

Supporting Information

A Facile Approach for Preparation of Poly(Benzothiophene-*alt*-Maleic Anhydride) Microspheres by Self-Stabilized Precipitation Polymerization

Tianxiao Chang, Hongyi Qi, Chenxi Liang, Yanbin Huang and Wantai Yang**

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China.

Corresponding Author

***Yanbin Huang**——Department of Chemical Engineering, Tsinghua University, Beijing 100084, China; orcid.org/0000-0002-5032-202X; Email: yanbin@tsinghua.edu.cn

***Wantai Yang**——Department of Chemical Engineering, Tsinghua University, Beijing 100084, China; orcid.org/0000-0002-7763-4947; Email: yangwantai@tsinghua.edu.cn

EXPERIMENTAL SECTION

Monomer conversion and microsphere yield

The monomer conversion and microsphere yield were determined gravimetrically. In the supernatant, there were still short-chain copolymers. So, the weight of copolymer products is the sum of the microspheres weight and the weight of the copolymer in the supernatant. The monomer conversion and the microsphere yield can be calculated according to the following equations:

$$\text{Monomer conversion \%} = W_c/W_m \times 100 \% \quad (1)$$

$$\text{Microsphere yield \%} = W_p/W_m \times 100 \% \quad (2)$$

where W_c is the weight of the copolymer formed, W_p is the weight of as-formed copolymer microspheres, and W_m is the weight of the monomers in the reaction system.

Size and particle size distribution of PBTMA microspheres

The particle size and size distribution of the PBTMA microspheres were determined by measuring over 100 microspheres in SEM images and calculated using the following formulas:

$$D_n = \frac{\sum_{i=1}^k D_i}{N} \quad (3)$$

$$D_w = \frac{\sum_{i=1}^k D_i^4}{\sum_{i=1}^k D_i^3} \quad (4)$$

$$PSD = D_w / D_n \quad (5)$$

$$CV = \sqrt{\frac{\sum_{i=1}^k (D_i - D_n)^2}{k - 1}} / D_n \times 100\% \quad (6)$$

where D_n is the number average diameter, D_w is the weight average diameter, D_i is the diameter of the determined microsphere, N is the total number of the measured microspheres, PSD stands for the particle size distribution. CV stands for the coefficient of variation in diameter.

RESULTS AND DISCUSSION

Solubility parameter calculated according to method of Hoftyzer and Van Krevelen¹

The solubility parameter components (δ) could be predicted from group contributions, using the following equations:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (7)$$

$$\delta_d = \frac{\rho \sum F_{di}}{M} \quad (8)$$

$$\delta_p = \frac{\rho \sqrt{\sum F_{di}^2}}{M} \quad (9)$$

$$\delta_h = \frac{\rho \sqrt{\sum E_{hi}}}{M} \quad (10)$$

where δ_d is theoretical estimate of dispersion forces; δ_p is theoretical estimate of polar forces; δ_h is theoretical estimate of hydrogen bonding; ρ represent the density of measured object; F means the molar attraction constant, as $\delta = \rho F/V$. M represent the relative molecular mass of measured object. (For $-\text{CH}_3$, $F_{di} = 420 (\text{MJ}/\text{m}^3)^{1/2} \cdot \text{mol}^{-1}$, $F_{pi} = 0 (\text{MJ}/\text{m}^3)^{1/2} \cdot \text{mol}^{-1}$, $E_{hi} = 0 \text{ J/mol}$; For $-\text{CH}_2-$, $F_{di} = 270 (\text{MJ}/\text{m}^3)^{1/2} \cdot \text{mol}^{-1}$, $F_{pi} = 0 (\text{MJ}/\text{m}^3)^{1/2} \cdot \text{mol}^{-1}$, $E_{hi} = 0 \text{ J/mol}$; For $-\text{COO}-$, $F_{di} = 390 (\text{MJ}/\text{m}^3)^{1/2} \cdot \text{mol}^{-1}$, $F_{pi} = 490 (\text{MJ}/\text{m}^3)^{1/2} \cdot \text{mol}^{-1}$, $E_{hi} = 7000 \text{ J/mol}$)

