Electronic Supplementary Material (ESI) for Chemical Communications. This journal is © The Royal Society of Chemistry 2021

## **Electronic Supplementary Information**

#### for

## Kinetically Controlled Synthesis of Supramolecular Block Copolymers with Narrow Dispersity and Tunable Block Lengths

Aritra Sarkar, Ranjan Sasmal, Angshuman Das, Sarit S. Agasti and Subi J George\*

New Chemistry Unit and School of Advanced Materials (SAMAt), Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur, Bangalore, India-560064. Email: george@jncasr.ac.in

## **Table of Contents**

- 1. General Methods
- 2. Experimental Section
- 3. Synthetic Schemes and Procedures
- 4. Supporting Figures
- 5. References

#### **1. General Methods**

**NMR Measurements:** NMR spectra were recorded with a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer and JEOL 600 MHz NMR spectrometer with chemical shifts reported in parts per million (ppm) with respect to TMS. Splitting patterns are designated as s, singlet; d, doublet; bs, broad singlet; m, multiplet; t, triplet; q, quartet; quin, quintet and br, broad.

**Optical Measurements:** Electronic absorption spectra were recorded on a Perkin Elmer Lambda 900 UV-Vis-NIR Spectrometer. Circular Dichroism (CD) spectra were recorded on a Jasco J-815 spectrometer where the sensitivity, time constant and scan rate were chosen appropriately. Emission spectra were recorded on Perkin Elmer LS 55 Luminescence Spectrometer.

**Transmission Electron Microscopy (TEM):** TEM measurements were performed on a JEOL, JEM 3010 operated at 300 kV. Samples were prepared by placing a drop of the solution on carbon-coated copper grids followed by drying at room temperature. The images were recorded with an operating voltage of 300 kV.

**Matrix-Assisted Laser Desorption Ionization (MALDI):** MALDI was performed on a Bruker daltonics Autoflex Speed MALDI TOF System (GT0263G201) spectrometer using trans-2-[3-(4-tert-Butylphenyl)-2methyl-2-propenylidene] malononitrile (DCTB) as the matrix.

**Structured Illumination Microscopy (SIM):** Optical setup for imaging in Structured Illumination Microscopy (SIM) method: The fluorescence images of supramolecular polymers were acquired using an inverted Zeiss 3 ELYRA PS1 microscope in structured illumination mode. Two lasers channel I - 488 nm (200 mW) (Green channel) and channel II - 561 nm (200 mW) (Red channel) have been used for respective excitation of 1 and 3 fluorophores. 10 % laser power from the objective top was used for structured illumination imaging. Imaging was performed using a Zeiss oil–immersion objective (Plan–apochromat 63x/1.40 Oil DIC M27, numerical aperture (NA) 1.40

oil). Fluorescence light was spectrally filtered with emission filters for the channel I - MBS-488+EF BP 495-575/LP 750 for laser line 488 nm (green channel) and channel II - MBS- 561+EF BP 570- 650/LP 750 for laser line 561 nm (red channel) and imaged using a PCO edge sCMOS camera (quantum yield > 70 %). Structured illumination images were processed using a structured illumination analysis package for Zen software (Zeiss). ImageJ was additionally used for processing images ). The channels were merged to investigate the spatial correlation between green and red-emitting fibers.

**Polydispersity index (PDI) calculation from SIM images:** SIM images were recorded for block copolymers (BCP) via merging channel I and channel II. Then 100 fibres were selected from different regions of the grid and analyzed using ImageJ software package developed by US, National Institute of Health to calculate the length of green stacks, red stacks and the overall length of the BCP. The average length and PDI were calculated using the following equations 1-3 equations. Where Ni is the number of fibres chosen for analysis and Li is the length of fibres for the sample.

Number average length, 
$$L_n = \sum_{i=1}^n \frac{N_i L_i}{N_i}$$
 (1)

Weight average length, 
$$L_w = \sum_{i=1}^n \frac{N_i L_i^2}{N_i L_i}$$
 (2)

Polydispersity index, 
$$PDI = \frac{L_w}{L_n}$$
 (3)

For details regarding the treatment of SIM images to calculate the length of the green segment, reg segment and overall block length please refer to figure S24.

## 2. Experimental Section

**Protocol I: Sample preparation protocol for 1 and 2 homopolymers:** A stock solution of **1** or **2** ( $c = 5 \times 10^{-3}$  M) was prepared in TCE. Required volumes of this stock is added to a TCE/MCH mixture and the solution was incubated for 2 hours to synthesize the homopolymers after which the spectroscopic investigations were performed.

For example, 12.5  $\mu$ L of 5×10<sup>-3</sup> M stock of **1** is added to a premixed solution of 112.5  $\mu$ L of toluene and in 2375  $\mu$ L of methylcyclohexane (MCH) to prepare the final self-assembling solution of 5×10<sup>-5</sup> M, 5 % toluene/MCH with total 2500  $\mu$ L sample volume.

