Electronic Supporting Information (ESI)

CS_2-Based one-pot multicomponent tandem polymerization toward functional polybenzothiazoles

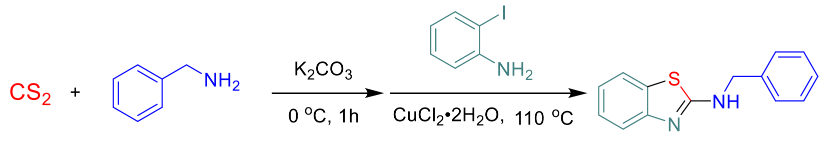
Dongming Liu,[a] Haoran Zhang,[a] Lijing Zhang,[a] Jia Wang,[b] Zhiyang Chang*[a] and Hailin Cong*[a]*

[a]School of Materials Science and Engineering, Shandong University of Technology, Zibo 255000, China. E-mail: conghailin@sdut.edu.cn, zychang2011@126.com

[b]Songshan Lake Materials Laboratory, Dongguan 523808, China. E-mail: wangjia@sslab.org.cn

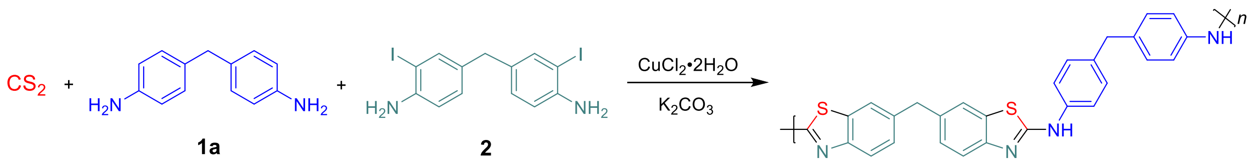
Table of Contents

Scheme S1 Synthetic route to model compound **3**.



3

Scheme S2 The three-component polymerization of CS_2, **1a** and **2**.



1a **2**

Formula S1 The calculation formula of polymer yields.

$$yield = \frac{m_a}{m_t} \times 100\% = \frac{m_a}{n\times(2M_{CS_2}+M_1-2M_H+2M_K+M_2)-(2n-1)M_{KI}-(2n-1)M_{H_2S}} \times 100\%^a$$

[a]Where m_a is the actual mass of the polymer, m_t is theoretical mass of the polymer, *n* is the amount of substance of monomers, and $M_{CS_2}, M_1, M_H, M_K, M_2, M_{KI}, M_{H_2S}$ are the molar mass of CS_2, monomer **1**, H atom, K atom, monomer **2**, KI and H_2S.

Table S1 Effect of solvent on the polymerization of CS_2, **1a** and **2**[a].

Entry	Solvent	Yield (%)	M_n[b]	M_w[b]	$Đ$[b]
1[c]	Toluene	trace	—	—	—
2[d]	Chloroform	No polymer			
3[d]	Tetrahydrofuran	23	4000	4800	1.2
4[c]	1, 4-Dioxane	trace	—	—	—
5	DMSO	77	10 600	18 500	1.7
6	DMF	84	8700	13 600	1.6
7	DMAc	82	7000	10 300	1.5

[a] The first step of this MCTP was carried out at 30 °C for 1 h, and the second step was carried out at 100 °C for 16 h. [**1a**] = 0.15 M, [**1a**]/[**2**]/[CS_2]/[$CuCl_2$•$2H_2O$] /[K_2CO_3] = 1:1:2.4:3:2. [b] Determined by gel-permeation chromatography (GPC) using *N,N*-dimethylformamide (DMF) containing 0.05 M LiBr as an eluent on the basis of a linear polymethyl methacrylate (PMMA) calibration. $Đ$ = polydispersity index (M_w/M_n, M_w = weight-average molecular weight, M_n = number-average molecular weight). [c] 90 °C for 4 h. [d] 50 °C for 10 h.

Table S2 Effect of $CuCl_2•2H_2O$ loading on the polymerization of CS_2, **1a** and **2**[a].

Entry	$CuCl_2•2H_2O$ (equiv.)	Yield (%)	M_n[b]	M_w[b]	$Đ$[b]
1	3	78	10 500	17 800	1.7
2	2	90	10 100	16 600	1.6
3	1	46	5300	6300	1.2

[a] The first step of this MCTP was carried out in DMSO at 30 °C for 1 h, and the second step was carried out in DMSO at 100 °C for 16 h. [**1a**] = 0.15 M, [**1a**]/[**2**]/[CS_2]/[K_2CO_3] = 1:1:2.4:2. [b] Determined by GPC using DMF containing 0.05 M LiBr as an eluent on the basis of a linear PMMA calibration. $Đ = M_w/M_n$.

