

# Supporting Information

## Chalcogenide Hybrid Inorganic/Organic Polymers (CHIPs) via Inverse Vulcanization and Dynamic Covalent Polymerizations

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#### I) Materials and Instrumentation

Sulfur (precipitated, 99.5%-100.5%, Sigma-Aldrich), Methylene Chloride- $d_2$  ( $CD_2Cl_2$ , Cambridge Isotope Laboratories), Chloroform- $d$  ( $CDCl_3$ , 0.01 % v/v TMS Cambridge Isotope Laboratories), 4-vinylbenzyl chloride (90%, Sigma-Aldrich), poly(ethylene glycol) methyl ether ( $M_n=550$  g/mol), octadecyl acrylate (97%, Sigma-Aldrich), *n*-butyl acrylate (99%, Sigma-Aldrich), 4-vinylbenzoic acid (92%, Matrix Scientific), methyl 3,5-dihydroxybenzoate (97%, Sigma-Aldrich), potassium carbonate (99%, Sigma-Aldrich), 18-crown-6 (99%, Sigma-Aldrich), allyl bromide (97%, Sigma-Aldrich), 1-bromooctadecane (97%, Sigma-Aldrich). Those chemicals were used as received. Styrene (99.5%, stabilized, Acros) was purified through an alumina column before use.

$^1H$  and  $^{13}C$  nuclear magnetic resonance (NMR) spectra were obtained using a Bruker DRX 500 MHz or a BrukerAvance III 400 MHz spectrometer. Chemical shifts are referenced to residual  $CHCl_3$  ( $\delta$  7.260 ppm) in  $CDCl_3$  and  $CH_2Cl_2$  ( $\delta$  5.320 ppm) in  $CD_2Cl_2$  for  $^1H$  NMR and residual  $CHCl_3$  ( $\delta$  77.0 ppm) for  $^{13}C$  NMR. Size exclusion chromatography (SEC) was performed in a tetrahydrofuran (THF) mobile phase with a Waters 1515 isocratic pump running three 5- $\mu m$  PLgel columns (Polymer Labs, pore size  $10^4$ ,  $10^3$  and  $10^2$  Å) at a flow rate of 1 mL/min with a Waters 2414 differential refractometer and a Waters 2487 dual-wavelength UV-vis spectrometer. Molar masses were calculated using the Empower software (Waters), calibrated against low polydispersity linear polystyrene standards.

#### II) Experimental procedures

1. Poly(S-*r*-Sty)

The poly(S-*r*-Sty) (90-50 wt% sulfur) was synthesized according to reported procedures.<sup>1</sup>

2. Poly(S-*r*-Sty-*r*-ODA).

- a. Poly(S-*r*-Sty-*r*-ODA) with 25 wt% S, 25 wt% Sty and 50 wt% ODA at 170 °C

To a 4 mL glass vial equipped with a magnetic stir bar was added 500 mg of poly(*S-r-Sty*) (50 wt% Sty) and 500 mg of octadecyl acrylate and heated to 170 °C in a thermostatic oil bath for 50 min yielding an orange wax.

b. Poly(*S-r-Sty-r-ODA*) with 25 wt% S, 25 wt%Sty and 50 wt% ODA at 150 °C

To a 4 mL glass vial equipped with a magnetic stir bar was added 500 mg of poly(*S-r-Sty*) (50 wt% Sty) and 500 mg of octadecyl acrylate and heated to 150 °C in a thermostatic oil bath for 30 h yielding an orange wax.

c. Poly(*S-r-Sty-r-ODA*) with 25 wt% S, 25 wt%Sty and 50 wt% ODA at 110 °C

To a 4 mL glass vial equipped with a magnetic stir bar was added 500 mg of poly(*S-r-Sty*) (50 wt% Sty) and 500 mg of octadecyl acrylate and heated to 110 °C in a thermostatic oil bath for 15 d yielding an orange wax.

d. Poly(*S-r-Sty-r-ODA*) with 35 wt% S, 15 wt%Sty and 50 wt% ODA at 170 °C

To a 4 mL glass vial equipped with a magnetic stir bar was added 500 mg of poly(*S-r-Sty*) (30 wt% Sty) and 500 mg of octadecyl acrylate and heated to 170 °C in a thermostatic oil bath for 15 d yielding an orange wax.

e. Poly(*S-r-Sty-r-ODA*) with 45 wt% S, 5 wt%Sty and 50 wt% ODA at 170 °C

To a 4 mL glass vial equipped with a magnetic stir bar was added 500 mg of poly(*S-r-Sty*) (10 wt% Sty) and 500 mg of octadecyl acrylate and heated to 170 °C in a thermostatic oil bath for 15 d yielding an orange wax.

