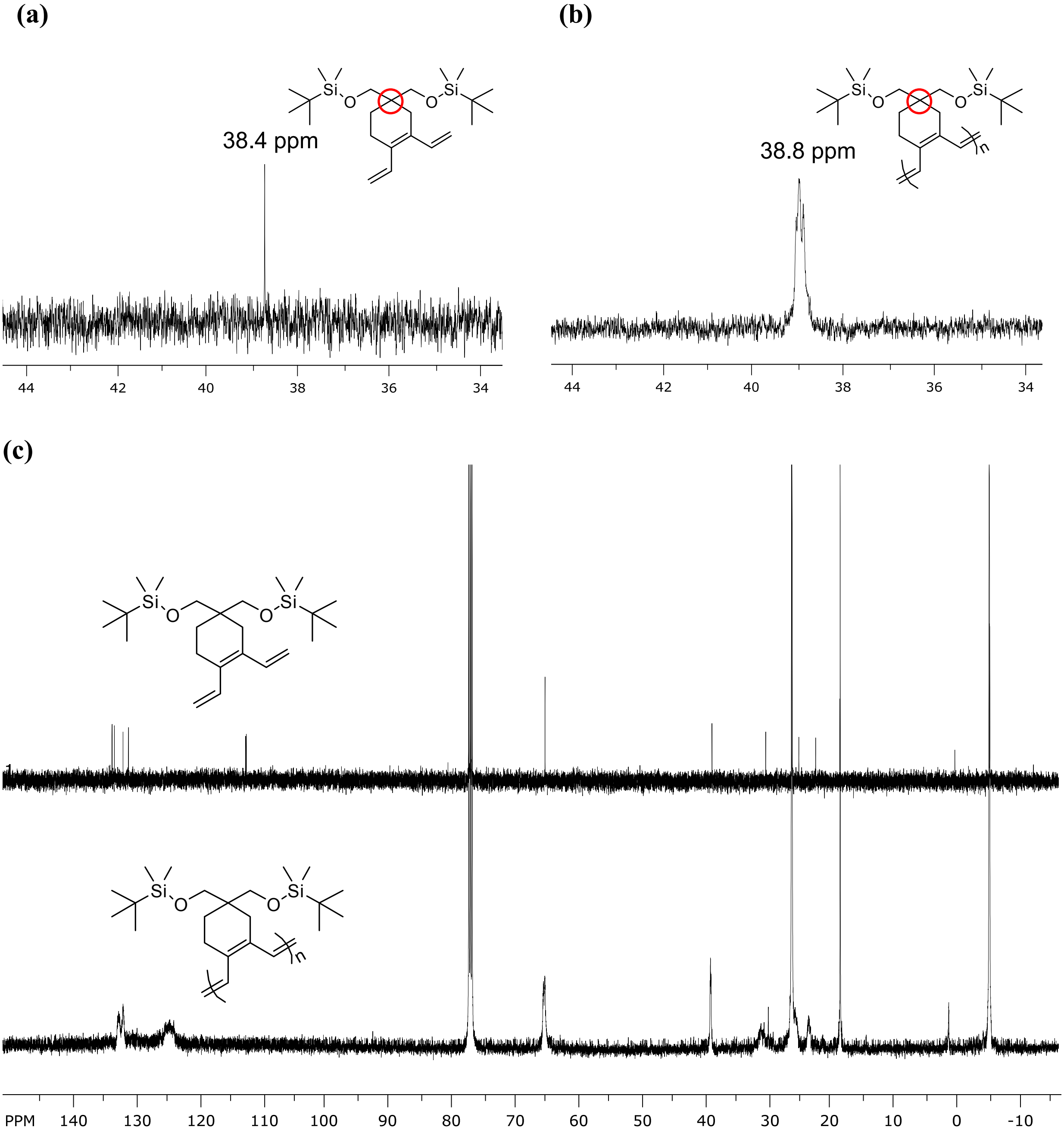


**Figure S1** $^{13}$C NMR peaks for (a) quaternary carbon of ene-yne reaction product **2**, (b) quaternary carbon of poly(**M4**). The broader peak around 38.8 ppm on the polymer might be caused by inevitable formation of head-to-head, head-to-tail, and tail-to-tail isomers. (c) Full $^{13}$C NMR of ene-yne reaction product **2** and full $^{13}$C NMR of poly(**M4**)

