Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

Reduction of the rate retardation effect in bulk RAFT radical polymerization under externally applied magnetic field

Ling Lv, Wenxuan Wu, Gang Zou, Qijin Zhang*

Key Laboratory of Soft Matter Chemistry, Key Laboratory of Optoelectronic Science and Technology, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Fax: +86 551 3601 704; E-mail: zqjm@ustc.edu.cn

Experimental Section

1. Reagents

Styrene monomer (CP, Sinopharm Chemical Reagent Co., Ltd) was distilled under reduced pressure after being washed three times with 15% sodium hydroxide aqueous solution and then distilled water. Benzoyl peroxide (BPO) (CP, Sinopharm Chemical Reagent Co., Ltd) was used after recrystallization in methanol. The chain transfer agent (2-cyano-2-propyl) dithiobenzoate (CPDB) was synthesized according to the literature procedure.[1] The purity of CPDB was better than 97% as verified by ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.9 (d, 2H, Ar H), 7.5 (t, 1H, Ar H), 7.4 (t, 2H, Ar H), 2.0 (s, 6H; CH_3).

2. External Applied Magnetic Field (EAMF)

The EAMF was generated by solenoid SB-100 (Changchun Yingpu Magneto-electric Corp) with a power supply. The strength of EAMF could be varied by changing electric current within 40A and voltage within 100V.

3. Polymerization

All the reactions conducted in this study were bulk polymerization of styrene under 60 ℃ in dilatometer of 25 mL. The dilatometer was designed with a jacket full of circulating water to adapt with the magnetic field and keep the polymerization temperature (see Figure 1). The kinetics of RAFT polymerization was calculated through the change rate of the height of liquid column of dilatometer.

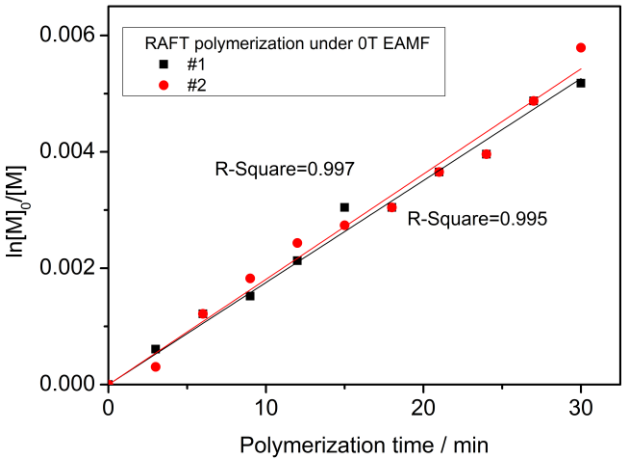
RAFT Polymerizations under different EAMF were conducted again to examine the reproducibility with the same dilatometer at 60℃. In the following experiments, [M]=

8.70 mol·L^{-1}, [BPO]= 0.0870 mol·L^{-1}, [CPDB]= 0.0435 mol·L^{-1}. The kinetics data is similar in parallel experiments (STable 1,2,3,4,5 and SFigure 1,2,3,4,5), and the change trend of apparent polymerization rate constant along with EAMF is the same.