Table S3 Effect of K_2CO_3 loading on the polymerization of CS_2, **1a** and **2**[a].

Entry	K_2CO_3 (equiv.)	Yield (%)	M_n[b]	M_w[b]	$Đ$[b]
1	2	89	7500	16 500	2.2
2	1	88	7700	14 600	1.9
3	0.5	87	8000	13 300	1.7
4	0	81	6400	11 300	1.8

[a] The first step of this MCTP was carried out in DMSO at 30 °C for 1 h, and the second step was carried out in DMSO at 100 °C for 16 h. [**1a**] = 0.15 M, [**1a**]/[**2**]/[CS_2]/[$CuCl_2•2H_2O$] = 1:1:2.4:2. [b] Determined by GPC using DMF containing 0.05 M LiBr as an eluent on the basis of a linear PMMA calibration. $Đ = M_w/M_n$.

Table S4 Effect of monomer concentration on the polymerization of CS_2, **1a** and **2**[a].

Entry	[**1a**] (mol/L)	Yield (%)	M_n[b]	M_w[b]	$Đ$[b]
1	0.10	88	7600	12 800	1.7
2	0.15	89	8300	14 800	1.8
3[c]	0.30	87	11 000	23 200	2.1
4[c]	0.40	Gel	–	–	–

[a] The first step of this MCTP was carried out in DMSO at 30 °C for 1 h, and the second step was carried out in DMSO at 100 °C for 16 h. [**1a**]/[**2**]/[CS_2]/[$CuCl_2•2H_2O$]/[K_2CO_3] = 1:1:2.4:2:1. [b] Determined by GPC using DMF containing 0.05 M LiBr as an eluent on the basis of a linear PMMA calibration. $Đ = M_w/M_n$.[c] For 10 h.

Table S5 Effect of temperature on the polymerization of CS_2, **1a** and **2**[a].

Entry	Temperature (°C)	Yield (%)	M_n[b]	M_w[b]	$Đ$[b]
1	120	93	8900	33 600	3.8
2	100	88	7200	21 600	3.0
3	80	86	7000	10 800	1.5

[a] The first step of this MCTP was carried out in DMSO at 30 °C for 1 h, and the second step was carried out in DMSO for 10 h. [**1a**] = 0.3 M, [**1a**]/[**2**]/[CS_2]/[$CuCl_2$•$2H_2O$]/[K_2CO_3] = 1:1:2.4:2:1. [b] Determined by GPC using DMF containing 0.05 M LiBr as an eluent on the basis of a linear PMMA calibration. $Đ = M_w/M_n$.

Table S6 Effect of CS_2 loading on the polymerization of CS_2, **1a** and **2**[a].

Entry	CS_2 (equiv.)	Yield (%)	M_n[b]	M_w[b]	$Đ$[b]
1	2.2	87	5500	9500	1.7
2	2.4	92	12 900	32 000	2.5
3	2.6	85	5100	7100	1.4

[a] The first step of this MCTP was carried out in DMSO at 30 °C for 1 h, and the second step was carried out in DMSO at 120 °C for 10 h. [**1a**] = 0.3 M, [**1a**]/[**2**]/[$CuCl_2$•$2H_2O$]/[K_2CO_3] = 1:1:2:1. [b] Determined by GPC using DMF containing 0.05 M LiBr as an eluent on the basis of a linear PMMA calibration. $Đ = M_w/M_n$.

Table S7 Time course of the polymerization of CS_2, **1a** and **2**[a].

Entry	Time (h)	Yield (%)	M_n[b]	M_w[b]	$Đ$[b]
1	2	35	4500	5400	1.2
2	4	58	6100	8300	1.4
3	6	87	9200	17 600	1.9
4	8	94	14 800	43 500	2.9
5	10	91	11 800	30 900	2.6

[a] The first step of this MCTP was carried out in DMSO at 30 °C for 1 h, and the second step was carried out in DMSO at 120 °C. [**1a**] = 0.3 M, [**1a**]/[**2**]/[CS_2]/[$CuCl_2$•$2H_2O$]/[K_2CO_3] = 1:1:2.4:2:1. [b] Determined by GPC using DMF containing 0.05 M LiBr as an eluent on the basis of a linear PMMA calibration. $Đ = M_w/M_n$.