**Protocol II: Sample preparation protocol for 1 and 2 to perform the kinetic experiment:** To spectroscopically monitor the kinetics of transformation of the metastable state of **1** and **2** into the homopolymeric state, we have added the required volume of stock into the TCE/MCH solvent mixture (see protocol I) to prepare respective solvent composition and concentration and have

immediately placed the cuvette into the spectrometer for spectroscopic probing of the transformation of metastable state into homopolymeric state.

**Protocol III: Preparation of supramolecular block copolymer:** A Seed solution of **1** was prepared by sonicating a hot solution (363 K) of **1** homopolymers (of different concentration) for 2 hours in an ultrasonic bath maintained at 298 K. The monomeric solution of **2** in TCE ( $5 \times 10^{-3}$  M) was then added into the sonicated seed solution and kinetics of the process was monitored following absorbance changes at 395 nm by immediately placing the cuvette into the spectrometer.

**3.** Synthetic Schemes and Procedures: Synthetic schemes for Synthesis of **1**, **2**, and **3** are shown in Scheme S1, Scheme S2 and Scheme S3. Molecules **S1**, **S2** and **S5** were synthesized following reported procedures. <sup>S1, S2</sup>

## 3.1. Synthetic Schemes



Scheme S1. Synthetic route to molecule 1



Scheme S2. Synthetic route to 2



Scheme S3. Synthetic route to 3

## **3.2. Synthetic Procedures**

Molecules S1 and S2 were synthesized following reported procedures.<sup>S1,S2</sup>

Synthesis of **S3**: Compound **S1** (461 mg, 1.08 mmol) was taken in a 100 mL round bottom (RB) flask and to it an acetic acid solution of **S2** (1.54 g, 3.25 mmol) was added. The reaction mixture was heated at 90 °C for 20 hrs. The extent of the reaction was monitored by thin layer chromatography. After completion of the reaction cold water was added to it and an orange coloured precipitate was obtained. The precipitate was filtered and washed thoroughly with water and methanol followed by drying at room temperature. The crude product obtained was loaded into 230-400 mesh silica gel and was purified using a gradient ranging from 1-2% MeOH/CHCl<sub>3</sub> to get the pure product as orange solid. The yield obtained was 14 %.<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, TMS): 8.99 (s, 2H), 5.12 (s, 2H), 4.93 (d, J= 5.4 Hz, 2H), 4.40 (t, J = 6 Hz, 4H), 4.24 (s, br, 2H), 3.59 (m, 4H), 2.2-1.95 (m, 4H), 1.9-1.6 (m, 10H), 1.59-1.25 (m, 14H), 0.97-0.85 (m, 52H), 0.67 (d, J = 9 Hz, 6H). MALDI-TOF (DCTB, negative mode): m/z calculated for C<sub>74</sub>H<sub>104</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>8</sub>: 1335.61; found: [M]<sup>±</sup> = 1336.00 (Molecular ion peak is observed as radical ions due to the electron deficient nature of naphthalene diimide cores). We could not record <sup>13</sup>C-NMR of **S3** due to low solubility in CDCl<sub>3</sub>.

Synthesis of **1**: Compound **S3** (209 mg, 0.156 mmol) was taken in a 2-necked 100 mL round bottom flask.  $K_2CO_3$  (216 mg, 1.565 mmol), excess ethane thiol (3 mL) and 40 mL chloroform was added to it and refluxed at 50 °C for 2 days. The reaction was monitored by thin layer chromatography. After completion the reaction the excess ethane thiol and chloroform were evaporated under reduced pressure and loaded into silica gel (230-400 mesh) and purified using a gradient ranging from 0.1-0.5 % MeOH/CHCl<sub>3</sub> to get a red coloured powder. The yield obtained was 83 %.<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, TMS): 8.58 (s, 2H), 5.37-5.14 (m, 4H), 4.38 (m, 6H), 3.60 (m, 4H), 3.23 (q, J = 6Hz, 4H), 2.13-1.86 (m, 4H), 1.83-1.52 (m, 10H), 1.5-1.42 (m, 20H), 1.35-0.85 (m, 52H), 0.66 (s, 6H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, TMS) = 162.44, 162.34, 162.08, 156.37, 149.08, 148.89, 139.76, 127.99, 122.54, 122.37, 74.28, 56.71, 56.67, 56.16, 49.95, 42.32, 40.71, 39.73, 39.53, 38.54, 37.00, 36.52, 36.20, 35.81, 31.87, 28.24, 28.02, 26.46, 24.29, 23.86, 22.82, 22.56, 21.03, 19.31, 18.72, 12.80, 11.87. Elemental analysis calculated for C<sub>78</sub>H<sub>112</sub>S<sub>2</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>8</sub>: C 72.18, H 8.70, N 4.32, S 4.94; found: C 72.52, H 8.91, N 4.69, S 4.47. MALDI-

TOF (DCTB matrix, negative mode): m/z calculated for  $C_{78}H_{112}S_2Br_2N_2O_8$  [M]<sup>+</sup> = 1297.80; found [M]<sup>-</sup> = 1297.51 (Molecular ion peak is observed as radical ions due to the electron deficient nature of naphthalene diimide cores).

