FULL PAPER

Controlled Bimodal Molecular-Weight-Distribution Polymers: Facile Synthesis by RAFT Polymerization**

Jian Qin, Lifen Zhang,* Hongjuan Jiang, Jian Zhu, Zhengbiao Zhang, Wei Zhang, Nianchen Zhou, Zhenping Cheng,* and Xiulin Zhu*^[a]

Abstract: The RAFT agents RAFT-1 and RAFT-2 were used for RAFT polymerization to synthesize well-defined bimodal molecular-weight-distribution (MWD) polymers. The system showed excellent controllability and "living" characteristics toward both the higher- and lower-molecular-weight fractions. It is important that bimodal higher-molecular-weight (HMW) polymers and block copolymers with both well-controlled molecular weight

Keywords: living radical polymerization • molecular-weight distribution • polymers • radical reactions • RAFT (MW) and MWD could be prepared easily due to the "living" features of RAFT polymerization. The strategy realized a mixture of higher/lower-molecular-weight polymers at the molecular level but also preserved the features of living radical polymerization (LRP) of the RAFT polymerization.

Introduction

The physical/mechanical properties and processing performance of polymers are greatly affected by their molecular (MWs) and molecular-weight weights distributions (MWDs). Polymers with higher molecular-weight (HMW) have higher strength but are difficult to process. On the contrary, lower-molecular-weight (LMW) polymers are endued with good toughness and rheological properties but possess lower rigidity. For some special applications, desirable mechanical properties and process abilities are both needed. In order to synchronously possess these characteristics, bimodal MWD polymers, which contain both HMW and LMW fraction polymers, effectively balance the processing performance (LMW component) and mechanical performance (HMW component) of materials under extreme conditions.^[1]

Until now, a number of approaches have been proposed to produce bimodal MWD polymers. 1) Physical blending is a traditional way to mix higher- and lower-molecular-weight polymers after the two components have been synthesized separately. This method is difficult to carry out on a molecu-

[**] RAFT: Reversible addition-fragmentation chain-transfer.

lar level. Therefore, the performance of the polymers is greatly influenced by the extent of mixing. 2) A two-step reaction^[2] is another strategy for synthesizing bimodal MWD polymers. In a two-step reaction, one kind of polymer would be synthesized first under certain polymerization conditions. The reaction conditions would then be changed in the second reaction step to obtain another kind of molecularweight polymer. 3) A mixed-hybrid-catalyst system in a single reactor is a commonly used method for the preparation of homogeneous bimodal MWD polymers on the molecular level. But the systems usually include expensive and toxic metal catalysts, such as cobalt complexes,^[3] Ziegler-Natta^[4] or metallocene catalyst components, and so on.^[5] These catalysts are hard to eliminate completely and therefore seriously affect the material properties. 4) Chain-transfer^[6] or crosslinking^[7] agents can also be used as modifiers in polymerization for the synthesis of bimodal MWD polymers. Generally, the HMW fraction is created by adding a certain amount of chain-transfer or crosslinking agents to the reaction system.

Actually, if the molecular weights for both HMW and LMW polymers can be adjusted during the polymerization according to the requirements of the application, it will provide a powerful tool for the synthesis of bimodal MWD polymers. However, all of the strategies mentioned above have failed to synthesize bimodal MWD polymers with both controlled MW and MWD at the same time, which has been a great challenge until now.

As we know, living/controlled radical polymerization (LRP)^[8] provides a simple way to achieve well-defined polymers with both controlled MW and MWD. However, few documents about the synthesis of bimodal MWD polymers are available for LRP techniques. Lenzi and co-workers^[9] prepared bimodal MWD polymer resins of polystyrene and poly(butyl acrylate) by using nitroxide-mediated polymeri-



[[]a] J. Qin, Dr. L. F. Zhang, H. J. Jiang, Dr. J. Zhu, Dr. Z. B. Zhang, Dr. W. Zhang, Dr. N. C. Zhou, Dr. Z. P. Cheng, Dr. X. L. Zhu Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering College of Chemistry, Chemical Engineering and Materials Science Soochow University, Suzhou 215123 (P. R. China) Fax: (+86)512-65882787 Fax: (+86)512-65112796 E-mail: chengzhenping@suda.edu.cn xlzhu@suda.edu.cn



zation combined with conventional free radical polymerization. Wan and co-workers^[10] reported the formation of bimodal MWD poly(methyl methacrylate) by using controlled radical polymerization catalyzed by a CuCl/bis(2-dimethylaminoethyl) ether (BDE) complex in an aqueous medium. Unfortunately, these reports with LRP methods have not overcome the drawbacks mentioned above; that is, they failed to synthesize bimodal MWD polymers with both controlled MW and MWD, due to the concurrent presence of conventional free radical polymerization^[11] in these systems. Therefore, only one kind of molecular weight, which was produced by living radical polymerization, could be controlled during the whole polymerization process.