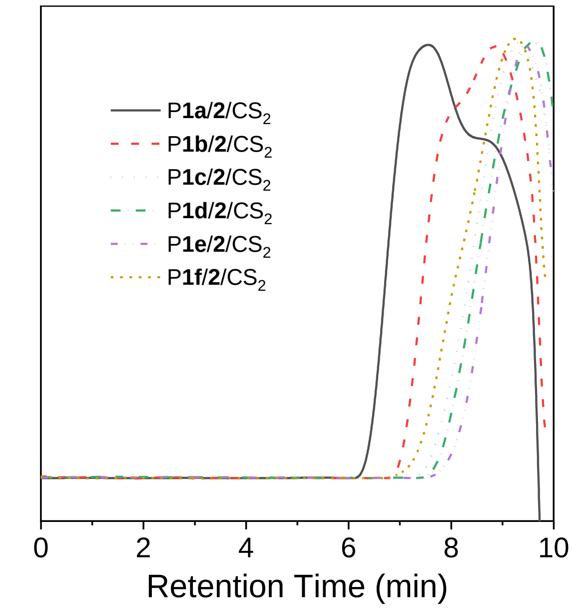


Fig. S1 The GPC curves of P**1a**/**2**/CS_2-P**1f**/**2**/CS_2.

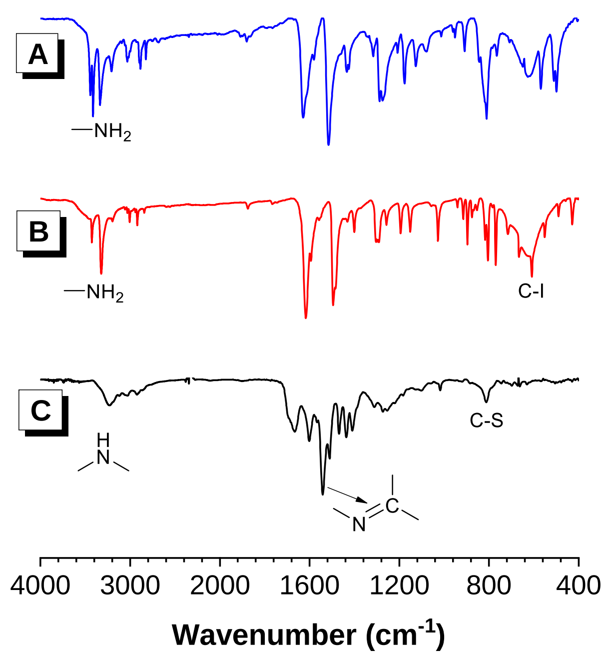


Fig. S2 FT-IR spectra of monomers **1a** (A) and **2** (B), and P**1a**/**2**/CS_2 (C).

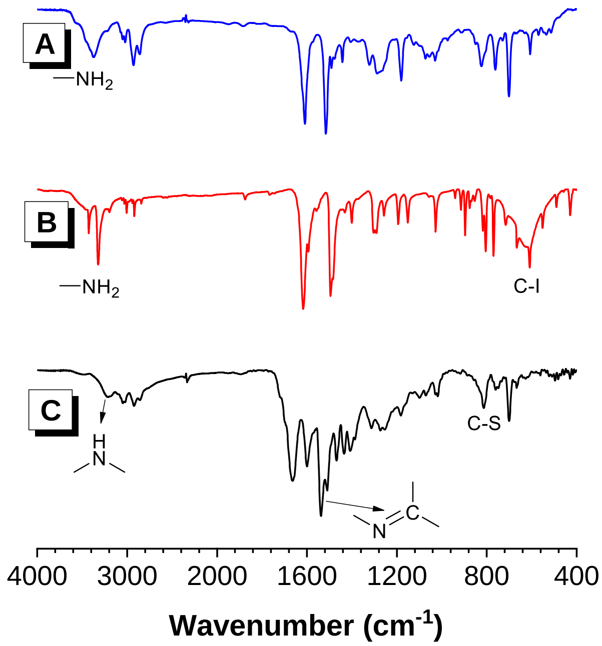


Fig. S3 FT-IR spectra of monomers **1b** (A) and **2** (B), and P**1b**/**2**/CS_2 (C).

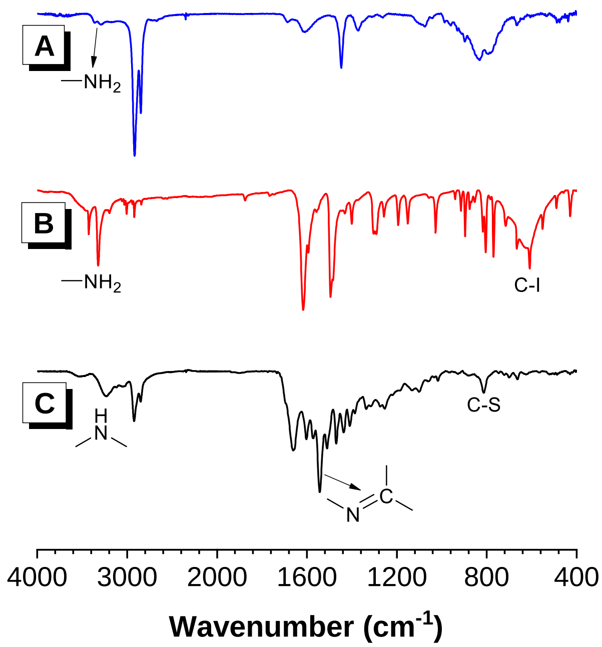


Fig. S4 FT-IR spectra of monomers **1c** (A) and **2** (B), and P**1c**/**2**/CS_2 (C).