3. Synthesis of 1,3-bis(allyloxy)-5-((octadecyloxy)methyl)benzene (BAO)

a. Synthesis of methyl 3,5-bis(allyloxy)benzoate

To a 200 mL round-bottom flask equipped with a magnetic stir bar was added 3.4 g (20.0 mmol) of methyl 3,5-dihydroxybenzoate, 7.0 g (50.7 mmol, 1.27 eq) of K<sub>2</sub>CO<sub>3</sub>, 2.6 g (1.0 mmol, 0.05 eq) of 18-crown-6, 4.3 mL (6.0 g, 49.6 mmol, 1.24 eq) of allyl bromide and 50 mL of acetone. The reaction mixture was refluxed overnight. The solid was removed by gravity filtration and acetone was removed by rot-vap. The crude product was dissolved with dichloromethane and extracted with 1 M NaOH(aq), 1M NaHSO<sub>4</sub> and brine and dried over Na<sub>2</sub>SO<sub>4</sub> and dichloromethane was removed by rot-vap. 4.2 g (17 mmol) of colorless liquid was collected (85% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.22 (m, 2H), 6.72 (m, 1H), 6.07 (ddt, J = 17.3, 10.5, 5.3 Hz, 2H), 5.45 (dq, J = 17.2, 1.6 Hz, 2H), 5.33 (dq, J = 10.5, 1.4 Hz, 2H), 4.58 (dt, J = 5.3, 1.5 Hz, 1H), 3.93 (s, 1H) ppm.

b. Synthesis of (3,5-bis(allyloxy)phenyl)methanol

1.14 g (30 mmol, 1.86 eq) of LiAlH<sub>4</sub> was suspended in 20 mL of tetrahydrofuran and cooled at 0 °C. 4.0 g (16.1 mmol) of methyl 3,5-bis(allyloxy)benzoate was dissolved in 10 mL of THF and added dropwise to the LiAlH<sub>4</sub> suspension. The reaction mixture was stirred at room temperature overnight and then quenched with Backstrom's reagent (Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O/celite, 1:1 wt ratio). Solid were removed from the reaction mixture by vacuum filtration. The solvent were removed by rot-vap and purified with column chromatography (hexans:DCM=1:1 v/v). 3.1 g (14 mmol) of colorless oil was collected (88% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 6.50 (m, 2H), 6.40 (m, 1H), 6.04 (m 2H), 5.41 (dq, J = 17.2, 1.6 Hz, 2H), 5.28 (dq, J = 10.3, 1.5 Hz, 1H), 4.52 (d, J=4.1 Hz, 2H), 4.47 (dt, J = 5.3, 1.6 Hz, 4H) ppm.

c. Synthesis of 1,3-bis(allyloxy)-5-((octadecyloxy)methyl)benzene (BAO)

2.8 g (20 mmol, 2.0 eq) of NaH was suspended in 20 mL THF. 2.2 g of (3,5-bis(allyloxy)phenyl)methanol was dissolved in 10 mL of THF and added to NaH suspension dropwise. 3.4 mL (3.3 g, 10 mmol, 1.0 eq) of 1-bromooctadecane was dissolved in 10 mL of THF and added to the reaction mixture dropwise. The reaction mixture was stirred at room temperature overnight. The reaction was quenched with brine and extracted with ether. The crude product was concentrated and purified by column chromatography (ethyl acetate:hexanes=1:4 v/v). 3.8 g light yellow liquid was collected (80% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 6.55 (m, 2H), 6.45 (m, 1H), 6.08 (m, 2H), 5.44 (dq, J = 17.2, 1.6 Hz, 2H), 5.31 (dq, J = 10.5, 1.5 Hz, 2H), 4.55 (m, 4H), 3.47 (m, 2H), 1.64 (m, 2H), 1.47 – 1.13 (m, 32H), 0.92 (t, J=6.9 Hz, 3H) ppm. HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>52</sub>O<sub>3</sub> 472.39; Found 473.39892