Supporting Data

STable 1. Data of RAFT polymerization under 0T EAMF

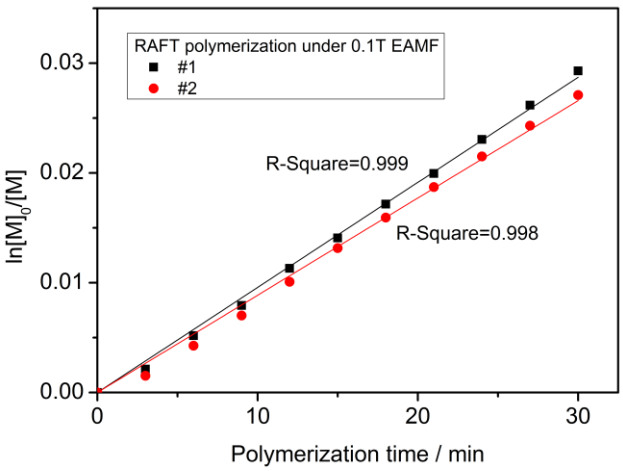
t/min	#1		#2	
	$Ln[M]_0/[M]$	Conversion	$Ln[M]_0/[M]$	Conversion
0	0	0	0	0
1	3.04E-4	3.04E-4	0	0
2	6.08E-4	6.08E-4	3.04E-4	3.04E-4
3	6.08E-4	6.08E-4	3.04E-4	3.04E-4
4	6.08E-4	6.08E-4	6.08E-4	6.08E-4
5	9.12E-4	9.12E-4	9.12E-4	9.12E-4
6	0.00122	0.00122	0.00122	0.00122
7	0.00152	0.00152	0.00152	0.00152
8	0.00152	0.00152	0.00152	0.00152
9	0.00152	0.00152	0.00182	0.00182
10	0.00182	0.00182	0.00213	0.00213
11	0.00182	0.00182	0.00243	0.00243
12	0.00213	0.00213	0.00243	0.00243
13	0.00243	0.00243	0.00274	0.00273
14	0.00274	0.00273	0.00274	0.00273
15	0.00304	0.00304	0.00274	0.00273
16	0.00304	0.00304	0.00304	0.00304
17	0.00304	0.00304	0.00304	0.00304
18	0.00304	0.00304	0.00304	0.00304
19	0.00304	0.00304	0.00335	0.00334
20	0.00304	0.00304	0.00335	0.00334
21	0.00365	0.00365	0.00365	0.00365
22	0.00396	0.00395	0.00365	0.00365
23	0.00396	0.00395	0.00396	0.00395
24	0.00396	0.00395	0.00396	0.00395
25	0.00426	0.00425	0.00426	0.00425
26	0.00457	0.00456	0.00457	0.00456
27	0.00487	0.00486	0.00487	0.00486
28	0.00487	0.00486	0.00518	0.00517
29	0.00518	0.00517	0.00548	0.00547
30	0.00518	0.00517	0.00579	0.00577



SFigure 1.Kinetics of RAFT polymerization under 0 T EAMF

STable 2. Data of RAFT polymerization under 0.1T EAMF

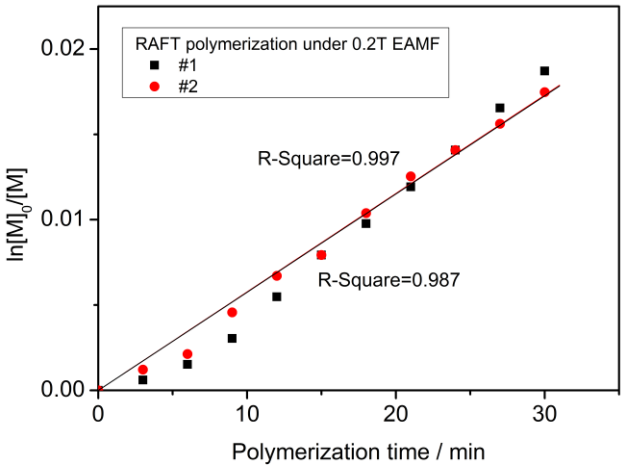
t/min	#1		#2	
	$Ln[M]_0/[M]$	Conversion	$Ln[M]_0/[M]$	Conversion
0	0	0	0	0
1	6.083E-4	6.08E-4	6.08E-4	6.08E-4
2	0.00122	0.00122	0.00122	0.00122
3	0.00213	0.00213	0.00152	0.00152
4	0.00335	0.00334	0.00243	0.00243
5	0.00426	0.00425	0.00304	0.00304
6	0.00518	0.00517	0.00426	0.00425
7	0.00640	0.00638	0.00487	0.00486
8	0.00732	0.00729	0.00610	0.00608
9	0.00793	0.00790	0.00701	0.00699
10	0.00946	0.00942	0.00793	0.00790
11	0.0101	0.0100	0.00916	0.0091
12	0.0113	0.0112	0.0101	0.0100
13	0.0125	0.0125	0.0113	0.0112
14	0.0135	0.0134	0.0119	0.0119
15	0.0141	0.0140	0.0132	0.0131
16	0.0150	0.0149	0.0141	0.0140
17	0.0159	0.0158	0.0150	0.0149
18	0.0172	0.0170	0.0159	0.0158
19	0.0181	0.0179	0.0169	0.0167
20	0.0187	0.0185	0.0175	0.0173
21	0.0200	0.0198	0.0187	0.0185
22	0.0212	0.0210	0.0196	0.0195
23	0.0221	0.0219	0.0206	0.0204
24	0.0231	0.0228	0.0215	0.0213
25	0.0243	0.0240	0.0224	0.0222
26	0.0252	0.0249	0.0234	0.0231
27	0.0262	0.0258	0.0243	0.0240
28	0.0268	0.0264	0.0255	0.0252
29	0.0280	0.0277	0.0262	0.0258
30	0.0293	0.0289	0.0271	0.0267