Synthesis of 2: Compound 1 (500 mg, 1.86 mmol) and S2 (2.2 g, 4.66 mmol) were taken in 250 mL 2-necked round bottom flask fitted with refluxed condenser and a continuous N<sub>2</sub> flow. Then 75 mL dry DMF was added to the reaction mixture and heated at 130 °C for 15-20 min until the compound gets dissolved in to the DMF. The heating is continued for another 10 hours. The progress of the reaction was monitored by thin layer chromatography. After 12 hrs when the reaction is completed the reaction mixture is allowed to cool down to room temperature. A precipitate was observed at the bottom of the round bottom flask. MeOH was added into it to complete the precipitation. The precipitate was filtered and washed thoroughly with MeOH and toluene mixture to remove the coloured portion of the precipitate. The white coloured precipitate obtained after washing with methanol and toluene was further washed with methanol to remove the excess of toluene. Finally the white solid obtained was kept for drying overnight under vacuum. Then the compound was loaded into normal silica gel (100 mesh) for further purification using a gradient ranging from 1-2% MeOH/CHCl<sub>3</sub>.The compound was obtained as white powder with a yield of 61 %. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>,  $\delta$  ppm, TMS): 8.75 (s, 4H), 5.15-4.99 (m, 4H), 4.39-4.28 (m, 6H), 3.59 (t, J = 7.8, 4H), 2.09-1.68 (m, 14H), 1.54-0.85 (m, 68H), 0.66 (s, 6H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, δ ppm, TMS) = 163.40, 156.61, 139.97, 131.37, 126.79, 122.61, 74.63, 56.90, 56.38, 50.19, 42.54, 40.71, 39.95, 39.77, 38.58, 37.12, 36.75, 36.43, 36.04, 32.11, 32.09, 28.47, 28.26, 28.20, 24.52, 24.09, 23.06, 22.80, 21.25, 19.54, 18.96, 12.09. Elemental analysis calculated for C<sub>74</sub>H<sub>104</sub>N<sub>4</sub>O<sub>8</sub>: C 75.47, H 8.90, N 4.76; found: C 75.31, H 8.81, N 5.20. MALDI-TOF (DCTB, negative mode): m/z calculated for  $C_{74}H_{104}N_4O_8$ : 1176.79; found: [M]<sup>+</sup> = 1176.92 (Molecular ion peak is observed as radical ions due to the electron deficient nature of naphthalene diimide cores).

Synthesis of **S6: S5** (1 g, 1.98 mmol) was taken in a round bottom flask and 200 mL of 1 M KOH in isopropanol solution was added to it and refluxed for 72 hours. After 72 hours, the excess isopropanol was evaporated and the residue obtained was directly used for the next reaction without further purification.

Synthesis of **3**: Compound **S5** (711 mg, 1.812 mmol) was taken in a 250 mL round bottom flask and a solution of **S2** in glacial acetic acid was added. The reaction mixture was heated at 90 °C for 20 hrs. The extent of reaction is monitored by thin layer chromatography. After completion of the reaction excess of water was added to it to get a light orange coloured precipitate. The precipitate was filtered and washed thoroughly with methanol and kept overnight for drying under vacuum. The crude obtained was loaded in to 230-400 mesh silica gel for further purification. The yield obtained was 14 %. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  (in ppm) = 8.45 (s, 2H), 5.17- 5.04 (m, 4H), 4.49 (q, J = 6.6 Hz, 4H), 4.36 (m, 6H), 3.57 (m, 4H), 2.16-2.13 (m, 4H), 2.01-1.7 (m, 8H), 1.61 (t, J = 6.6 Hz, 6H), 1.55-1.01 (m, 20H), 0.97-0.86 (m, 48H), 0.67 (s, 6H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (in ppm) = 162.69, 161.27, 160.02, 156.33, 139.74, 126.97, 123.55, 122.38, 119.63, 110.42, 74.25, 66.35, 56.63, 56.11, 49.91, 42.28, 40.23, 39.68, 39.50, 38.38, 36.88, 36.49, 36.16, 35.79, 31.83, 29.69, 28.21, 28.00, 27.96, 24.26, 23.83, 22.81, 22.54, 20.99, 19.28, 18.69, 14.78, 11.83. Elemental analysis calculated for C<sub>78</sub>H<sub>112</sub>N<sub>2</sub>O<sub>10</sub>: C 74.01, H 8.92, N 4.43; found: C 73.45, H

8.80, N 4.81. MALDI-TOF (DCTB matrix, negative mode): m/z calculated for  $C_{78}H_{112}N_2O_{10}$  [M]<sup>+</sup> = 1264.84; found [M]<sup>+</sup> = 1265.24 (Molecular ion peak is observed as radical ions due to the electron deficient nature of naphthalene diimide cores).