A facile LRP method, reversible addition-fragmentation chain-transfer (RAFT) polymerization,^[12] has been developed as a vital technique to synthesize well-defined polymers with designed structures since its first advent in 1998. Lovestead and co-workers studied the chain-length dependence of the termination-rate coefficient for disparate average-size radicals generated by a RAFT agent and a macro-RAFT species in the same system.^[13] For the first time, in this work, the RAFT polymerization method has been developed to establish a new strategy for synthesizing bimodal MWD polymers with both higher- and lower-molecularweight fractions controlled in MW and MWD by a one-step/ one-pot method. Herein, we describe the use of a pair of RAFT agents (a monofunctional RAFT agent: {2-bromo-2methyl-propionic acid 4-[2-(carbazole-9-carbodithioate)-2methyl-propionyloxy]phenyl ester} (BMCCDP, RAFT-1), and a difunctional RAFT agent: {1,4-[2-(carbazole-9-carbodithioate)-2-methyl-propionic acid] phenyl ester} (BCCDP, RAFT-2; Scheme 1) with similar structure in the same polymerization system.



Scheme 1. Synthetic route to BMCCDP and BCCDP. THF: tetrahydrofuran; TEA: triethylamine; BMPB: 1,4-(2'-bromo-2'-methylpropionato)benzene; DMSO: dimethylsulfoxide.

Results and Discussion

Synthesis of bimodal molecular-weight-distribution polystyrene: Figure 1 shows the GPC curves of the polystyrene (PS)



Figure 1. GPC curves of obtained polystyrenes with different molar ratios of RAFT-1/RAFT-2. [St]/[AIBN]/[RAFT-1]/[RAFT-2]_0 ratios of a) 1200:1.66:2.5:5; b) 1200:1:2.5:2.5; c) 1200:1.33:5:2.5; temperature = 75 °C; volume of styrene (V_{st}) = 3.0 mL.

obtained by this strategy in the presence of different molar ratios of RAFT-1/RAFT-2 (1:2, 1:1, and 2:1, respectively) by using styrene (St) as the monomer and 2,2'-azobisisobutyronitrile (AIBN) as the initiator at 75 °C. From Figure 1, it can be seen that two peaks (representing the HMW and LMW polymers, respectively) were discernable, which indicated that bimodal MWD polymers were successfully obtained.

To further investigate the polymerization behavior for this strategy, the kinetics of the RAFT polymerization of St were studied first. Figure 2a shows the kinetic plot for the RAFT polymerization of St with a molar ratio for [St]₀/[AIBN]₀/[RAFT-1]₀/[RAFT-2]₀ of 1200:1:2.5:2.5. A linear plot with respect to the monomer concentration and without an obvious induction period at the beginning of the polymerization indicated that the polymerizations were approximately first order and the concentration of propagating radicals remained constant during the polymerization. It can be seen from Figure 2b that both of the number-average molecular weights $(M_{n,GPC})$ of the resultant polymers increased linearly with monomer conversion, from 3850 gmol⁻¹ to 12250 gmol⁻¹ for the LMW polymer and from 8550 gmol⁻¹ to 27900 gmol⁻¹ for the HMW polymer, respectively. These values were consistent with the corresponding theoretical ones. Moreover, very low values for the weight-average molecular weight $(M_w)/M_n$ (<1.10) were obtained for both HMW and LMW polymers. All these results suggest that RAFT-1 and RAFT-2 were effective RAFT agents for the synthesis of bimodal MWD polymers.

Thermal RAFT polymerization of St and RAFT polymerization of methyl acrylate and acrylonitrile: Thermal polymerization without the AIBN initiator was carried out at 110 °C. The result is shown in entry 1 of Table 1. The polymerization could still be well-conducted to produce bimodal

6016 -



Figure 2. ln([M]₀/[M]) as a function of time and $M_{n,GPC}$ and M_w/M_n values versus conversion for the bulk RAFT polymerization of St in the presence of a pair of RAFT agents RAFT-1/RAFT-2 (a and b) or in the presence of RAFT-1 or RAFT-2 as individual RAFT agents, respectively (c and d). Polymerization conditions: a and b) [St]₀/[AIBN]₀/[RAFT-1]₀/[RAFT-2]₀=1200:1:2.5:2.5, V_{st} =3.0 mL, temperature =75 °C; c and d) [St]₀/[AIBN]₀/[RAFT-1]₀=600:0.33:2.5, [St]₀/[AIBN]₀/[RAFT-2]₀=600:0.33 or 0.66:2.5, V_{st} =3.0 mL, temperature =75 °C.

Table 1. Polymerizations of MA and AN and thermal polymerization of St with monofunctional BMCCDP and difunctional BCCDP as RAFT agents.

Entry	Ratio ^[a]	<i>t</i> [h]	Conv. ^[b] [%]	$M_{n,th}^{[c]}(LMW/HMW)$ [gmol ⁻¹]	$M_{n,GPC}(LMW)/HMW)$ [g mol ⁻¹]	$M_{ m w}/M_{ m n}$ (LMW/ HMW)
1 ^[d]	1200:0:2.5:2.5	28	91.0	15800/31000	14700/30400	1.08/1.04
2 ^[e]	600:1:2.5:2.5	7.5	79.6	6100/11650	10100/21000	1.04/1.08
3 ^[e]	1200:1:2.5:2.5	9.3	86.8	12600/24600	22900/46300	1.04/1.09
4 ^[e]	2400:1:2.5:2.5	19	98.0	27600/54700	40900/86000	1.06/1.09
5 ^[e]	4800:1:2.5:2.5	7.0	≈ 100	55700/113500	64600/176000	1.15/1.25
6 ^[f]	1200:1:2.5:2.5	2.0	84.0	7700/14950	23 000/44 600	1.03/1.07