## $^1$H NMR analysis for six-membered ring of poly(3)

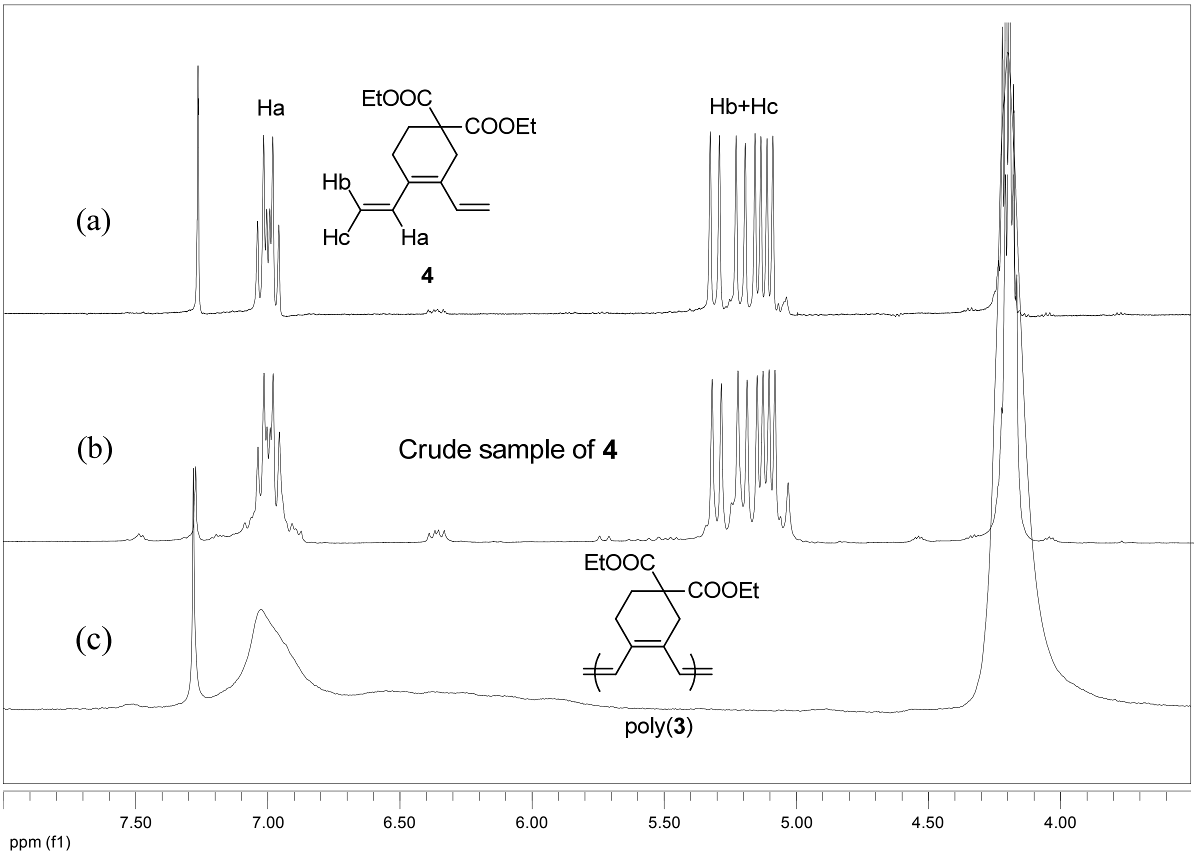


**Figure S2** $^1$H NMR spectrum for (a) olefinic NMR spectrum of **4**, (b) crude NMR spectrum of **4** before purification, and (c) olefinic NMR spectrum of poly(**3**). It suggests that only six-membered ring product is synthesised through olefin metathesis reaction.