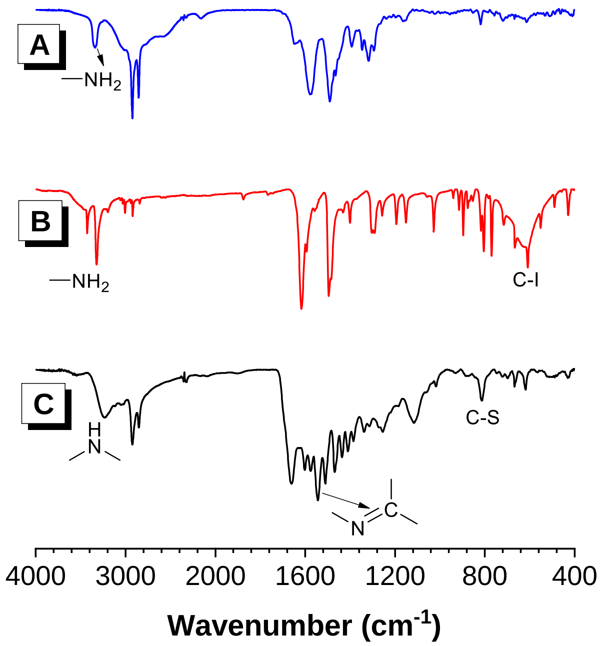


Fig. S5 FT-IR spectra of monomers **1e** (A) and **2** (B), and P**1e**/**2**/CS_2 (C).

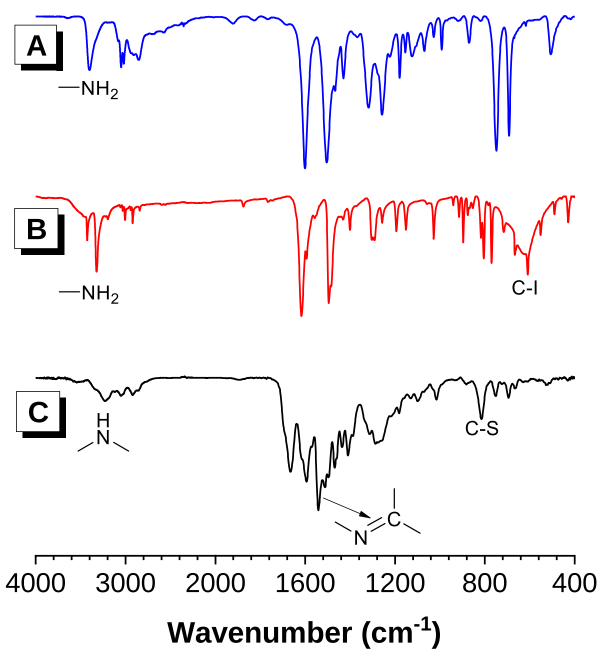


Fig. S6 FT-IR spectra of monomers **1f** (A) and **2** (B), and P**1f**/**2**/CS_2 (C).

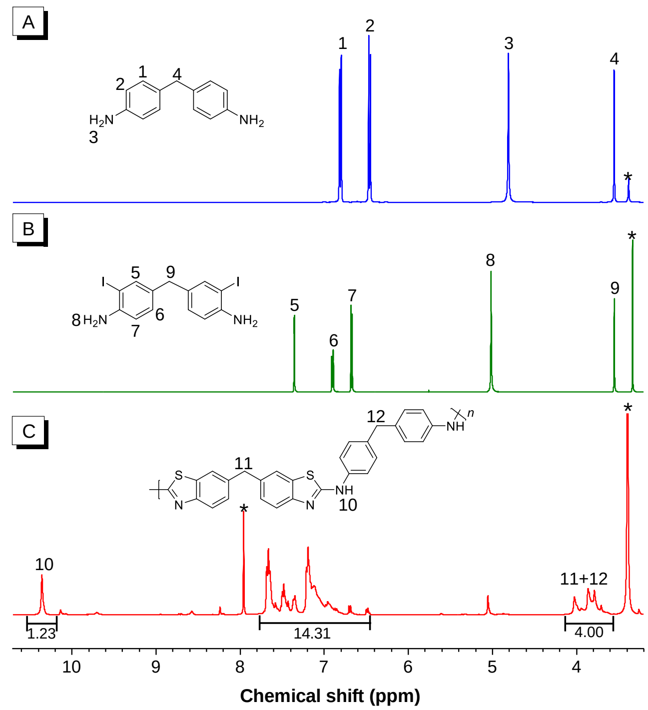


Fig. S7 ^{1}H NMR spectra of monomers **1a** (A) and **2** (B), and P**1a**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