[a] Ratio of [Monomer]₀/[AIBN]₀/[BMCCDP]₀/[BCCDP]₀. [b] Conv.: conversion. [c] $M_{n,th(LMW)} = \{[M]_0/([BMCCDP]_0 + 2 \times [BCCDP]_0]\} \times M_{w(M)} \times \text{conversion \% +} M_{w(BMCCDP}; M_{n,th} (HMW) = 2 \times \{[M]_0/([BMCCDP]_0 + 2 \times [BCCDP]_0]\} \times M_{w(M)} \times \text{conversion \% +} M_{w(BCCDP)}.$ [d] Thermal polymerization of St; temperature = 110 °C, $V_{\text{St}} = 3.0 \text{ mL}.$ [e] Solution polymerization of AA; MA/anisole = 1:1 (v/v), temperature = 75 °C. [f] Solution polymerization of AN; AN/DMSO = 1:2 (v/v), temperature = 75 °C.

MWD polymers, even in the absence of the conventional free-radical initiator (AIBN).

Monomers such as methyl acrylate (MA) and acrylonitrile (AN) were also used for the preparation of bimodal MWD polymers to validate the extensive application of this strategy for other monomers. The results of the polymerization of MA are shown in entries 2–5 of Table 1. Although the $M_{n,GPC}$ values of the polymers (HMW and LMW fractions, respectively) were slightly higher than the theoretical values

FULL PAPER

 $(M_{n,th})$ at lower ratios of monomer/RAFT agents, the M_w/M_n ratio (HMW and LMW fractions, respectively) of the polymers remained low (<1.09). An increase in the ratio of monomer/RAFT agents resulted in good consistency between the $M_{n,GPC}$ and $M_{n,th}$ values (entry 5 in Table 1). AN was another monomer that could be used for the preparation of bimodal MWD polymers with this pair of RAFT agents (entry 6 in Table 1).

Analysis of chain end and chain extension: To evaluate the "living" characteristics of the RAFT polymerization for the synthesis of bimodal MWD polymers, ¹H NMR spectroscopy was used to analyze the chain end of the PS prepared in the presence of thermal freeradical initiator (AIBN). As illustrated in Figure 3, a peak at $\delta = 4.50 - 4.85 \text{ ppm}$ (f in Figure 3) corresponded to the methenyl protons of the styrene unit, which were attached to

the polymer chain ends linked to the S-C(=S) moieties. The characteristic signals at $\delta = 8.3$, 7.9, and 7.3 ppm (a-c in Figure 3) were assigned to the protons of the carbazole group at the chain end. The peak at $\delta = 1.0$ ppm (d in Figure 3) corresponded to the methyl protons connected to the ester group. The signal at $\delta = 3.77$ ppm (e in Figure 3) was attributed to the methyl group at another chain end; this deviates from the chemical shift ($\delta = 1.0$ ppm, d in Figure 3) of the other methyl groups because of the electron-attracting functionality of the Br atom. Signals at $\delta = 1.2-2.2$ and 6.2–7.2 ppm (h and g in Figure 3, respectively) were assigned to styrene units in polymers. Furthermore, the ratio of the integrals of peaks H_a and H_f was 2:1. These results suggest that the PS chains obtained were capped by the BMCCDP and BCCDP moieties at the polymer chain ends, a result that is consistent with the mechanism of RAFT polymerization.

The chain-extension reaction is another way to verify the functionality of the polymers. Therefore, the obtained PS was used as a macro-RAFT agent to polymerize fresh St monomer. Figure 4 shows the GPC curves of the original and chain-extended polymers of PS. The bimodal elution peaks of the macro-RAFT agent obviously shifted to the chain-extended PS with $M_{n,GPC}$ =28000/62000 gmol⁻¹ and



Figure 3. ¹H NMR spectrum of PS ($M_{n,GPC}$ = 3850/8550 g mol⁻¹, M_w/M_n = 1.06/1.05) obtained in the absence of oxygen with CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal standard. Polymerization conditions: [St]₀/[AIBN]₀/[BMCCDP]₀/[BCCDP]₀ = 1200:1:2.5:2.5, V_{St} = 3.0 mL, temperature = 75 °C.



Figure 4. GPC curves before and after chain extension with PS as a macro-RAFT agent. Polymerization conditions for original PS: $[St]_0/[AIBN]_0/[BMCCDP]_0/[BCCDP]_0 = 1200:1:2.5:2.5, V_{St} = 3.0 \text{ mL}, time = 2 \text{ h, conversion} = 15.6 \%, temperature = 75 °C. Polymerization conditions for chain-extended PS: <math>[St]_0/[AIBN]_0/[PS]_0 = 2400:1:2.5, V_{St} = 3.0 \text{ mL}, time = 34 \text{ h, conversion} = 68.8 \%, temperature = 75 °C.$

low M_w/M_n values (1.08/1.07). The successful chain-extension reaction further verified the "living" features of the RAFT polymerization of St.