Solubility parameter of PBTMA copolymer determined by the cloud point titration method

80 mg of PBTMA copolymer was dissolved in 10 mL of acetone (the good solvent) and then transferred 1 mL solution in a test tube. Hexane (the poor solvent) was added dropwise until the solution began to appear turbidity. The solubility parameter of PBTMA can be calculated according to the following equation:

$$\delta(\text{PBTMA}) = \varphi_1 \delta_1 + \delta_2 \varphi_2 \quad (11)$$

where δ_1 is the solubility parameter of good solvent; φ_1 is the volume percentage of good solvent; δ_2 is the solubility parameter of poor solvent; φ_2 is the volume percentage of poor solvent. ($\delta(\text{n-hexane}) = 14.94 \text{ J}^{1/2} \cdot \text{cm}^{3/2}$; $\delta(\text{cyclohexane}) = 16.78 \text{ J}^{1/2} \cdot \text{cm}^{3/2}$; $\delta(\text{n-hexane}) = 19.2 \text{ J}^{1/2} \cdot \text{cm}^{3/2}$)

The experiment was also determined in acetone-cyclohexane system and ethyl formate-*n*-hexane system. The $\delta(\text{PBTMA})$ was $18.3 \text{ J}^{1/2} \cdot \text{cm}^{3/2}$, $18.6 \text{ J}^{1/2} \cdot \text{cm}^{3/2}$, $18.1 \text{ J}^{1/2} \cdot \text{cm}^{3/2}$ determined in acetone-*n*-hexane system, acetone-cyclohexane system and ethyl formate-*n*-hexane system respectively. The average value was $18.3 \text{ J}^{1/2} \cdot \text{cm}^{3/2}$.

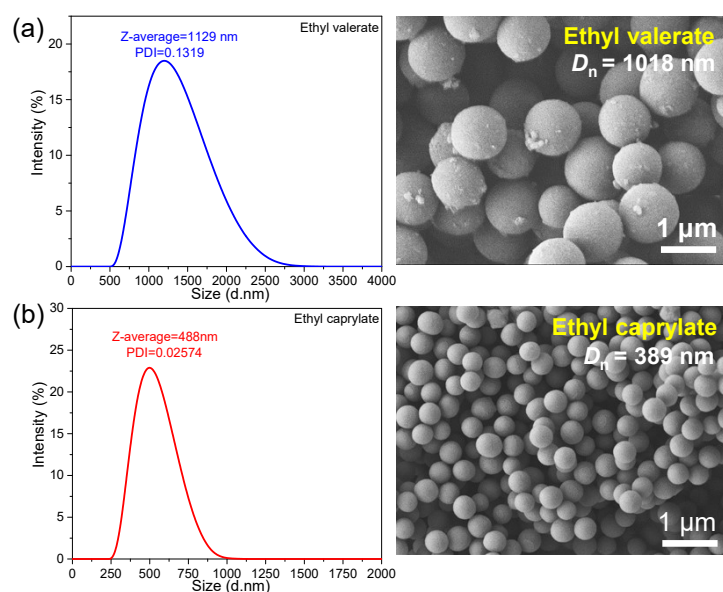


Fig. S1 Particle size of microspheres obtained in (a) ethyl valerate and (b) ethyl caprylate measured by dynamic light scattering (DLS) and SEM.

Table S1. Formation process of PBTMA microspheres

Reaction time	Particle yield	Monomer conversion	M_n (g/mol)	M_w (g/mol)	Dispersity	D_n (nm)	D_w (nm)	PSD	CV (%)
10 min	7%	13%	12100	24200	2.00	703	705	1.017	7.71
20 min	26%	40%	11000	21300	1.94	924	931	1.008	5.17
30 min	47%	61%	8200	19800	2.41	1446	1459	1.009	5.58
40 min	55%	68%	7300	15300	2.08	1467	1485	1.012	6.39
60 min	60%	79%	6400	14000	2.19	1630	1644	1.009	5.48
120 min	76%	82%	6700	15700	2.33	1741	1772	1.018	7.71
240 min	78%	88%	4600	11600	2.55	1664	1692	1.017	7.64
360 min	80%	91%	4300	11200	2.63	1726	1740	1.007	5.13