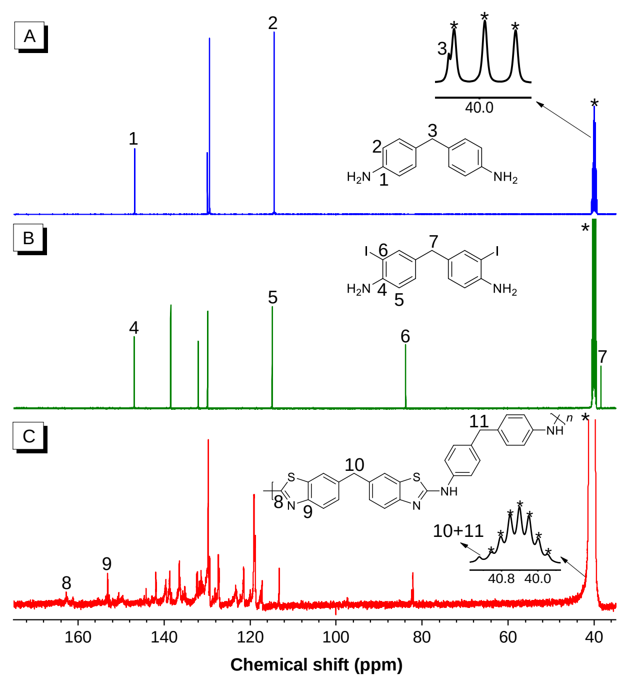


Fig. S8 ^{13}C NMR spectra of monomers **1a** (A) and **2** (B), and P**1a**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

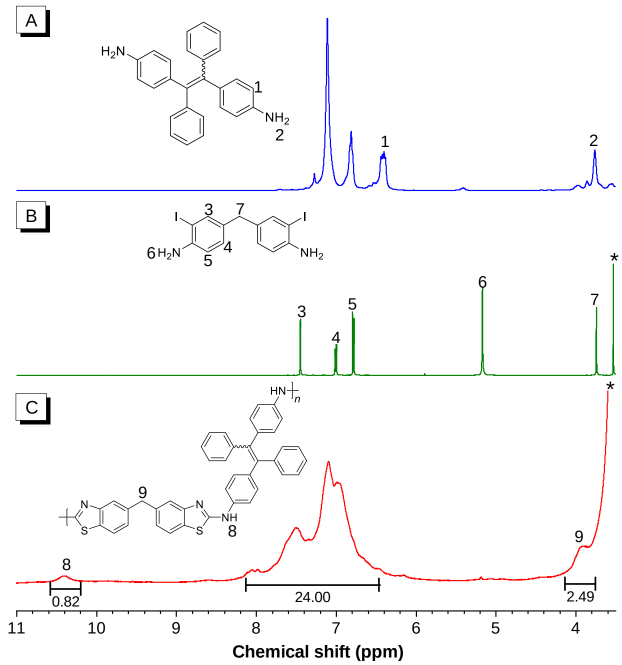


Fig. S9 [1]H NMR spectra of monomers **1b** (A) and **2** (B), and P**1b**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

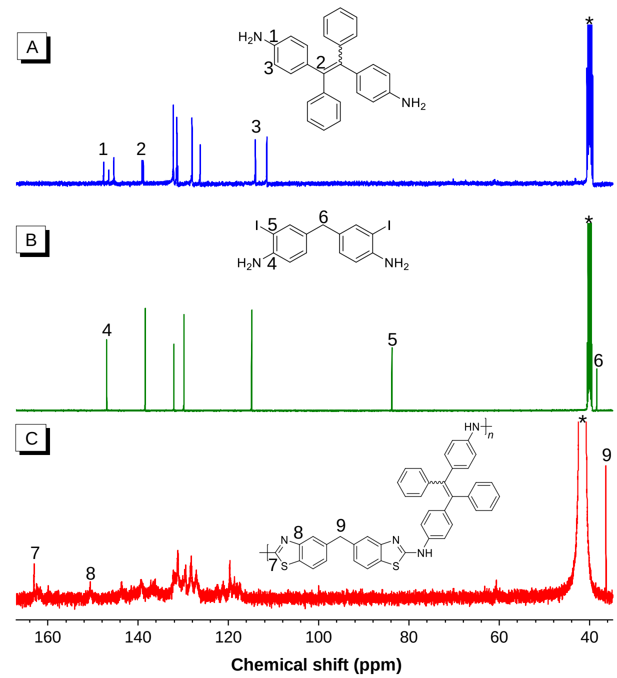


Fig. S10 [13]C NMR spectra of monomers **1b** (A) and **2** (B), and P**1b**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