# 4.Supporting figures

**Figure S1.** Solvent composition dependent a) absorption, b) CD, and c) emission ( $\lambda_{ex}$ = 490 nm) spectra of molecule **1**. Normalized absorption spectra of molecule **1** in homopolymeric and monomeric state at d) 530 nm and e) 370 nm. Normalized f) emission spectra ( $\lambda_{ex}$  = 490 nm) and g) excitation spectra of molecule **1** in homopolymeric and monomeric state. h) Lifetime decay profile ( $\lambda_{ex}$  = 532 nm,  $\lambda_{coll}$  = 600 nm) in monomeric (TCE) and homopolymeric (TCE/MCH, 5/95 (v/v) states of **1**. ([**1**] = 2.5×10<sup>-5</sup> M, l = 10 mm).

**Note:** Molecule **1** remains in its monomeric state in TCE and in its self-assembled state in TCE/MCH solvent mixture (TCE/MCH, 10/90 (v/v) to TCE/MCH, 1/99 (v/v)) which is evident from change in intensity between vibronic transitions of  $\pi$ - $\pi$ \* absorption band (from A<sub>370</sub> /A<sub>353</sub> = 1.2 in TCE to 1.0 in TCE/MCH, 5/95 (v/v)) for **1** and broadening and shift in n- $\pi$ \* absorption band. This is accompanied by an appearance of CD spectrum corresponding to the n- $\pi$ \* absorption band, a red shift in emission maximum and red-shifted excitation spectra in case of homopolymers compared to monomeric state. Lifetime decay profile indicated a different lifetime decay profile for homopolymeric state compared to the monomeric state. These changes

in spectral properties are in accordance with  $\pi$ -stacking between the chromophores.<sup>S3</sup> Although the changes in absorption spectra (red shift in intermediate solvent composition to broadening and hypochromic shift at a higher percentage of MCH) are not in line with the formation of Jaggregates, the different emission maximum, excitation spectra and lifetime decay profile of homopolymeric state indicated the formation of fluorescent aggregates. Since the exact derivation of molecular packing to interpret the observed absorption spectral changes would require computational investigation, we could not assign the formation of H- or J-aggregates. However, the mentioned changes in emission spectra, excitation spectra, and lifetime points towards the formation of fluorescent aggregates helped to visualize the homopolymers and block copolymers under the SIM microscope.

TCE/MCH (v/v)	$\lambda_{coll}$ (nm)	t1 (ns)	t2 (ns)	t₃ (ns)
100/0	590	1.12 (6.44 %)	5.00 (20.11 %)	0.04 (73.45 %)
5/95	590	1.49 (32.88 %)	5.35 (2.02 %)	0.7 (65.10 %)

**Table S1.** Lifetime data of monomeric **1** in TCE and homopolymeric **1** in TCE/MCH, 5/95 (v/v). ([**1**] =  $2.5 \times 10^{-5}$  M).



**Figure S2.** Solvent composition-dependent a) absorption, b) CD spectra of molecule **2**. c) LD spectrum of the self-assembled **2** and its comparison with CD spectrum in the self-assembled state. d) Emission spectra of monomeric **2** in TCE and homopolymeric **2** in TCE/MCH, 1/99 (v/v). (TCE/MCH, 5/95 (v/v)). ([**2**] =  $2.5 \times 10^{-5}$  M, I = 10 mm).

**Note:** The solvent composition-dependent absorption spectra show a change in intensity between the vibronic transition of  $\pi$ - $\pi^*$  absorption band (A<sub>380</sub>/A<sub>360</sub> = 1.13 in TCE to 1.08 in TCE/MCH), and appearance of CD signal corresponding to  $\pi$ - $\pi^*$  absorption band which is evidence of  $\pi$ -stacking between chromophores at higher percentages of MCH. The overlayed LD spectrum (Fig. S2c) suggests the CD spectrum of homopolymeric **2** is contaminated with LD. We

have observed a similar shift in solvent composition-dependent absorption spectrum (red shift in intermediate solvent composition which moves back to monomer absorption spectrum at higher % of MCH) as seen during solvent composition-dependent studies for **1**. The exact derivation of packing between chromophores leading to these changes will require computational investigation and is beyond the scope of the current manuscript. However, the emission changes suggested a quenching of emission for **2** upon homopolymerization, hence we have visualized the homopolymers of **2** using 1 % of fluorescent **3** as a fluorescent marker.