## $^{13}$C NMR analyses for six-membered ring unit of poly(3)

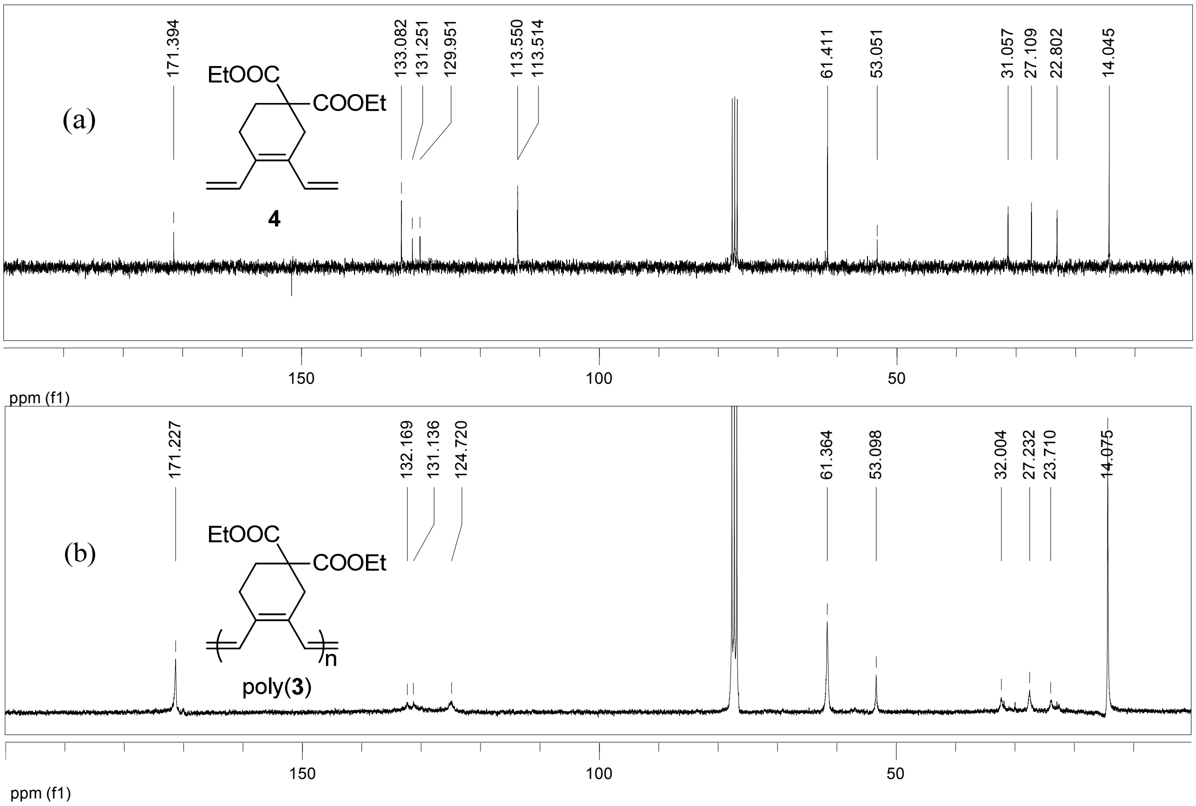
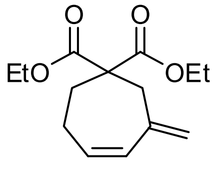