Polymerization conditions: [benzothiophene]/[MAh]= 1:1, monomer concentration 50 wt%, AIBN 1 wt%, in xylene, at 70 °C

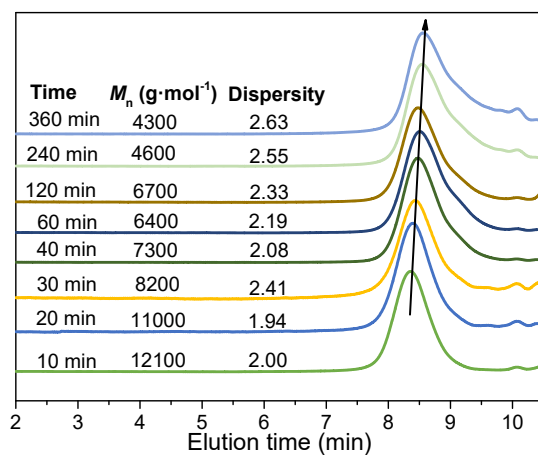
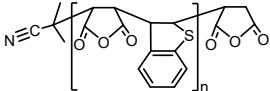
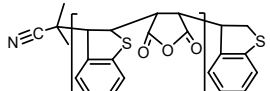
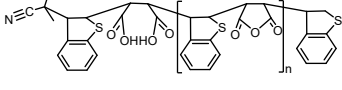
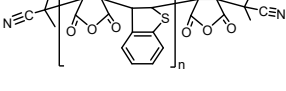
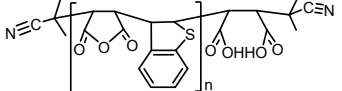
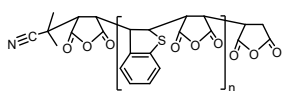
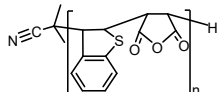
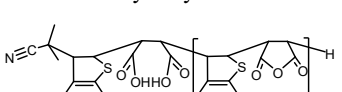
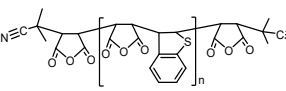
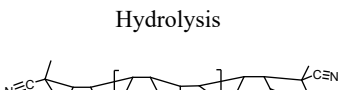
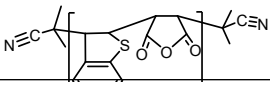


Fig. S2 GPC traces of the polymers synthesized at different reaction time.

Table S2. Sequence analysis of PBTMA copolymer by MALDI-TOF MS

Structural formula	Hydrolysis and Cation		n	Peak	(m/z) ^{Found} (g·mol ⁻¹)	(m/z) ^{calcd.} (g·mol ⁻¹)	Difference
	Na ⁺		7	A	1815.025	1815.860	0.835
	K ⁺		7	B	1831.547	1831.970	0.423
	Na ⁺		7	C	1850.458	1851.992	1.534
	K ⁺		7	D	1867.722	1868.102	0.3797
		Na ⁺	6		Mixed in peak D	1870.118	
		K ⁺	6	E	1885.197	1886.118	0.921
	Na ⁺		7		Mixed in peak E	1882.950	
	K ⁺		7		Mixed in peak F	1899.060	
		Na ⁺	7	F	1901.710	1900.966	0.744
		K ⁺	7		Mixed in peak G	1917.076	
	Na ⁺		7	G	1919.800	1919.082	0.718
	K ⁺		7	I	1935.609	1935.192	0.417
	Na ⁺		7		Mixed in peak G	1913.916	
	K ⁺		7	H	1929.501	1930.026	0.525
	Na ⁺		8	J	1949.306	1950.048	0.742
	K ⁺		8	K	1965.435	1966.158	0.723
		Na ⁺	7		Mixed in peak K	1968.064	
		K ⁺	7	L	1983.360	1984.174	0.814
	Na ⁺		7		Mixed in peak L	1981.006	
	K ⁺		7		Mixed in peak M	1997.116	
		Na ⁺	7	M	1999.896	1999.022	0.874
		K ⁺	7		Mixed in peak N	2015.132	
	Na ⁺		8	N	2017.240	2017.138	0.102
	K ⁺		8	O	2032.367	2033.248	0.8810