Preparation of bimodal molecular-weight-distribution block copolymers: According to the mechanism of RAFT polymerization, the polymers obtained are "living". The chainend analysis and chain-extension experiment verified the successful attachment of RAFT-agent moieties in the bimodal MWD polymers (see Figures 2 and 3). To further confirm the "living" features of the obtained bimodal MWD polymers, poly(methyl acrylate) (PMA) and poly(acrylonit-rile) (PAN) prepared by the method mentioned above (Table 1) were used as macro-RAFT agents to synthesize block copolymers with other fresh monomers. Solvents were added to obtain a homogeneous reaction system. Figure 5



Figure 5. GPC curves before and after block copolymerization with bimodal PSt and PMA as macro-RAFT agents. The polymerization conditions were the same as those listed in Table 2. PNIPAM: poly(N-isopropylacry-lamide).

shows the GPC curves before and after block copolymerization. The obtained polymers were used as bimodal macro-RAFT agents, with AIBN as the initiator and MA, N-isopropylacrylamide (NIPAM), and St as the monomers at 75°C. Four different bimodal MWD block copolymers, PS-b-PMA, PS-b-PNIPAM, PS-b-PAN, and PMA-b-PS were obtained successfully. Obviously, the bimodal elution peaks of the macro-RAFT agents shifted to those of the corresponding block copolymers, and the results are listed in Table 2. From Table 2, we can see that good control over the MW and MWD could be attained during block copolymerization. The bimodal peak remains good, with narrow polydispersities (<1.14). This is the first time that bimodal MWD block copolymers with both well-defined MW and MWD have been synthesized, which demonstrates the advantages of this strategy over the other reported methods mentioned above.

Effect of the molar ratio of mono/difunctional RAFT agents on bimodal MWD PS: As discussed above, all chain ends of the polymers prepared by mono/difunctional RAFT agents have equal chances to grow further. In this work, different molar ratios of RAFT-1 to RAFT-2 (1:100–100:1) were used in the polymerization to control the proportions of higher-/ lower-molecular-weight fractions in the bimodal MWD poly-

FULL PAPER

Table 2. Preparation of bimodal MWD block copolymers by RAFT polymerization with bimodal MWD macro-RAFT agents.

Entry	Copolymers	Ratio ^[a]	<i>t</i> [h]	Conv. [%]	$M_{n,GPC}^{[b]}$ (LMW/ HMW) [g mol ⁻¹]	$M_{n,GPC}^{[c]}$ (LMW/ HMW) [gmol ⁻¹]	$M_{\rm w}/M_{\rm n}$ (LMW/ HMW)
1 ^[d]	PS-b-PMA	2400:1:2.5	50.5	86.3	2900/5750	33 000/80 300	1.12/1.14
2 ^[d]	PS- <i>b</i> - PNIPAM	1200:1:2.5	50.5	≈ 100	2900/5750	19700/35700	1.02/1.07
3 ^[e] 4 ^[d]	PS- <i>b</i> -PAN PMA- <i>b</i> -PS	2400:1:2.5 2400:1:2.5	9.3 70.0	49.7 27.8	4850/9950 10100/21000	15 000/31 200 19 400/35 000	1.06/1.07 1.02/1.08

[a] Ratio of [Monomer]₀/[AIBN]₀/[macro-RAFT agent]₀; the first blocks of the copolymers were used as macro-RAFT agents. [b] Molecular weights of the first blocks (macro-RAFT agents). [c] Molecular weights of block copolymers. [d] Anisole used as solvent, monomer/anisole=1:1 (v/v), temperature=75°C, molecular weights measured by GPC in THF. [e] DMSO used as solvent, monomer/DMSO=1:1 (v/v), temperature=75°C, molecular weights measured by GPC in *N*,*N*-dimethylformamide (DMF) as $M_{n,GPC}/2.5$ with acceptable errors.^[14]

Table 3. Effect of molar ratio of mono/difunctional RAFT agents on RAFT polymerization of styrene.

Entry	Ratio ^[a]	<i>t</i> [h]	Conv. [%]	$M_{n,th}$ (LMW/HMW) [gmol ⁻¹]	$M_{n,GPC}$ (LMW/ HMW) [gmol ⁻¹]	$M_{\rm w}/M_{\rm n}$ (LMW/ HMW)	$m_{ m th}^{[b]}$ [%]	$m_{\rm GPC}^{[c]}$ [%]
1 ^[d]	1:2	26	75.0	15650/30700	14080/33470	1.10/1.06	20.0	29.4
2 ^[e]	1:3	26	82.8	12450/24350	10680/25900	1.09/1.05	14.3	26.4
3 ^[f]	1:20	23.8	76.5	9950/19400	7200/18900	1.11/1.06	2.5	15.7
4 ^[g]	1:50	16	≈ 100	5600/10600	3750/10200	1.07/1.06	1.0	12.5
5 ^[h]	1:100	16	≈ 100	5600/10600	3850/9550	1.06/1.06	0.5	11.0
6 ^[i]	2:1	70	80.5	20700/41000	22 250/48 200	1.09/1.05	50.0	51.8
7 ^[i]	3:1	70	84.9	17600/34700	20150/42850	1.08/1.05	60.0	58.0
8 ^[k]	20:1	40.2	66.1	15650/30750	20900/43700	1.07/1.03	90.9	87.9
9 ^[1]	50:1	40	76.7	8000/15450	10300/22900	1.10/1.02	96.1	92.7
10 ^[m]	100:1	40	83.3	8800/17050	7900	1.14	98.0	100