4. Poly(S-*r*-Sty-*r*-BAO) with 35 wt% S, 15 wt% Sty and 50 wt% BAO

To a 4 mL glass vial equipped with a magnetic stir bar was added 50 mg of poly(S-*r*-Sty) (70 wt% Sty), 50 mg of 1,3-bis(allyloxy)-5-((octadecyloxy)methyl)benzene and 0.05 mL of dichlorobenzene and heated to 170 °C in a thermostatic oil bath for 2h until BOA was consumed. The crude product was precipitated in methanol to afford 92 mg of orange solid (92%yield).

5. Poly(S-*r*-BAO-*r*-TAT) with 40 wt% S, 40 wt% BAO and 20 wt% TAT

To a 4 mL glass vial equipped with a magnetic stir bar was added 50 mg of elemental sulfur, 50 mg of 1,3-bis(allyloxy)-5-((octadecyloxy)methyl)benzene and 0.05 mL of dichlorobenzene and heated to 170 °C in a thermostatic oil bath for 2h until BOA was consumed. 25 mg of 2,4,6-Triallyloxy-1,3,5-triazine was added to the reaction mixture and heated for 4 h until TAT was consumed. The crude product was precipitated in methanol to afford 117 mg of orange solid (94%yield).

6. Synthesis of 4-(poly(ethylene glycol)) styrene

315 mg (13.1 mmol, 2 eq) of NaH was suspended in 10 mL of dry THF. 3.3 mL of poly(ethylene glycol) methyl ether (6.55 mmol, 1 eq) was dissolved in 10 mL of dry THF and transferred to NaH/THF via a syringe. 0.93 mL of vinylbenzyl chloride was dissolved in 5 mL of THF and added to the reagent mixture. The reaction mixture was stirred at room temperature overnight and quenched with brine, extracted with ether and purified with flash chromatography using a gradient eluent from ethyl acetate/hexanes 1/10 (v/v) to methanol/ethyl acetate 1/20 (v/v). 3.7 g of light orange liquid was collect (84 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.40 (m, 2H), 7.32 (m,2H), 6,73 (dd, J=17.6, 10.9 Hz, 1H), 5.76 (dd, J=17.6, 0.95 Hz, 1H), 5,26 (dd, J=10.9, 0.95 Hz, 1H), 4.57 (S, 2H), 3.56-3.66 (m, 48H), 3.40 (s, 3H)

7. Poly(S-*r*-Sty-*r*-(poly(ethylene glycol) styrene)) with 50 wt% S, 20 wt% Sty and 30 wt% PEGSty

To a 4 mL glass vial equipped with a magnetic stir bar was added 500 mg of poly(S-*r*-Sty) (70 wt% Sty) and 200 mg (0.30 mmol) of 4-(poly(ethylene glycol)) styrene and heated at 130 °C for 30 min until 4-(poly(ethylene glycol)) styrene was completely consumed, yielding a red fluid.

8. Poly(S-*r*-Sty-*r*-vinylbenzoic acid) with 58 wt% S, 25 wt% Sty and 17 wt% vinylbenzoic acid

To a 4 mL glass vial equipped with a magnetic stir bar was added 500 mg of poly(S-*r*-Sty) (70 wt% Sty) and 100 mg (0.67 mmol) of 4-vinylbenzoic acid and heated at 170 °C for 30 min until 4-vinylbenzoic acid was completely consumed, yielding a red fluid.