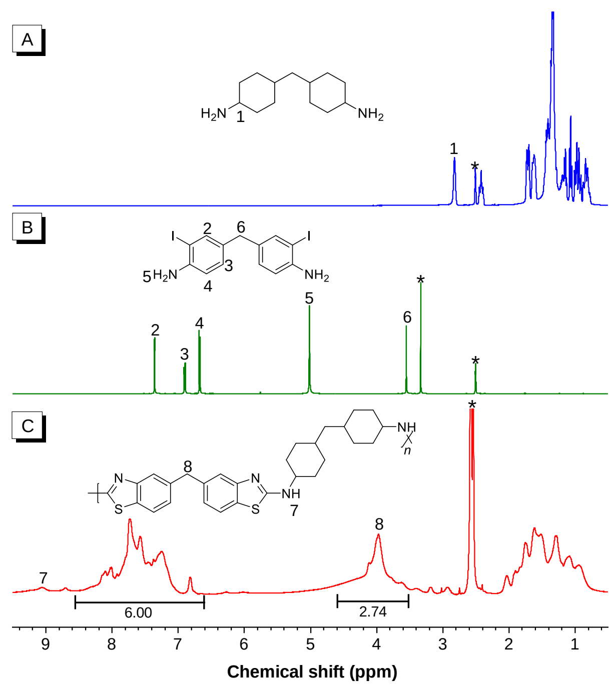


Fig. S11 [1]H NMR spectra of monomers **1c** (A) and **2** (B), and P**1c**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

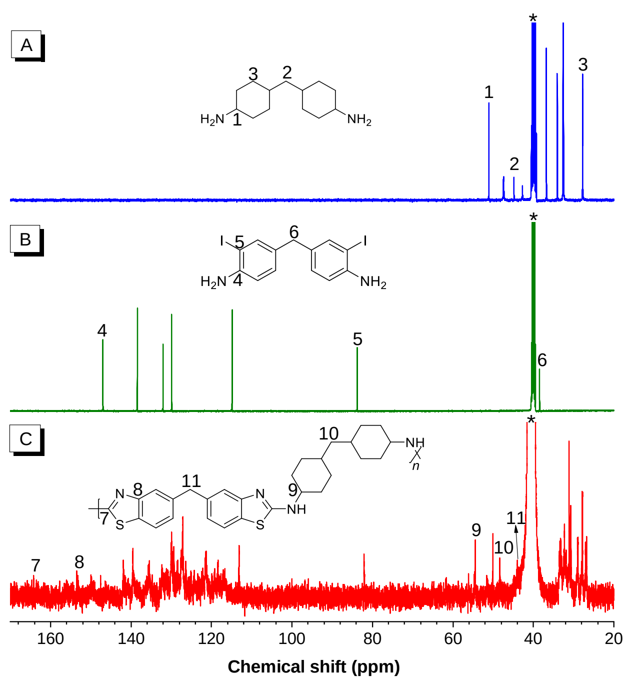


Fig. S12 [13]C NMR spectra of monomers **1c** (A) and **2** (B), and P**1c**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

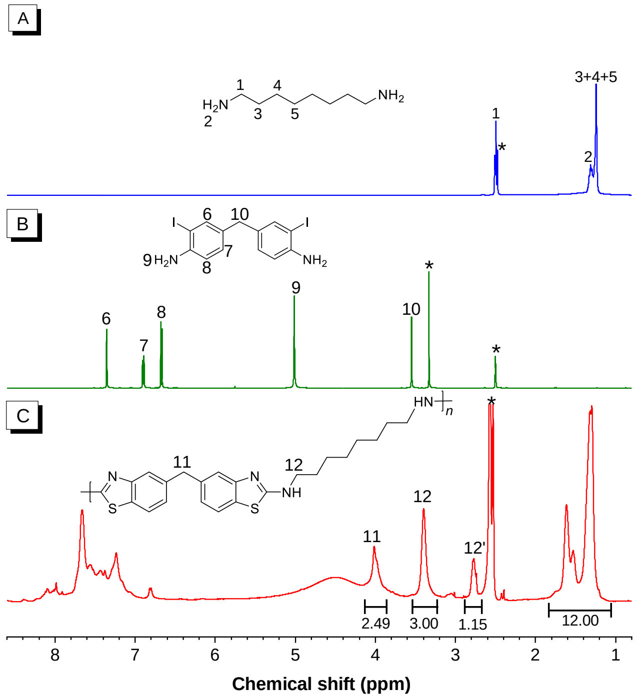


Fig. S13 ^{1}H NMR spectra of monomers **1e** (A) and **2** (B), and P**1e**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