[a] Ratio of [RAFT-1]₀/[RAFT-2]₀. Polymerization conditions: $V_{st} = 3.0 \text{ mL}$; temperature =75 °C. [b] m_{th} =Ratio/(Ratio+2)×100% = the theoretical mass concentration (%) of PS with lower molecular weight calculated from the feed molar ratio. [c] m_{GPC} =ALMW/(AHMW+ALMW)×100% = the mass concentration (%) of PS with lower molecular weight calculated from the corresponding peak areas (A) measured by GPC. [d-m] [St]₀/[AIBN]₀/[RAFT-1]₀/[RAFT-2]₀: d) 2400:1.66:2.5:5, e) 2400:2.33:2.5:7.5, f) 4800:5.46:1:20, g) 4800:13.5:1:50, h) 9600:26.8:1:100, i) 2400:1.33:5:2.5, j) 2400:1.66:7.5:2.5, k) 4800:2.9:20:1, l) 4800:6.93:50:1, m) 9600:13.6:100:1, respectively.

mers. As shown in Table 3, bimodal MWD polystyrenes with low M_w/M_n values (HMW and LMW fractions, respectively) could be obtained even though the ratios of RAFT-1 to RAFT-2 were from 1:100 to 50:1. The $M_{n,GPC}$ values of the polymers were close to the $M_{n,th}$ values (HMW and LMW fractions, respectively). However, the peak of the HMW fraction became weak if the ratio of RAFT-1 to

RAFT-2 was increased to 100:1 (entry 10 in Table 3). In addition, it can also be seen that each fraction of higher or lower molecular weights in the bimodal MWD polymers can be controlled by changing the molar ratio of RAFT-1 to RAFT-2 (Table 3). The experimental mass concentrations were close to the corresponding theoretical ones. For example, when a ratio of 2:1 for RAFT-1 to RAFT-2 was used (entry 6 in Table 3), the HMW is almost twice the LMW for all of the obtained bimodal MWD polymers in our work. This is because this strategy is based on the idea that a RAFT polymerization is carried out in the concurrent presence of two different RAFT agents, one monofunctional RAFT agent (RAFT-1) and one difunctional RAFT agent (RAFT-2). According to the mechanism of RAFT polymerization, polymers with the

Table 4.	Bimodal MV	WD PS wit	1 higher	molecular	weight	from	RAFT	polymerization.
----------	------------	-----------	----------	-----------	--------	------	------	-----------------

Entry	Ratio ^[a]	<i>t</i> [h]	Conv. [%]	$M_{ m n,th}$ (LMW/ HMW) [gmol ⁻¹]	$M_{ m n,GPC}$ (LMW/ HMW) [gmol ⁻¹]	M _w /M _n (LMW/ HMW)
1	2400:1:2.5:2.5	33.5	70.9	24250/47950	22800/49000	1.07/1.05
2	3600:1:2.5:2.5	33.5	65.0	33 100/65 700	31 100/66 900	1.07/1.05
3	4800:1:2.5:2.5	33	61.5	41 600/82 700	38800/84400	1.07/1.06
4	6000:1:2.5:2.5	65.5	63.8	53 800/10 7100	46800/107800	1.10/1.10
5	9600:1:2.5:2.5	65	54.6	73 400/14 6300	64700/149900	1.09/1.10
6	12000:1:2.5:2.5	24	61.0	102100/203700	88000/237000	1.18/1.13
7	36000:1:2.5:2.5	53	45.3	227000/453000	146000/407000	1.16/1.11
8	48000:1:2.5:2.5	24	50.7	33 8000/67 5000	23 1000/87 1000	1.36/1.08

[a] Ratio of $[St]_0/[AIBN]_0/[RAFT-1]_0/[RAFT-2]_0$. Polymerization conditions: $V_{St} = 3.0$ mL, temperature = 75 °C.

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

www.chemeurj.org

the experimental mass concentration for the lower molecular weight from the GPC results was 51.8%, which is close to the theoretical value of 50%.

Synthesis of higher-molecularweight PS: The synthesis of HMW polystyrenes by using this pair of RAFT agents was also attempted. The retention of functional chain ends is crucial in synthesizing HMW polymers. A HMW PS with narrow MWD was obtained. The polymerization rate decreased with an increase in the molar ratio [St]₀/[RAFT-1]₀/[RAFT-2]₀, of due to the corresponding lower concentration of AIBN initiator, as expected. As shown in Table 4, both higher- and lowermolecular-weight fractions had low $M_{\rm w}/M_{\rm n}$ values (≈ 1.2), even MW the was up to $871\,000 \text{ g mol}^{-1}$ (entry 8 in Table 4). The $M_{n,GPC}$ values were close to the predicted theoretical values. The above results demonstrate that RAFT polymerization with this pair of RAFT agents, without any additional treatments, could synthesize bimodal HMW polymers with excellent controllability.