### III) Results and Discussion

# 1. Kinetic study of IDC of poly(*S-r-Sty*) and ODA

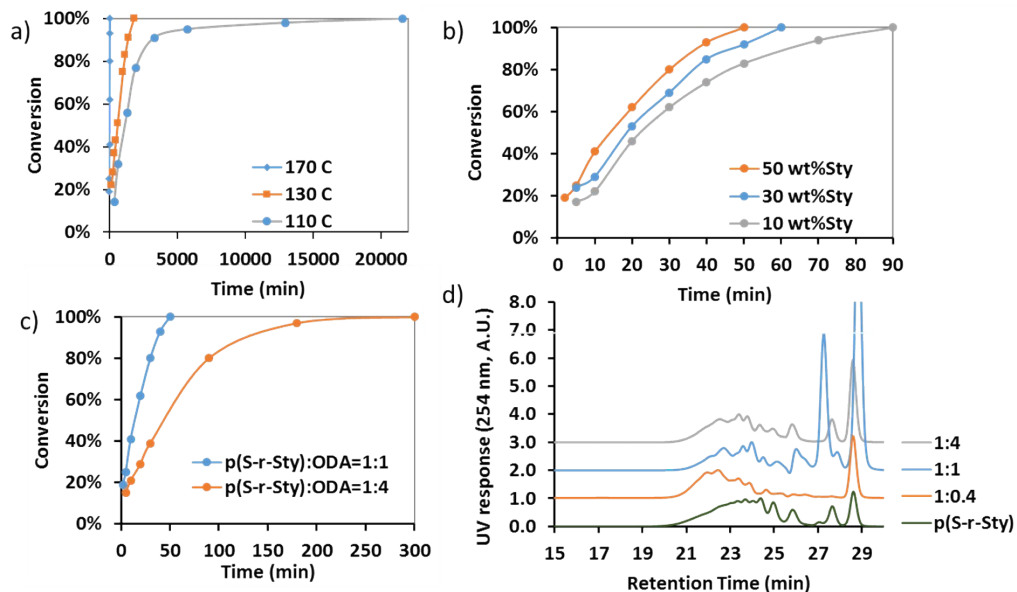


Figure S1. a) kinetic study of IDC at different temperatures. b) kinetic study of IDC with different composition of poly(*S-r-Sty*). c) kinetic study of IDC with different feed ratio of poly(*S-r-Sty*) and ODA. d) SEC analysis of poly(*S-r-Sty-r-ODA*) with different feed ratio of poly(*S-r-Sty*) and ODA.