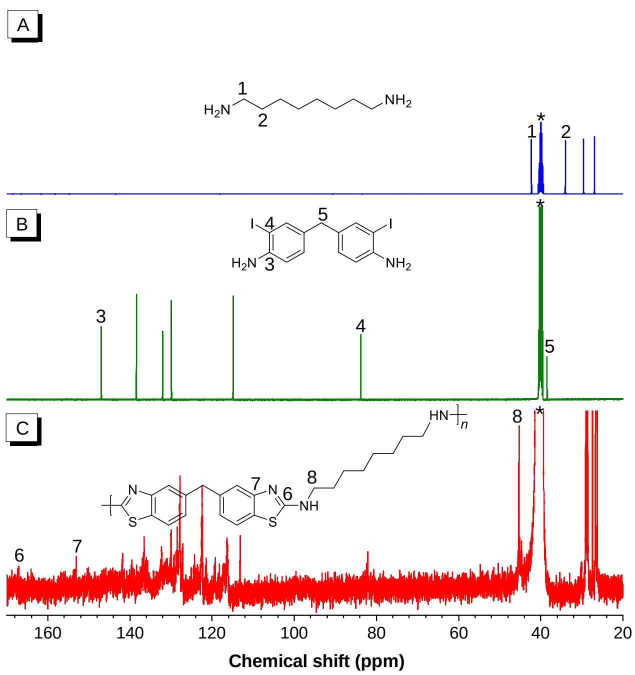


Fig. S14 ^{13}C NMR spectra of monomers **1e** (A) and **2** (B), and P**1e**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

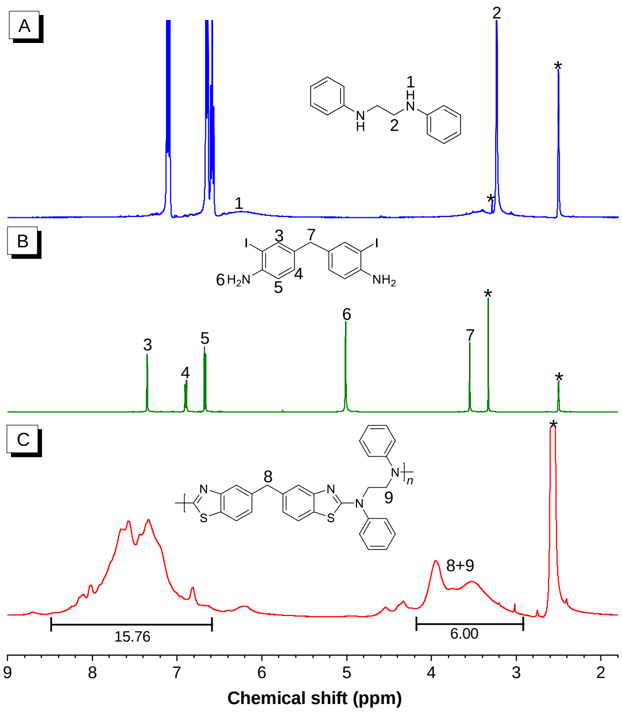


Fig. S15 [1]H NMR spectra of monomers **1f** (A) and **2** (B), and P**1f**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

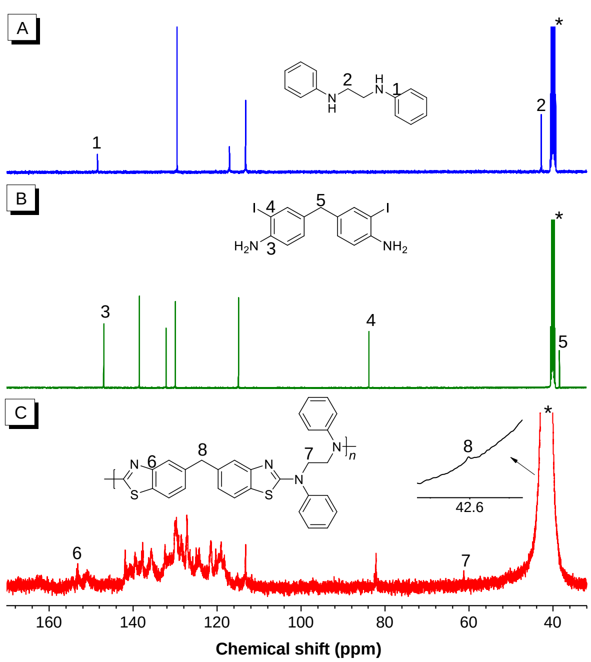


Fig. S16 [13]C NMR spectra of monomers **1f** (A) and **2** (B), and P**1f**/**2**/CS_2 (C) in DMSO-d_6. The solvent peaks are marked with asterisks.