It is worth pointing out that

structure of $R-[monomer]_n-S-C(=S)-Z$ could be obtained by using a monofunctional RAFT-1 with the structure R-S-C(=S)-Z. Similarly, difunctional RAFT-2, with the structure Z-(S=)C-S-R-S-C(=S)-Z, can be used to synthesize polymers with the structure $Z-(S=)C-S-[monomer]_n-R [monomer]_n$ -S-C(=S)-Z. Therefore, the MWs of polymers prepared with difunctional RAFT-2 were twice those of polymers prepared with monofunctional RAFT-1. The key to preparing bimodal MWD polymers is that the structures of the pair of RAFT agents should have equal chances to be addition and fragmentation radicals. In order to confirm the hypothesis, RAFT-1 or RAFT-2, respectively, was used as a RAFT agent in the polymerization of St. The results are shown in Figure 2c and d. As determined from the kinetic plots shown in Figure 2c, the apparent rate constant of the polymerization, k_p^{app} $(R_p = -d[M]/dt = k_p[P_n \cdot][M] = k_p^{\text{app}}[M];$ R_{p} : polymerization rate; M: monomer; P_{n} : propagating radical) with difunctional RAFT-2 ([St]₀/[AIBN]₀/[RAFT-2]₀= 600:0.66:2.5) was calculated as 0.0782 s^{-1} , which was approximately twice that of monofunctional RAFT-1 (0.0395 s^{-1}) under the same polymerization conditions (the same ratio of $[AIBN]_0/[S-C(=S) \text{ segments}]_0; [St]_0/[AIBN]_0/[RAFT-1]_0 =$ 600:0.33:2.5). From Figure 2d, it can be seen that all of the molecular weights obtained from GPC results were consistent with the corresponding theoretical ones in three cases. These results confirmed that all S-C(=S) groups in this pair of RAFT agents have the same "living" for the RAFT polymerization and, therefore, result in bimodal MWD polymers in the presence of this pair of RAFT agents by the one-step/ one-pot method.

Conclusion

Bimodal MWD polymers were successfully synthesized by using a pair of mono/difunctional RAFT agents in RAFT polymerization. The system showed excellent controllability and "living" characteristics for both higher- and lower-molecular-weight fractions. The $M_{n,GPC}$ values of the polymers (for the HMW and LMW fractions, respectively) were close to the theoretical $M_{n,th}$ values. The M_w/M_n ratio (for the HMW and LMW fractions, respectively) of the polymers was kept low (<1.10) during the polymerization process. Bimodal HMW polymers and block copolymers with both well-controlled MW and MWD could be prepared easily due to the "living" features of RAFT polymerization. The strategy produced a mixture of higher-/lower-molecularweight polymers at the molecular level but also preserved the features of LRP of RAFT polymerization.

Experimental Section

Materials and reagents: Unless otherwise specified, all chemicals were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). The monomers, methyl acrylate (MA, +99%), *N*-isopropylacrylamide (NIPAM, +99%), acrylonitrile (AN, +99%), and styrene (St, +99%),

were passed through an alumina column and stored at -18 °C. 2,2-Azobisisobutyronitrile (AIBN, chemically pure), dimethylsulfoxide (DMSO, +99%), tetrahydrofuran (THF, +99%), anisole (+99%), and all other chemicals were used as received unless mentioned. 2-Bromo-2-methylpropionyl bromide (98%) was purchased from Aldrich Chemical Co.

Characterizations: The number-average molecular weight $(M_{n,GPC})$ and molecular weight distribution (M_w/M_n) of the polymers were determined by using a Waters 1515 gel permeation chromatograph equipped with a Waters 2414refractive-index detector, with HR1, HR2, and HR4 columns $(7.8 \times 300 \text{ mm}^2, 5 \text{ mm} \text{ bead size})$ with measurable molecular weights in the range of 10^2 –5×10⁵ gmol⁻¹. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹, at 30 °C. The GPC samples were injected by using a Waters 1515 plus autosampler and calibrated with polystyrene standards from Waters (PMA was calibrated with poly(methyl methacrylate) standards). For PAN, DMF with added LiBr (0.05 mol L⁻¹) was used as the eluent at a flow rate of 0.8 mLmin⁻¹, also at 30 °C. In this case, the GPC samples were injected by using a Waters 1515 plus autosampler and calibrated with polystyrene standards from Waters. ¹H NMR spectra were recorded on an Inova 400 MHz NMR instrument with CDCl3 or (CD₃)₂SO as the solvent and tetramethylsilane (TMS) as the internal standard at ambient temperature.

Synthesis of 1,4-[2-(carbazole-9-carbodithioate)-2-methyl-propionic acid] phenyl ester (BCCDP): Carbazole (1.67 g, 0.01 mol) was added to a suspension of KOH (0.56 g, 0.01 mol) in DMSO (25 mL) under vigorous stirring. The solution was stirred for 3 h at 30 °C, and then carbon disulfide (0.76 g, 0.01 mol) was added dropwise. The resultant reddish solution was stirred for 5 h at 30 °C, and then 1,4-(2'-bromo-2'-methylpropionato)benzene (BMPB; 2.04 g, 0.005 mol; synthesized according to reference [15]) was added. The mixture was stirred for 24 h at 30 °C and was then poured into a large amount of deionized water (\approx 300 mL). A yellow solid was obtained. The crude product was purified by washing with acetone three times. ¹H NMR ((CD₃)₂SO, 400 MHz): δ =1.99 (s, 12H), 7.31 (s, 4H), 7.41–7.45 (m, 4H), 7.51–7.55 (m, 4H), 8.22–8.24 (d, 4H), 8.37–8.39 ppm (d, 4H).