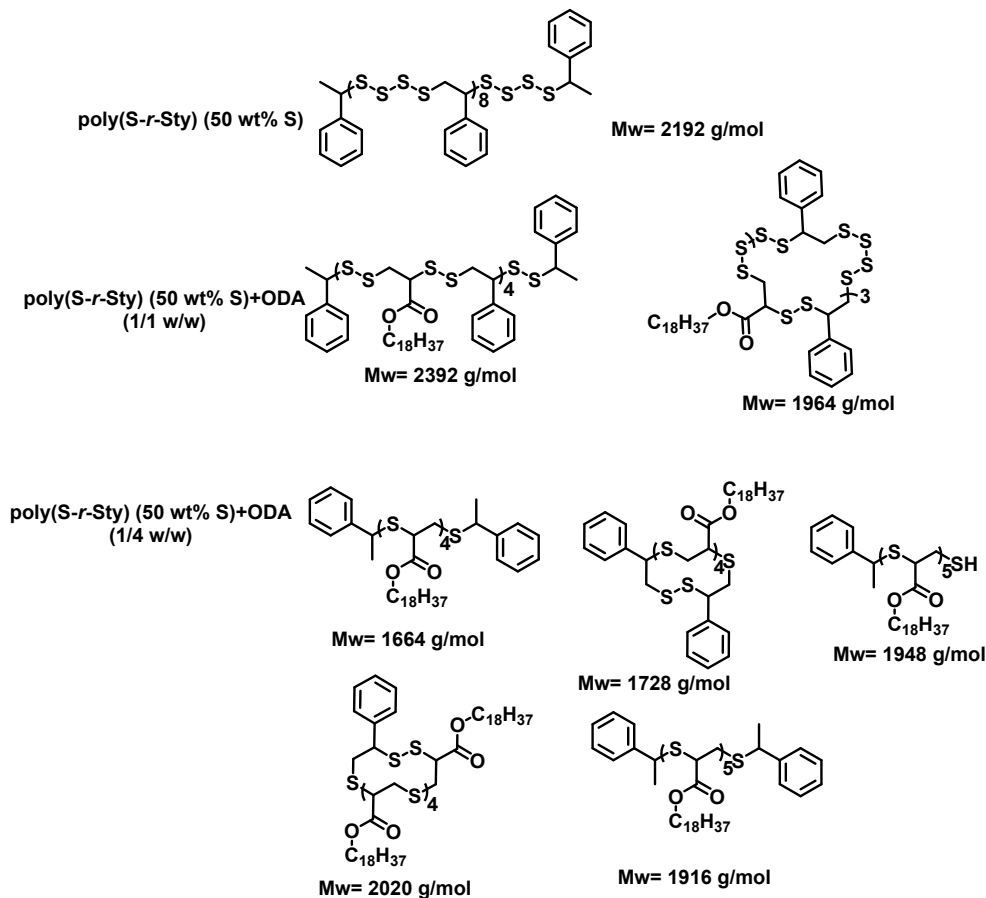


Figure S2. Possible structures for poly(*S-r-Sty-r-ODA*)

The IDC with poly(*S-r-Sty*) and ODA with (1:1 w/w) feed ratio can be conducted at different temperatures (110-170 °C) and the conversion of ODA vs. reaction time is shown in Fig. S1a. For the reaction at 170 °C, it takes 50 min to achieve 100% conversion, 30 h at 130 °C and 15 d at 110 °C. The composition of poly(*S-r-Sty*) also effects the rate of IDC and the IDC of poly(*S-r-Sty*) (90-50 wt% S) and ODA with 1:1 feed ratio at 170 °C was shown in Fig. S1b. Poly(*S-r-Sty*) with 50 wt% sulfur content exhibits highest rate of ODA consumption while poly(*S-r-Sty*) with 90 wt% sulfur exhibits lowest rate. The SEC analysis of IDC of poly(*S-r-Sty*) (50 wt% S,  $M_n = 1095$  g/mol,  $M_w/M_n=1.3$ ) and ODA with 1:1 (w/w) feed ratio at 170 °C was shown in Fig. S1d. With low ODA feed ratio (1:0.4 w/w of poly(*S-r-Sty*) and ODA), the reaction affords  $M_n=1554$  g/mol ( $M_w/M_n=1.3$ ) terpolymers. The IDC with 1:1 feed ratio affords  $M_n=1256$  g/mol ( $M_w/M_n=1.3$ ) terpolymers and 1:4 feed ratio affords  $M_n=1156$  g/mol ( $M_w/M_n=1.3$ ) terpolymers. The possible microstructure of the terpolymer was shown in Fig. S2.