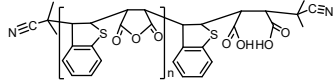
	Na ⁺	7	P	2036.478	2035.154	1.324
	K ⁺	7	Q	2052.151	2051.264	0.887

Table S3. Copolymerization results of benzothiophene and MAh *via* 2SP method in different solvents^a

Run	Solvent type	Reaction media	Solubility parameter (J ^{1/2} ·cm ^{3/2})	Observation	Particle size (nm)	M _n (g·mol ⁻¹)	M _w (g·mol ⁻¹)	Dispersity
1	Heterocyclic compound	1,4-Dioxane	20.5 ^b	Solution	/	3600	6100	1.68
2		Ethyl benzoate	19.8 ^b	Solution	/	5000	8500	1.71
3		Ethyl formate	19.2 ^b	Solution	/	4700	8000	1.69
4		Ethyl acetate	18.6 ^b	Solution	/	5600	9600	1.71
5		Ethyl propionate	17.9 ^b	Solution	/	5800	9800	1.70
6	Ester	Ethyl butyrate	17.4 ^c	Dispersion	1846	7700	11900	1.55
7		Ethyl valerate	17.3 ^c	Dispersion	1018	4300	7600	1.75
8		Ethyl heptanoate	17.1 ^c	Dispersion	591	5300	9100	1.74
9		Ethyl caprylate	17.0 ^c	Dispersion	389	5500	9500	1.72
10		Ethyl nonanoate	16.7 ^c	Dispersion	437	5000	8700	1.74
11		Ethyl caprate	16.8 ^c	Dispersion	552	4000	6800	1.73
12	Aromatic hydrocarbon	Toluene	18.2 ^b	Dispersion	1148	2400	4200	1.75
13		Xylene	~18.0 ^b	Dispersion	1156	1400	2400	1.71
14	Haloalkane	1,3,5-Trimethyl benzene	18.0 ^b	Dispersion	1368	1500	2600	1.73
15		Chloroform	19.0 ^b	Dispersion	2958	8000	13700	1.71
16		Dichloromethane	20.2 ^b	Coagulation	/	10300	15800	1.54

^a Polymerization condition: [benzothiophene]/[MAh]= 1:1, monomer concentration 20 wt%, AIBN 1 wt%, 6 h, 70 °C.

^b Experimental data.

^c Calculated by method of Hoftyzer and Van Krevelen.

Table S4. Effects of reaction medium on particle size and particle size distribution of PBTMA microspheres

Run	Solvent	Solubility parameter (J ^{1/2} ·cm ^{3/2})	D _n (nm)	D _w (nm)	PSD	CV (%)
1	Ethyl butyrate	17.4	1846	1988	1.077	16.69
2	Ethyl valerate	17.3	1018	1025	1.007	5.02
3	Ethyl caprylate	17.0	389	398	1.023	8.92
4	Ethyl nonanoate	16.7	437	443	1.013	6.92
5	Ethyl caprate	16.8	552	561	1.016	7.43
6	Xylene	~18.0	1156	1177	1.018	7.95
7	Toluene	18.2	1148	1171	1.021	8.79
8	Chloroform	19.0	2958	3119	1.054	14.06

Polymerization condition: [benzothiophene]/[MAh] =1:1, AIBN 1 wt%, monomer concentration 20 wt%, 6 h, 70 °C

Table S5. Effects of monomer concentration on monomer conversion, yield, particle size and particle size distribution of PBTMA microspheres

Monomer concentration	Particle yield	Monomer conversion	M_n (g/mol)	M_w (g/mol)	Dispersity	D_n (nm)	D_w (nm)	PSD	CV (%)
10 wt%	20%	46%	1000	1560	1.56	106	111	1.04	12.49
20 wt%	49%	58%	1400	2400	1.71	115	117	1.01	7.95
30 wt%	74%	90%	1900	3400	1.79	121	123	1.01	7.51
40 wt%	77%	88%	3000	5600	1.87	126	128	1.02	8.39
50 wt%	80%	91%	4300	11200	2.63	172	174	1.00	5.13