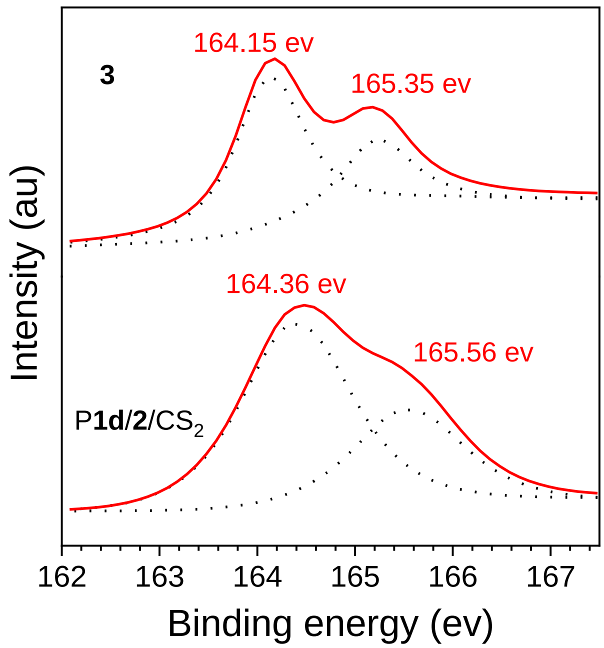


Fig. S17 S 2p XPS of **3** and P**1d**/**2**/CS_2.

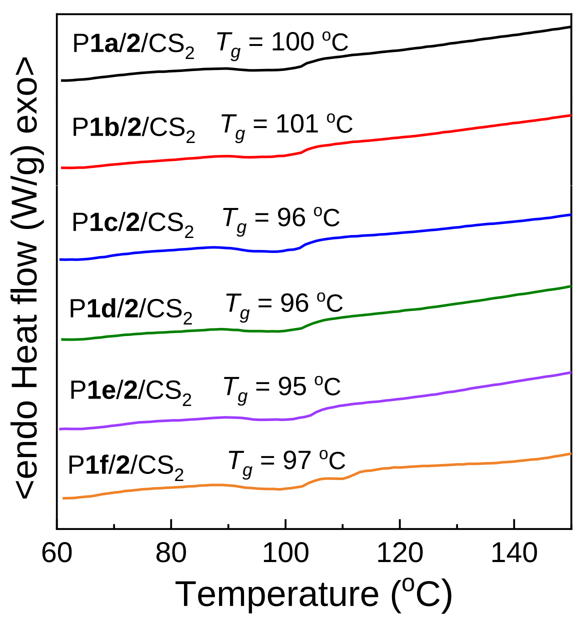


Fig. S18 DSC curves of the PBTs recorded under nitrogen.

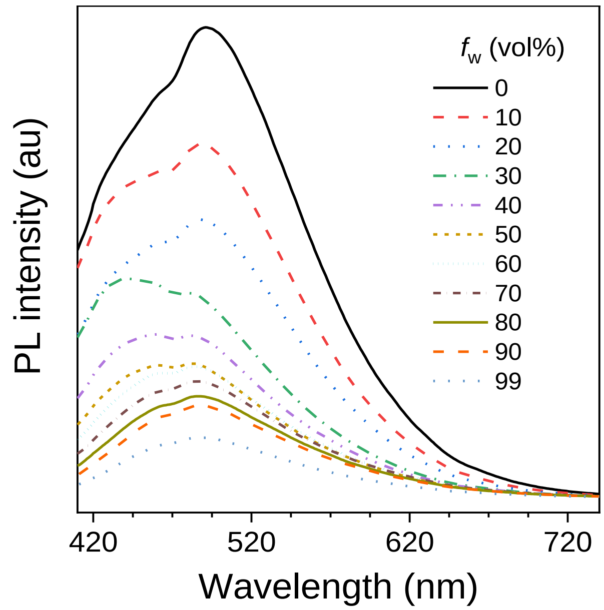


Fig. S19 PL spectra of P**1b**/**2**/CS_2 in DMSO/water mixtures with different water fractions (f_w). Solution concentration: 10 μM; excitation wavelength: 350 nm.