Synthesis of 2-bromo-2-methyl-propionic acid 4-[2-(carbazole-9-carbodithioate)-2-methyl-propionyloxy]phenyl ester (BMCCDP): BMCCDP was synthesized by using a similar method to that used for BCCDP, except that the amount of BMPB was increased to 6.12 g (0.015 mol). The crude product was purified first by column chromatography on silica oxide with a mixture of petroleum ether and ethyl acetate (10:1) as the eluent and then by recrystallization three times from acetone. ¹H NMR (CDCl₃, 400 MHz): δ = 2.06–2.11 (d, 12 H), 7.19–7.22 (d, 2 H), 7.28–7.30 (d, 2 H), 7.39–7.43 (m, 2 H), 7.48–7.52 (m, 2 H), 8.03–8.05 (d, 2 H), 8.45–8.48 ppm (d, 2 H).

Typical bulk RAFT polymerization of St: AIBN (3.5 mg, 0.022 mmol), RAFT-1 (37.5 mg, 0.055 mmol), RAFT-2 (42.0 mg, 0.055 mmol), and St (3.0 mL, 26.2 mmol) were added in that order to a dried ampoule under stirring. The ampoule was thoroughly bubbled with argon for 20 min to eliminate the dissolved oxygen in the solution. The ampoule was then flame sealed and transferred into an oil bath, held at 75 °C by a thermostat, to allow polymerization in the mixture under stirring. After the desired polymerization time, the ampoule was cooled by immersing it into iced water. Afterwards, it was opened and the contents were dissolved in THF (2 mL); the contents from the polymerization of AN were dissolved in DMF (2 mL). The products were then precipitated in a large amount of methanol (\approx 200 mL). The polymer obtained by filtration was dried under vacuum until constant weight was achieved at 50°C. The conversion of monomer was determined gravimetrically. The procedures for MA and AN polymerization and for the block copolymerization were similar to that of St polymerization except that a certain amount of anisole or DMSO was added to the reaction system to form a homogeneous solution. In addition, for block copolymerization, the macro-RAFT agents were used in place of RAFT-1 and RAFT-2.

Chain extension of the PS macro-RAFT agent with St: Predetermined quantities of AIBN and PS (obtained by RAFT polymerization of St with RAFT-1 and RAFT-2 agents at 75 °C) were dissolved in St (3.0 mL) in a dried ampoule. The rest of the procedure was the same as that de-

6020 ·

FULL PAPER

scribed above. The chain-extension polymerization was carried out under stirring at 75 °C.

Acknowledgements

Financial support from the National Natural Science Foundation of China (nos. 20974071 and 21174096), the Specialized Research Fund for the Doctoral Program of Higher Education (no. 20103201110005), the Project of Science and Technology Development Planning of Suzhou (no. SYG201026), the Project of International Cooperation of the Ministry of Science and Technology of China (no. 2011DFA50530), the Qing Lan Project, the Program of Innovative Research Team of Soochow University, the Project Funded by Jiangsu Key Lab Carbon Based Functional Materials & Devices, and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) is gratefully acknowledged.

- a) R. Radicevic, S. Kisin, I. Krakovsky, *Chromatographia* **2004**, *59*, 621–624; b) X. Sun, H. Shen, B. Xie, W. Yang, M. Yang, *Polymer* **2011**, *52*, 564–570.
- [2] a) S. Abedi, N. Hassanpour, J. Appl. Polym. Sci. 2006, 101, 1456– 1462; b) G. Maschio, T. Bello, C. Scali, Chem. Eng. Sci. 1994, 49, 5071–5086.
- [3] a) G. Britovsek, M. Bruce, V. Gibson, B. Kimberley, P. Maddox, S. Mastroianni, S. McTavish, C. Redshaw, G. Solan, S. Strömberg, A. White, D. Williams, J. Am. Chem. Soc. 1999, 121, 8728-8740; b) Q. Wang, H. Yang, Z. Fan, Macromol. Rapid Commun. 2002, 23, 639-642; c) K. Radhakrishnan, H. Cramail, A. Deffieux, P. Francois, A. Momtaz, Macromol. Rapid Commun. 2003, 24, 251-254; d) E. P. Talsi, D. E. Babushkin, N. V. Semikolenova, V. N. Zudin, V. N. Panchenko, V. A. Zakharov, Macromol. Chem. Phys. 2001, 202, 2046-2051; e) L. Deng, P. Margl, T. Ziegler, J. Am. Chem. Soc. 1999, 121, 6479-6481.
- [4] a) F. Fim, T. Machado, D. Sá, P. Livotto, Z. Rocha, N. Basso, G. Galland, J. Polym. Sci. Part A: Polym. Chem. 2008, 46, 3830–3841;
 b) Y. V. Kissin, R. I. Mink, A. J. Brandolini, T. E. Nowlin, J. Polym. Sci. Part A: Polym. Chem. 2009, 47, 3271–3285;
 c) D. Ribour, V. B. Benoit, V. Monteil, R. Spitz, J. Polym. Sci. Part A: Polym. Chem. 2007, 45, 3941–3948;
 d) H. Zhang, Y. Lee, J. Park, D. Lee, K. Yoon, J. Appl. Polym. Sci. 2011, 120, 101;
 e) M. I. Nikolaeva, T. B. Mikenas, M. A. Matsko, L. G. Echevskaya, V. A. Zakharov, J. Appl. Polym. Sci. 2010, 115, 2432–2439.
- [5] a) J. Liu, E. Rytter, Macromol. Rapid Commun. 2001, 22, 952–956;
 b) K. Yamamoto, Y. Ishihama, K. Sakata, J. Polym. Sci., Part A: Polym. Chem. 2010, 48, 3722–3728;
 c) J. B. P. Soares, J. D. Kim, J. Polym. Sci., Part A: Polym. Chem. 2000, 38, 1408–1416.