Polymerization conditions: [benzothiophene]/[MAh] =1:1, AIBN 1 wt%, in xylene, 6 h, 70°C

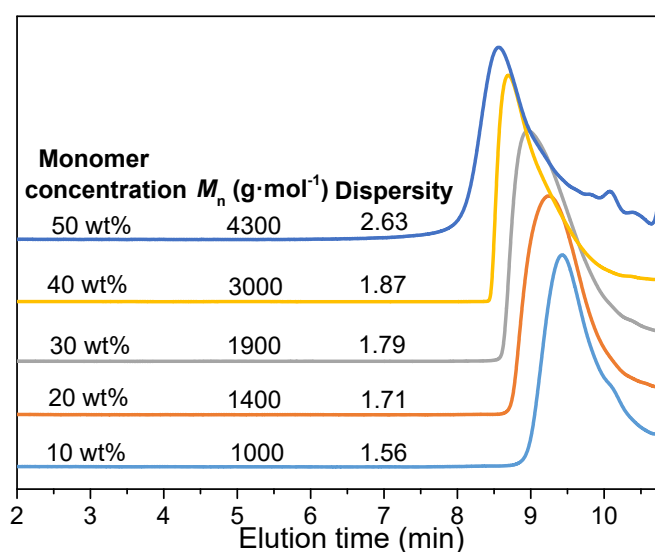


Fig. S3 GPC traces of the polymers synthesized at different monomer concentrations.

Table S6. Effects of initiator concentration on monomer conversion, yield, particle size and particle size distribution of PBTMA microspheres

Initiator concentration	Particle yield	Monomer conversion	M_n (g/mol)	M_w (g/mol)	Dispersity	D_n (nm)	D_w (nm)	PSD	CV (%)
1 wt%	77%	88%	3000	5600	1.87	1260	1285	1.020	8.39
2 wt%	79%	91%	2700	5100	1.89	1384	1435	1.037	11.21
2.5 wt%	77%	88%	2400	5100	2.12	1284	1324	1.031	9.99

3 wt%	76%	87%	1900	4000	2.10	1314	1351	1.028	9.25
3.5 wt%	80%	91%	1700	3600	2.12	1257	1282	1.020	8.11
4 wt%	87%	94%	700	1500	2.14	1255	1273	1.015	7.28
5 wt%	78%	85%	800	1900	2.37	1331	1552	1.166	22.32

Polymerization conditions: [benzothiophene]/[MAh] = 1:1, monomer concentration 40 wt%, in xylene, 6 h, 70 °C

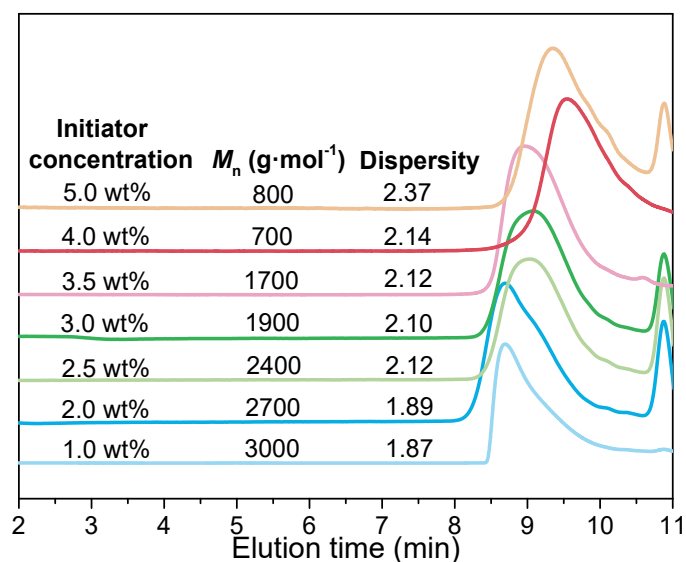


Fig. S4 GPC traces of the polymers synthesized at different initiator concentrations.

REFERENCES

1. D. W. Krevelen, and K. Nijenhuis, *Properties of Polymers*, Fourth Edition, Elsevier, 2009.