SFigure 2.Kinetics of RAFT polymerization under 0.1 T EAMF

STable 3. Data of RAFT polymerization under 0.2T EAMF

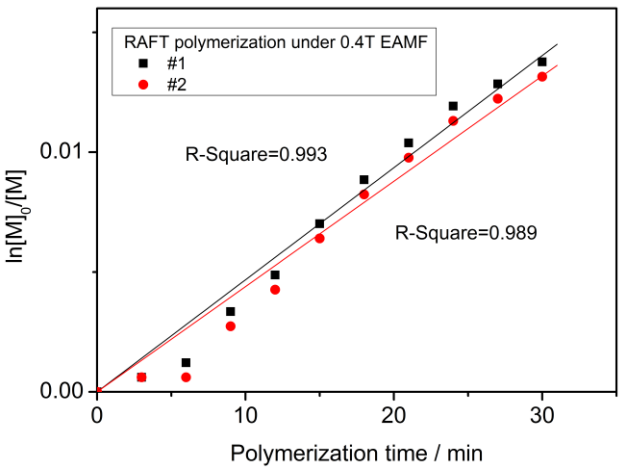
t/min	#1		#2	
	$Ln[M]_0/[M]$	Conversion	$Ln[M]_0/[M]$	Conversion
0	0	0	0	0
1	3.04E-4	3.04E-4	6.08E-4	6.08E-4
2	3.04E-4	3.04E-4	9.12E-4	9.12E-4
3	6.08E-4	6.08E-4	0.00122	0.00122
4	9.12E-4	9.12-4	0.00152	0.00152
5	0.00122	0.00122	0.00152	0.00152
6	0.00152	0.00152	0.00213	0.00213
7	0.00182	0.00182	0.00274	0.00273
8	0.00243	0.00243	0.00396	0.00395
9	0.00304	0.00304	0.00457	0.00456
10	0.00396	0.00395	0.00518	0.00517
11	0.00457	0.00456	0.0061	0.00608
12	0.00548	0.00547	0.00671	0.00668
13	0.00610	0.00608	0.00701	0.00699
14	0.00701	0.00699	0.00732	0.00729
15	0.00793	0.0079	0.00793	0.0079
16	0.00885	0.00881	0.00885	0.00881
17	0.00946	0.00942	0.00977	0.00972
18	0.00977	0.00972	0.0104	0.01033
19	0.0104	0.0103	0.0110	0.0109
20	0.0113	0.0112	0.0116	0.0116
21	0.0119	0.0119	0.0125	0.0125
22	0.0128	0.0128	0.0128	0.0128
23	0.0135	0.0134	0.0135	0.0134
24	0.0141	0.0140	0.0141	0.0140
25	0.0150	0.0149	0.0147	0.0146
26	0.0159	0.0158	0.0150	0.0149
27	0.0165	0.0164	0.0156	0.0155
28	0.0169	0.0167	0.0165	0.0164
29	0.0181	0.0179	0.0169	0.0167
30	0.0187	0.0185	0.0175	0.0173