## 2. Sulfur-vinylbenzoic acid reaction and IDC of poly(*S-r-Sty*) and vinylbenzoic acid (VBA)

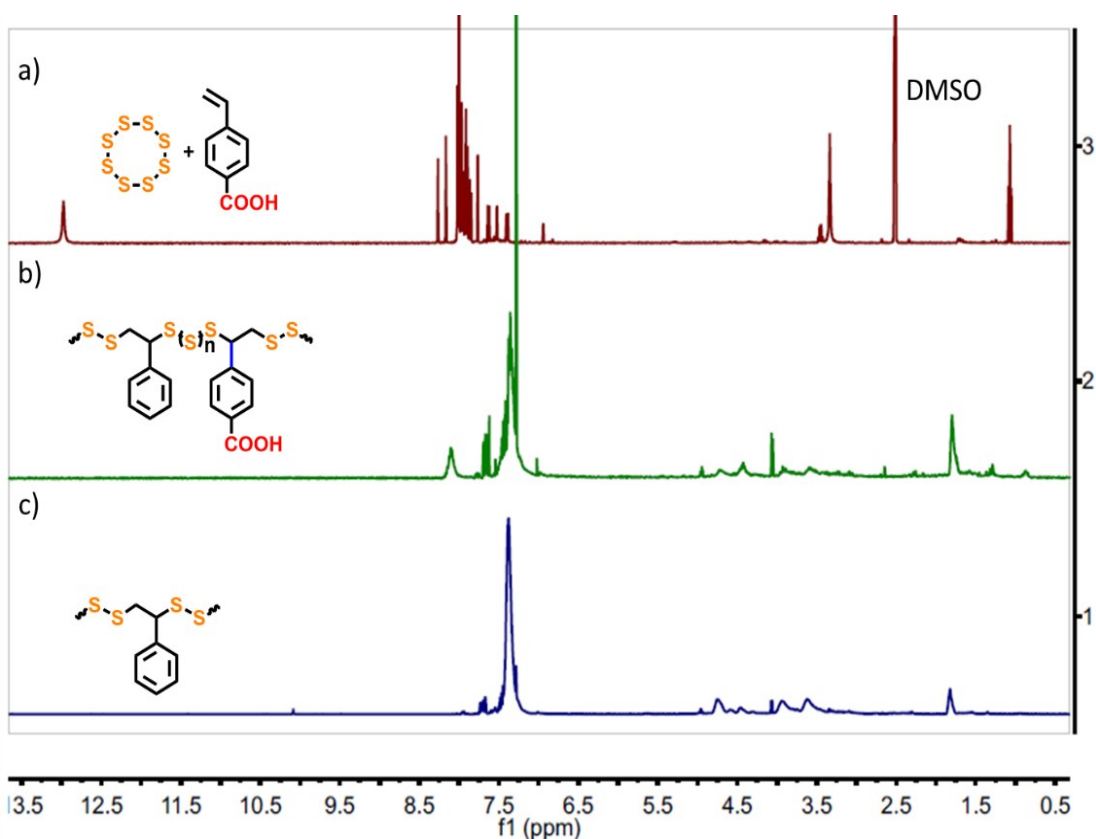


Figure S3. <sup>1</sup>H NMR spectra of a) the product of sulfur-vinylbenzoic acid reaction in DMSO-d<sub>6</sub> b) poly(*S-r-Sty-r-VBA*) in CDCl<sub>3</sub> c) poly(*S-r-Sty*) in CDCl<sub>3</sub>

When 4-vinylbenzoic acid is not soluble in liquid sulfur. When heating elemental sulfur and vinylbenzoic acid in dichlorobenzene solution at 170 °C for 2 h, the NMR spectrum shows that the monomer was consumed but no sulfur copolymer was formed (Fig. S4a). However, 4-vinylbenzoic acid is soluble in poly(*S-r-Sty*) (70 wt% sulfur) and the VBA unit can be incorporated with the polysulfide with IDC approach (Fig. S4b)

### 3. SEC analysis of poly(S-*r*-Sty-*r*-PEGSty)

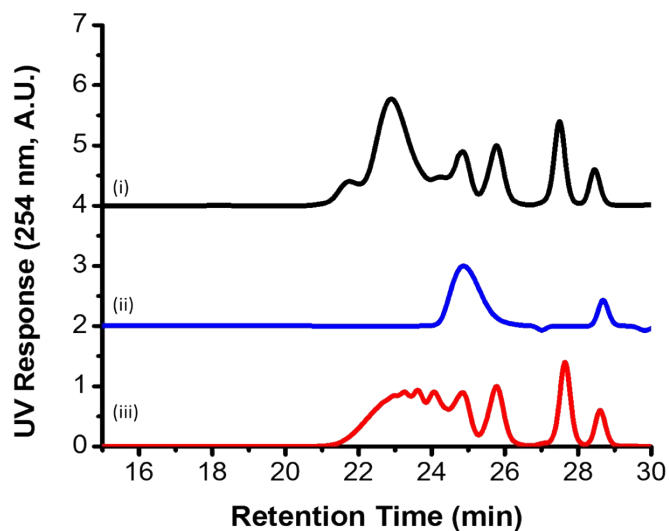


Figure S4. SEC analysis of (i) poly(S-*r*-Sty-*r*-PEGSty) (50 wt% S, 20 wt% Sty, 30 wt% PEGSty) ( $M_n=1364$  g/mol,  $M_w/M_n = 1.3$ ), (ii) PEGSty ( $M_n=671$  g/mol,  $M_w/M_n=1.06$ ), (iii) poly(S-*r*-Sty) (70 wt% S) ( $M_n=1159$  g/mol,  $M_w/M_n = 1.3$ )

#### IV) Reference

- 1 Y. Zhang, J. J. Griebel, P. T. Dirlam, N. A. Nguyen, R. S. Glass, M. E. Mackay, K. Char and J. Pyun, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 107-116.