- [6] a) C. Sayer, G. Arzamendi, J. Asua, E. Lima, J. Pinto, Comput. Chem. Eng. 2001, 25, 839–849; b) M. Vicente, S. Benamor, L. Gugliotta, J. Leiza, J. Asua, Ind. Eng. Chem. Res. 2001, 40, 218–227; c) M. Thomson, N. Smeets, J. Heuts, J. Meuldijk, M. Cunningham, Macromolecules 2010, 43, 5647–5658.
- [7] a) H. Tobita, N. Aoyagi, S. Takamura, *Polymer* 2001, 42, 7583–7587;
 b) H. Tobita, *J. Polym. Sci. Part A: Polym. Chem.* 2002, 40, 3426–3433.
- [8] a) G. Moad, E. Rizzardo, S. H. Thang, Aust. J. Chem. 2006, 59, 669–692; b) B. M. Rosen, V. Percec, Chem. Rev. 2009, 109, 5069–5119; c) M. Ouchi, T. Terashima, M. Sawamoto, Chem. Rev. 2009, 109, 4963–5050; d) C. J. Hawker, A. W. Bosman, E. Harth, Chem. Rev. 2001, 101, 3661–3688.
- [9] M. Lenzi, M. Cunningham, E. Lima, J. Pinto, Ind. Eng. Chem. Res. 2005, 44, 2568–2578.
- [10] X. Wan, Y. Liu, S. Ying, J. Appl. Polym. Sci. 2002, 83, 3076-3081.
- [11] a) N. Tsarevsky, T. Sarbu, B. Goebelt, K. Matyjaszewski, Macromolecules 2002, 35, 6142–6148; b) K. Matyjaszewski, S. Coca, S. Gaynor, M. Wei, B. Woodworth, Macromolecules 1998, 31, 5967–5969; c) K. Matyjaszewski, D. Shipp, J. Wang, T. Grimaud, T. Patten, Macromolecules 1998, 31, 6836–6840; d) H. Fischer, J. Polym. Sci. Part A: Polym. Chem. 1999, 37, 1885–1901; e) P. A. Costello, I. K. Martin, A. T. Slark, D. C. Sherrington, A. Titterton, Polymer 2002, 43, 245–254.
- [12] a) J. Chiefari, Y. Chong, F. Ercole, J. Krstina, J. Jeffery, T. Le, R. Mayadunne, G. Meijs, C. Moad, G. Moad, E. Rizzardo, S. Thang, *Macromolecules* 1998, *31*, 5559–5562; b) A. Favier, M. T. Charreyre, *Macromol. Rapid Commun.* 2006, *27*, 653–692; c) S. Perrier, P. Takolpuckdee, J. Polym. Sci. Part A: Polym. Chem. 2005, *43*, 5347–5393; d) G. Moad, E. Rizzardo, S. H. Thang, Aust. J. Chem. 2005, *58*, 379–410; e) J. Liu, V. Bulmus, D. L. Herlambang, C. Barner-Kowollik, M. H. Stenzel, T. P. Davis, Angew. Chem. 2007, *119*, 3159–3163; Angew. Chem. 1nt. Ed. 2007, *46*, 3099–3103; f) M. Semsarilar, S. Perrier, *Nat. Chem.* 2010, *2*, 811–820; g) M. Benaglia, J. Chiefari, Y. K. Chong, G. Moad, E. Rizzardo, S. H. Thang, J. Am. Chem. Soc. 2009, *131*, 6914–6915; h) C. Boyer, V. Bulmus, T. P. Davis, V. Ladmiral, J. Q. Liu, S. Perrier, *Chem. Rev.* 2009, *109*, 5402–5436; i) Handbook of *RAFT Polymerization* (Ed.: C. Barner-Kowollik), Wiley-VCH, Weinheim, 2008.
- [13] T. M. Lovestead, A. Theis, T. P. Davis, M. H. Stenzel, C. Barner-Kowollik, *Macromolecules* 2006, 39, 4975–4982.
- [14] a) H. C. Dong, W. Tang, K. Matyjaszewski, *Macromolecules* 2007, 40, 2974–2977; b) Q. F. Chen, Z. B. Zhang, N. C. Zhou, Z. P. Cheng, Y. F. Tu, X. L. Zhu, *J. Polym. Sci. Part A: Polym. Chem.* 2011, 49, 1183–1189.
- [15] D. Haddleton, C. Waterson, Macromolecules 1999, 32, 8732-8739.

Received: December 14, 2011 Published online: April 4, 2012