**Figure S3** $^{13}$C NMR spectrum of (a) **4** and (b) poly(**3**).



**5**

**5** is the previously reported diethylmalonate derived compounds with seven-membered ring.[3]

$^{13}$C NMR spectrum of aliphatic carbons on poly(**3**), **4** and **5** are

Poly(**3**) : 14.08, 23.71, 27.34, 32.00, 53.10

**4** (six-membered ring): 14.04, 22.79, 27.10, 31.05, 53.05

**5** (seven-membered ring): 14.26, 24.67, 33.81, 39.72, 57.34

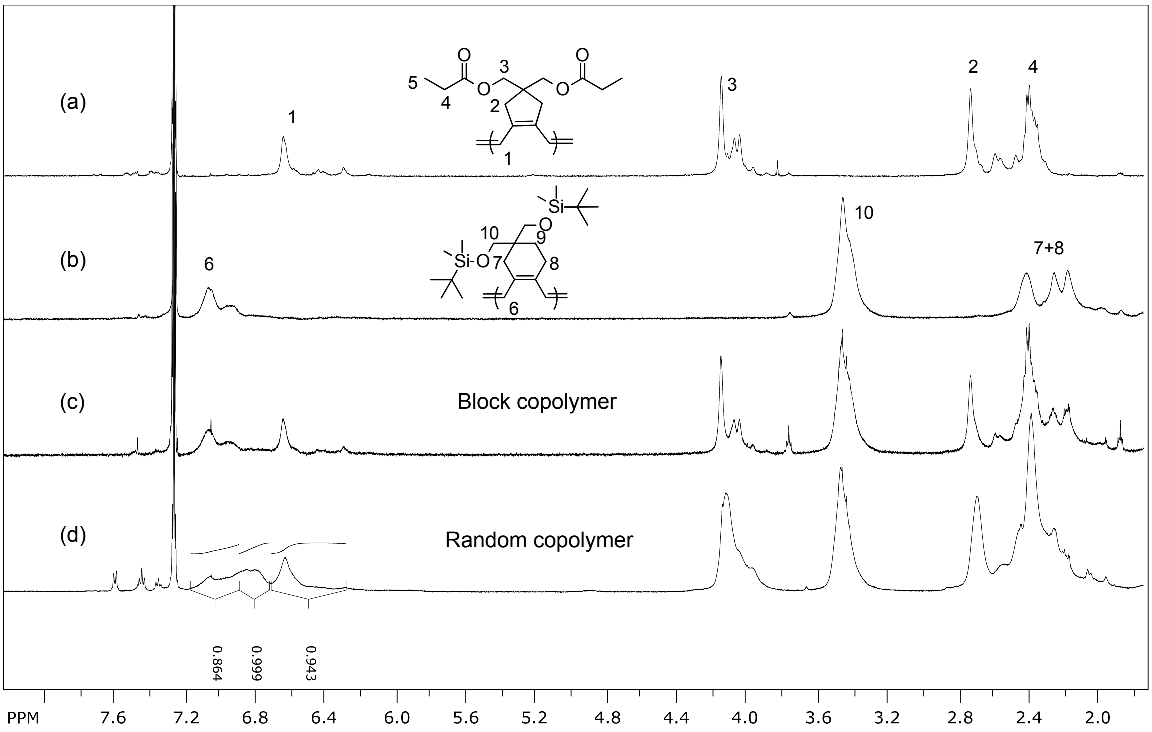


**Figure S4** $^1$H NMR spectrum of (a) poly(**M5**), (b) poly(**M4**), (c) poly[(**M5**)$_{25}$-*b*-(**M4**)$_{50}$] and (d) random copolymer (**M4M4**(6):**M5M4**(13):**M5M5**(5) = 0.86:1.00:0.94, It indicated that this polymer is random (statistical) polymer)