**Figure S3.** a) Normalized absorption (solid lines) and emission (dotted lines,  $\lambda_{ex}$  = 490 nm) spectra of the monomeric (TCE) and homopolymeric (TCE/MCH, 5/95 (v/v)) states of 1. b) Normalized aborption spectra of monomeric (TCE) and homopolymeric (TCE/MCH, 5/95 (v/v)) 2.



**Figure S4.** Time dependent a) CD changes and b) absorbance changes monitored at 563 nm, which shows, evolution of metastable state of **1** into homopolymeric state at various percentages of TCE/MCH solvent mixtures. ([**1**] =  $2.5 \times 10^{-5}$  M).



**Figure S5.** a) Time dependent absorbance changes monitored at 395 nm for **2** which shows, transformation of metastable **2** into homopolymeric state at various percentages of MCH/TCE solvent composition. b-d) Fitting of time dependent kinetic data of Figure S4a into Watzky-Finke model<sup>S4</sup> to extract the nucleation ( $k_{nu}$ ) and elongation ( $k_e$ ) rate constants. Plot of calculated e)  $k_{nu}$  and f)  $k_e$  against percentage of TCE. ([**2**] = 2.5×10<sup>-5</sup> M).



**Figure S6.** a) Fitting of time dependent absorbance changes of Figure S4b into Watzky-Finke model<sup>S4</sup> to extract the nucleation ( $k_{nu}$ ) and elongation ( $k_e$ ) rate constants. Plot of calculated b)  $k_{nu}$  and c)  $k_e$  against percentage of TCE. ([**1**] =  $2.5 \times 10^{-5}$  M).



**Figure S7.** a-c) Calculation of kinetic parameters for **1** using the solvent composition dependent kinetic data of Figure S4b: (lag time ( $t_{lag}$ ), time at which the rate is maximum ( $t_m$ ), time required for 50 % conversion of the process ( $t_{50}$ ) and maximum rate ( $v_{max}$ )). d) Plot of  $t_{lag}$ ,  $t_m$ ,  $t_{50}$  and  $v_{max}$  against percentage of TCE showing an increasing trend with decrease in TCE %. ([**1**] =  $2.5 \times 10^{-5}$  M).

**Note:** The rate of conversion of metastable **1** into homopolymeric **1** increases with decrease in % of TCE in MCH.



**Figure S8.** a-c) Calculation of kinetic parameters for **2** using the solvent composition dependent kinetic data of Figure S5a: (lag time ( $t_{lag}$ ), time at which the rate is maximum ( $t_m$ ), time required for 50 % conversion of the process ( $t_{50}$ ) and maximum rate ( $v_{max}$ )). d) Plot of  $t_{lag}$ ,  $t_m$ ,  $t_{50}$ ,  $v_{max}$ , against % of TCE showing an increasing trend with decrease in TCE %. (TCE/MCH, 5/95 (v/v)).

**Note:** The rate of conversion of metastable **2** into homopolymeric **2** increases with decrease in % of TCE in MCH.



**Figure S9.** Concentration dependent a) absorbance and b) CD changes monitored at 563 nm, which shows, conversion of metastable state of **1** into homopolymeric state of **1**. (TCE/MCH, 5/95 (v/v)).



**Figure S10.** a) Fitting of concentration dependent kinetic data of Figure S9b into Watzky-Finke model to extract the nucleation ( $k_{nu}$ ) and elongation ( $k_e$ ) rate constants. Plot of b)  $k_{nu}$  and c)  $k_e$  against concentration. (TCE/MCH, 5/95 (v/v)).

**Note:** The sigmoidal growth kinetics of Figure S8b could be fitted to an autocatalytic nucleation elongation model, which tells the transformation of metastable state into a thermodynamically stable state goes via nucleation and elongation processes.



**Figure S11.** a-c) Kinetic parameters calculated for **1** using the concentration dependent kinetic data of Figure S9b: (lag time ( $t_{lag}$ ), time at which the rate is maximum ( $t_m$ ), time required for 50 % conversion of the process ( $t_{50}$ ) and maximum rate ( $v_{max}$ )). d) Plot of  $t_{lag}$ ,  $t_m$ ,  $t_{50}$ ,  $v_{max}$ , against concentration. (TCE/MCH, 5/95 (v/v)).

**Note:** The lag time of this conversion process extends with a decrease in concentration which designates an on-pathway formation of metastable **1** *en route* to homopolymeric state of **1**.



**Figure S12.** a) Concentration dependent kinetics data obtained by monitoring the absorbance changes at 395 nm which shows, evolution of metastable state of **2** into homopolymeric state. b-d) Fitting of concentration dependent kinetic data of Figure S12a an into Watzky-Finke model to extract the nucleation ( $k_{nu}$ ) and elongation ( $k_e$ ) rate constants. Plot of e)  $k_{nu}$  and f)  $k_e$  against concentration. (TCE/MCH, 5/95 (v/v)).