SFigure 3.Kinetics of RAFT polymerization under 0.2 T EAMF

STable 4. Data of RAFT polymerization under 0.4T EAMF

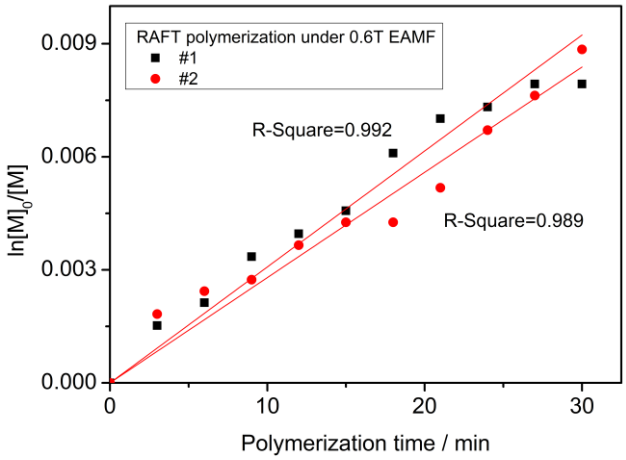
t/min	#1		#2	
	$Ln[M]_0/[M]$	Conversion	$Ln[M]_0/[M]$	Conversion
0	0	0	0	0
1	3.04E-4	3.04E-4	3.04E-4	3.04E-4
2	3.04E-4	3.04E-4	6.08E-4	6.08E-4
3	6.08E-4	6.08E-4	6.08E-4	6.08E-4
4	6.08E-4	6.08E-4	6.08E-4	6.08E-4
5	9.12E-4	9.12E-4	6.08E-4	6.08E-4
6	0.00122	0.00122	6.08E-4	6.08E-4
7	0.00152	0.00152	9.12E-4	9.12E-4
8	0.00243	0.00243	0.00182	0.00182
9	0.00335	0.00334	0.00274	0.00273
10	0.00396	0.00395	0.00335	0.00334
11	0.00457	0.00456	0.00396	0.00395
12	0.00487	0.00486	0.00426	0.00425
13	0.0061	0.00608	0.00548	0.00547
14	0.00671	0.00668	0.00610	0.00608
15	0.00701	0.00699	0.00640	0.00638
16	0.00763	0.00760	0.00701	0.00699
17	0.00824	0.00820	0.00763	0.00760
18	0.00885	0.00881	0.00824	0.00820
19	0.00916	0.00912	0.00854	0.00851
20	0.00977	0.00972	0.00916	0.00912
21	0.0104	0.0103	0.00977	0.00972
22	0.0107	0.0106	0.0101	0.0100
23	0.0113	0.0112	0.0107	0.0106
24	0.0119	0.0119	0.0113	0.0112
25	0.0122	0.0122	0.0116	0.0116
26	0.0125	0.0125	0.0119	0.0119
27	0.0128	0.0128	0.0122	0.0122
28	0.0128	0.0128	0.0122	0.0122
29	0.0132	0.0131	0.0125	0.0125
30	0.0138	0.0137	0.0132	0.0131



SFigure 4.Kinetics of RAFT polymerization under 0.4 T EAMF

STable 5. Data of RAFT polymerization under 0.6T EAMF

	#1		#2	
t/min	$Ln[M]_0/[M]$	Conversion	$Ln[M]_0/[M]$	Conversion
0	0	0	0	0
1	6.08E-4	6.08E-4	6.08E-4	6.08E-4
2	0.00122	0.00122	0.00122	0.00122
3	0.00152	0.00152	0.00182	0.00182
4	0.00182	0.00182	0.00213	0.00213
5	0.00182	0.00182	0.00213	0.00213
6	0.00213	0.00213	0.00243	0.00243
7	0.00274	0.00273	0.00274	0.00273
8	0.00304	0.00304	0.00274	0.00273
9	0.00335	0.00334	0.00274	0.00273
10	0.00365	0.00365	0.00304	0.00304
11	0.00365	0.00365	0.00304	0.00304
12	0.00396	0.00395	0.00365	0.00365
13	0.00396	0.00395	0.00396	0.00395
14	0.00426	0.00425	0.00396	0.00395
15	0.00457	0.00456	0.00426	0.00425
16	0.00518	0.00517	0.00426	0.00425
17	0.00579	0.00577	0.00426	0.00425
18	0.00610	0.00608	0.00426	0.00425
19	0.00640	0.00638	0.00457	0.00456
20	0.00671	0.00668	0.00457	0.00456
21	0.00701	0.00699	0.00518	0.00517
22	0.00701	0.00699	0.00579	0.00577
23	0.00732	0.00729	0.00610	0.00608
24	0.00732	0.00729	0.00671	0.00668
25	0.00732	0.00729	0.00732	0.00729
26	0.00763	0.00760	0.00763	0.00760
27	0.00793	0.00790	0.00763	0.00760
28	0.00824	0.00820	0.00793	0.00790
29	0.00824	0.00820	0.00854	0.00851
30	0.00793	0.00790	0.00885	0.00881



SFigure 5.Kinetics of RAFT polymerization under 0.6 T EAMF

Reference

1 (a) J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules*, 1998, **31**, 5559-5562; (b) S. Perrier, C. Barner-Kowollik, J. F. Quinn, P. Vana, T. P. Davis, *Macromolecules*, 2002, **35**, 8300-8306.