## UV-vis analysis of Poly(M4)

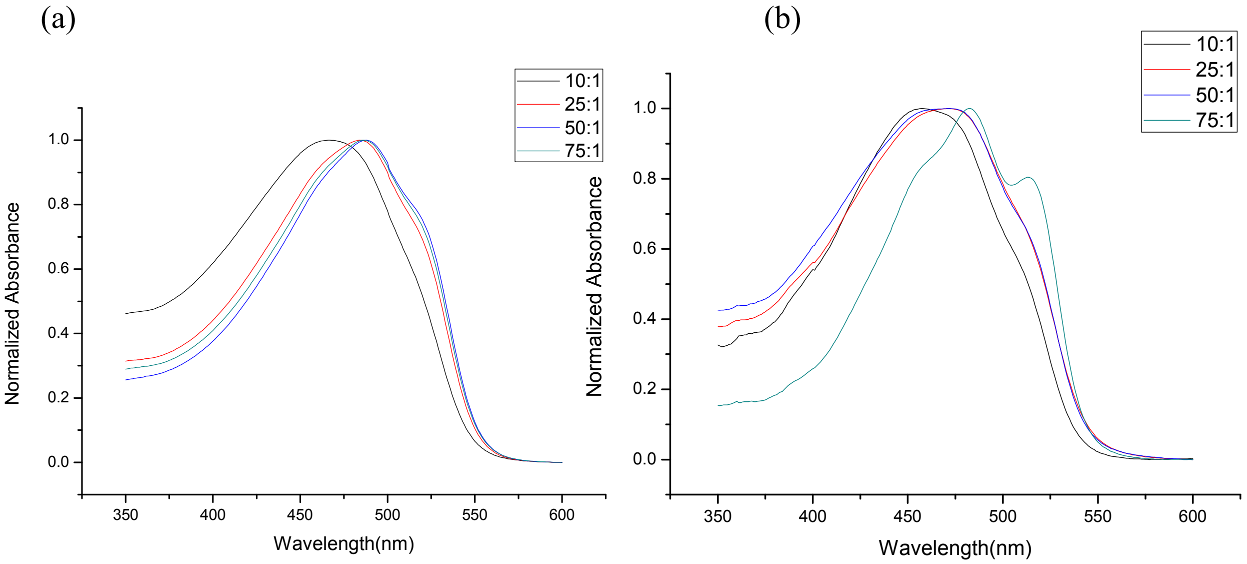


**Figure S5** UV spectra of poly(**M4**) (a) in $CHCl_3$ solution and (b) in thin film with different DPs (n = 10–75)

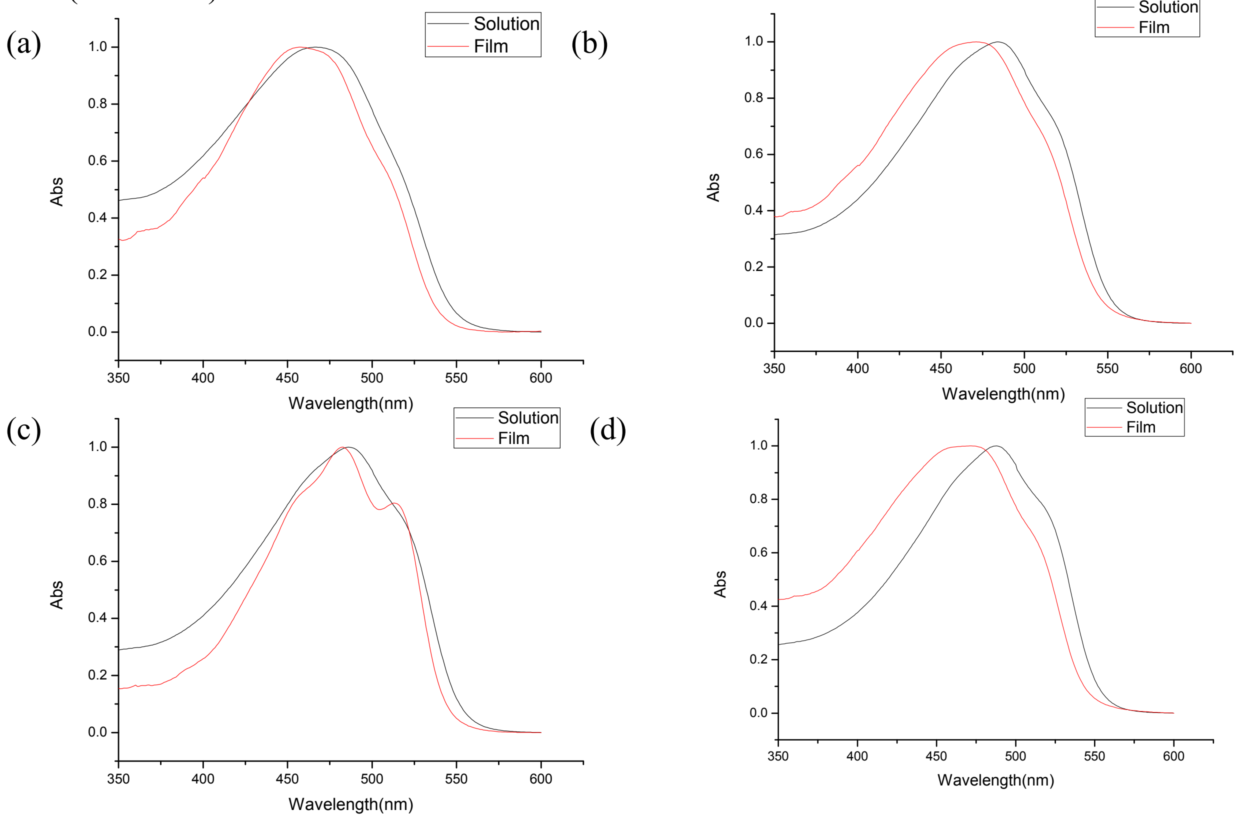


**Figure S6** UV spectra of poly(**M4**) (a) DP=10. $\lambda_{max}$ = 467 nm in $CHCl_3$ solution and 458 nm in thin film. (b) DP=25. $\lambda_{max}$ = 484 nm in $CHCl_3$ solution and 471 nm in thin film. (c) DP=50. $\lambda_{max}$ = 488 nm in $CHCl_3$ solution and 472 nm in thin film. (d) DP=75. $\lambda_{max}$ = 486 nm in $CHCl_3$ solution and 482, 513 nm in thin film.

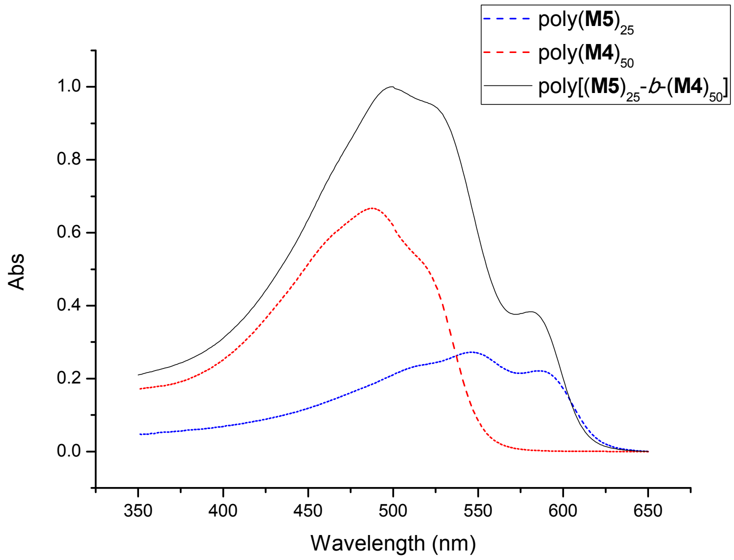