**Note:** The sigmoidal growth kinetics of Figure S11a could be fitted to an autocatalytic nucleation elongation model, which tells us, the conversion of metastable state into a thermodynamically stable state consist of nucleation and elongation processes



**Figure S13.** a-d) Kinetic parameters calculation for 2 using concentration dependent kinetic data of Figure S12a. e) Plot of  $t_{lag}$ ,  $t_m$ ,  $t_{50}$ ,  $v_{max}$ , against concentration. (TCE/MCH, 5/95 (v/v)).



**Figure S14.** Spectroscopic investigation of metastable state of **1** and **2**. a) Absorption and b) emission spectrum of metastable state of molecule **1** ( $\lambda_{ex} = 490 \text{ nm}$ ) ([**1**] = 2.5×10<sup>-5</sup> M) and its comparison with monomeric and homopolymeric state. c) Excitation spectra of metastable state ( $\lambda_{coll} = 590 \text{ nm}$ ), and its comparison with **1** homopolymers ( $\lambda_{coll} = 600 \text{ nm}$ ) and **1** monomers ( $\lambda_{coll} = 600 \text{ nm}$ ). d) Time dependent emission spectra during conversion of metastable state into homopolymeric state. e) DLS spectrum of metastable state of **1** and its comparison with DLS spectra of homopolymeric and monomeric state. (TCE/MCH, 5/95 (v/v), [**1**] = 2.5×10<sup>-5</sup> M). f) Absorption, g) CD, and h) DLS spectrum of metastable state of **2** and its comparison with homopolymeric and monomeric state. (TCE/MCH, 5/95 (v/v), [**2**] = 2.5×10<sup>-5</sup> M).

**Note:** Metastable state showed a change in the ratio between vibronic bands of  $\pi$ - $\pi^*$  absorption maximum (A<sub>370</sub>/A<sub>353</sub> 1.2 for monomers, 1 for homopolymers, and 1.05 for metastable state) and emission spectra depicted a broadening and appearance of weak emission at higher wavelength (585 nm,  $\lambda_{ex}$  = 490 nm) compared to the absorption and emission spectra of monomer in TCE (560 nm,  $\lambda_{ex}$  = 490 nm). Further excitation spectra collected at the emission maximum of metastable state showed the presence of a blue-shifted excitation spectrum compared to the monomeric state. DLS spectra of metastable state shows a different size for metastable state is CD inactive in comparison to homopolymeric state. The different absorption, emission, CD and DLS spectral features compared to monomeric and aggregated species, indicate less ordered small aggregates as metastable states prior to the nucleation and elongation event.



**Figure S15.** Temperature dependent a, b) <sup>1</sup>H-NMR spectrum of molecule **2** in CDCl<sub>3</sub> ([**2**] =  $2.5 \times 10^{-4}$  M, 600 mHz). Figure S15b represents the zoomed in portion corresponding to amide hydrogen of molecule **2**. The arrows are to direct the eye to the temperature dependent changes. c) The NH chemical shift against Temperature plot (obtained using Figure S15b) to more clearly iterate the temperature dependent changes in chemical shift ( $\delta$ ) of amide hydrogen of molecule **2** in chloroform. d, e) Normalized absorption spectra of molecule 2 in 100 % TCE and CHCl<sub>3</sub> and in 100% CHCl<sub>3</sub> at two different concentration ( $2.5 \times 10^{-5}$ M and  $2.5 \times 10^{-4}$ M), respectively. The normalized absorption spectra in 100% CHCl<sub>3</sub> showing the molecule **2** is in monomeric state at both concentration.(I = 1 mm)

**Note:** To decipher the nature of the metastable state we have performed temperaturedependent <sup>1</sup>H-NMR measurement, which depicts an up-field shift of carbamate hydrogen (4.96 ppm at 25°C to 4.89 ppm at 55 °C) with the increase in temperature. The NH chemical shift against Temperature graph more clearly depicts the upfield shift of amide hydrogen with increase in temperature. This measurements indicates a possible intramolecular hydrogen-bonded state at room temperature which gets disrupted at high temperature.<sup>55</sup> To rule out that the observed temperature dependent chemical shifts in NMR are not due to aggregation of molecule **2** in chloroform we have now recorded the absorption spectra at two different concentration  $(2.5 \times 10^{-5} \text{ and } 2.5 \times 10^{-4} \text{ M})$ . We have observed an identical absorption spectrum at  $2.5 \times 10^{-5}$  and  $2.5 \times 10^{-4}$  M, which unambiguously proves the molecularly dissolved nature of molecule **2** in chloroform. The temperature dependent absorption spectra of molecule **2** at  $2.5 \times 10^{-4}$  M concentration depicts absence of any shift at high temperature, again pointing towards molecularly dissolved nature of molecule **2** in chloroform. Thus, we believe the intramolecular hydrogen bonding between carbamate hydrogen and imide oxygen is the origin of the metastable state seen in these derivatives.