**Figure S7** UV spectra of poly[(**M5**)$_{25}$-*b*-(**M4**)$_{50}$] ($\lambda_{max}$ = 500, 581 nm in $CHCl_3$ solution), poly(**M5**)$_{25}$ ($\lambda_{max}$ = 546, 586 in $CHCl_3$ solution state) and poly(**M4**)$_{50}$ ($\lambda_{max}$ = 488 in $CHCl_3$ solution state).

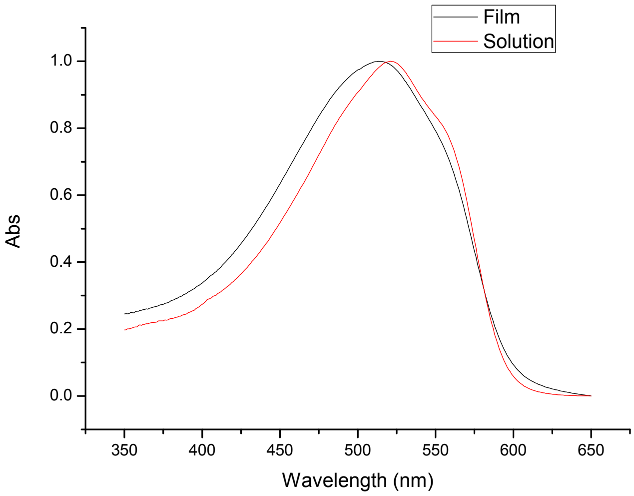


**Figure S8** UV spectra of random copolymer ($\lambda_{max}$ = 521 nm in $CHCl_3$ solution and 513 nm in thin film)

## References

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