**Figure S16.** TEM images of a) homopolymers of **1** and b) homopolymers of **2**. (TCE/MCH, 5/95 (v/v),  $[\mathbf{1}] = [\mathbf{2}] = 2.5 \times 10^{-5}$  M).



**Figure S17.** SIM images of homopolymers of **1** in a) green channel ( $\lambda_{ex}$  = 488 nm,  $\lambda_{coll}$  = 495–575 nm) and b) red channel ( $\lambda_{ex}$  = 561 nm,  $\lambda_{coll}$  = 570–650 nm). (TCE/MCH, 5/95 (v/v), [**1**] = 2.5×10<sup>-5</sup> M).



**Figure S18.** a) Absorption spectrum and b) emission spectrum ( $\lambda_{ex}$ = 430 nm) of molecule **3** in TCE and TCE/MCH, 5/95 (v/v). c) SIM microscopy images of self-assembled **3** depicting absence of any ordered supramolecular polymers. ([**3**] = 2.5×10<sup>-5</sup> M, I = 10 mm).



**Figure S19.** SIM images of homopolymers of **2** mixed with 1 % of **3** as a fluorescence marker in green channel ( $\lambda_{ex}$  = 488 nm,  $\lambda_{coll}$  = 495–575 nm) and b) red channel ( $\lambda_{ex}$  = 561 nm,  $\lambda_{coll}$  = 570-650 nm) depicting its selective excitation and visualization in the green channel. (TCE/MCH, 5/95 (v/v), [**2**] = 2.5×10<sup>-5</sup> M).



**Figure S20.** Comparison of a) CD and b) absorption spectra of **2** homopolymers and **2** homopolymers in presence of **1** % of **3**. (TCE/MCH, 5/95 (v/v), [**2**] =  $2.5 \times 10^{-5}$  M).



**Figure S21.** a) SIM microscopy images of prepared  $\mathbf{1}_{seed}$  solution in red channel after sonication of **1** homopolymers for 2 hours in an ultrasonic bath. b) Absorption spectra of **1** homopolymers and its comparison with sonicated solution of **1** homopolymer. c) Length distribution analysis of the seed solution prepared by sonicating **1** homopolymers for 2 hours in an ultrasonic bath. (red channel:  $\lambda_{ex} = 561 \text{ nm}$ ,  $\lambda_{coll} = 570-650 \text{ nm}$ , [**1**] =  $10^{-5}$  M, TCE/MCH, 5/95 (v/v)).



**Figure S22.** a) Plot of kc\* value as a function of equivalent of  $\mathbf{1}_{seed}$  with respect to  $\mathbf{2}_{monomer}$  showing a linear relationship. b) Absorption and c) CD spectra of prepared supramolecular BCP and its comparison with individual homopolymers. Time dependent d) CD and e) Absorption spectra showing stability of the synthesized block copolymer with time ([1] =  $10^{-5}$  M, TCE/MCH, 5/95 (v/v)).

**Note:** The time dependent absorption and CD spectra of the synthesized block copolymer did not show any changes over 120 minutes, which suggests high kinetic stability of the blocks and low dynamics of the system.



**Figure S23.** Visualization of the supramolecular BCP ( $[1_{seed}]$ : $[2_{monomer}] = 1:1$ ) by merging SIM images collected at red channel ( $\lambda_{ex} = 561 \text{ nm}$ ,  $\lambda_{coll} = 570-650 \text{ nm}$ ) and bright field image. ( $[1_{seed}] = 1 \times 10^{-5} \text{ M}$ , TCE/MCH, 5/95 (v/v)).



**Figure S24.** a) Time course of the supramolecular polymerization on addition  $2_{monomer} + 1 \% 3$  on various equivalent of  $1_{seed}$  ([2] =  $1.0 \times 10^{-5}$  M). b) Absorption and c) CD spectra of prepared supramolecular BCP in presence of 1 % of 3 and its comparison with pure supramolecular block copolymer between 1 and 2. Time dependent d) absorption and e) CD spectra showing stability of the synthesized block copolymer with time ([1] =  $10^{-5}$  M, TCE/MCH, 5/95 (v/v)).

**Note:** The addition of  $\mathbf{1}_{\text{seed}}$  to the metastable state of **2** mixed with 1 % of **3** resulted in an instantaneous non-sigmoidal growth with a faster polymerization ( $t_{1/2}$  for 2039 seconds for unseeded and 40 seconds for seeded assembly) rate depicting heterogeneous nucleation and copolymerization. The rate of transformation can be further accelerated by increasing the concentration of the seed.



**Figure S25.** a) SIM microscopy images of synthesized supramolecular BCPs between  $\mathbf{1}_{seed}$  and  $\mathbf{2}_{monomer}$  stained with 1% of **3** with a  $\mathbf{1}_{seed}$ : $\mathbf{2}_{monomer}$  ratio of 1:1 in merged, green and red channel showing formation of supramolecular BCPs. b) Treatment of the extracted intensity profile (of the marked fiber using white line) from the SIM image to calculate the overall length (black line), green segments length (green line), and red segments length (red line). (red channel:  $\lambda_{ex} = 561$  nm,  $\lambda_{coll} = 570-650$  nm; green channel:  $\lambda_{ex} = 488$  nm,  $\lambda_{coll} = 495-575$  nm [**1**] =  $1.0 \times 10^{-5}$  M, TCE/MCH, 5/95 (v/v)).



**Figure S26.** SIM microscopy images of synthesized supramolecular BCPs between  $\mathbf{1}_{seed}$  and  $\mathbf{2}_{monomer}$  stained with 1% of 3 with a  $\mathbf{1}_{seed}$ : $\mathbf{2}_{monomer}$  ratio of 1:2 in merged, green and red channel showing formation of supramolecular BCPs. (red channel:  $\lambda_{ex} = 561 \text{ nm}$ ,  $\lambda_{coll} = 570-650 \text{ nm}$ ; green channel:  $\lambda_{ex} = 488 \text{ nm}$ ,  $\lambda_{coll} = 495-575 \text{ nm}$ ,  $[\mathbf{1}] = 1.0 \times 10^{-5} \text{ M}$ , TCE/MCH, 5/95 (v/v)).

[S]:[M]	L <sub>n</sub> (nm)	Lw	PDI
1:1	1031	1078	1.04
1:2	1382	1463	1.05

**Table S2.** Calculated L<sub>n</sub>, L<sub>w</sub> and PDI of overall block supramolecular copolymer at [S]:[M] ratio of 1:1 and 1:2.

[S]:[M]	L <sub>n</sub> (nm)	Lw	PDI
1:1	410	437	1.06
1:2	582	627	1.07

**Table S3.** Calculated  $L_n$ ,  $L_w$  and PDI of green component of block supramolecular copolymer at [S]:[M] ratio of 1:1 and 1:2.

[S]:[M]	L <sub>n</sub> (nm)	Lw	PDI
1:1	668	700	1.04
1:2	684	707	1.03

**Table S4.** Calculated  $L_n$ ,  $L_w$  and PDI of red component of block supramolecular copolymer at [S]:[M] ratio of 1:1 and 1:2.



**Figure S27**. SIM microscopy images of synthesized supramolecular BCPs of  $\mathbf{1}_{\text{seed}}$ : $\mathbf{2}_{\text{monomer}}$  ratio of 1:3 with 1 % of **3** as a fluorescent stain in the merged channel (red channel + green channel). (red channel:  $\lambda_{\text{ex}}$  = 561 nm,  $\lambda_{\text{coll}}$  = 570-650 nm; green channel:  $\lambda_{\text{ex}}$  = 488 nm,  $\lambda_{\text{coll}}$  = 495-575 nm, [**1**] = 10<sup>-5</sup> M, TCE/MCH, 5/95 (v/v)).



Figure S28. <sup>1</sup>H-NMR spectrum of molecule 1.



Figure S29. <sup>13</sup>C-NMR spectrum of molecule 1.



Figure S30. <sup>1</sup>H-NMR spectrum of molecule 2.



Figure S31. <sup>13</sup>C-NMR spectrum of molecule 2.



Figure S32. <sup>1</sup>H-NMR spectrum of molecule 3.



Figure S33. <sup>13</sup>C-NMR spectrum of molecule 3.

#### 5. References:

(S1) R. S. K. Kishore, V. Ravikumar, G. Bernardinelli, N. Sakai, S. Matile, J. Org. Chem. 2008, 73, 738-740.

(S2) R. Balamurugan, Y.-S. Zhang, S. Fitriyani and J.-H. Liu, Soft Matter, 2016, 12, 5214.

(S3) C. Kulkarni, S. J. George, *Chem. Eur. J.* 2014, **20**, 4537-4541; H. Shaoa, J. R. Parquette, *Chem. Commun.*, 2010, **46**, 4285-4287; M. Kumar, N. L Ing, V. Narang, N. K. Wijerathne, A. I. Hochbaum, R. V. Ulijn, *Nat. Chem.* 2018, **10**, 696-703; S. Ogi, V. Stepanenko, J. Thein, F. Würthner, *J. Am. Chem. Soc.* 2016, **138**, 670-678; M. Endo, T. Fukui, S. H. Jung, S. Yagai, M. Takeuchi, K. Sugiyasu, *J. Am. Chem. Soc.* 2016, **138**, 14347-14353.

(S4) L. Bentea, M. A. Watzky, R. G. Finke, J. Phys. Chem. C 2017, 121, 5302-5312.

(S5) G. P. Dado, S. H. Gellman, J. Am. Chem. Soc. 1994, 116, 1054-1062.