

# Molar Mass Dispersity Control by Iodine-mediated Reversible-deactivation Radical Polymerization

Jin-Ying Wang<sup>†</sup>, Yuan-Yuan Ni<sup>†</sup>, Jian-Nan Cheng, Li-Fen Zhang<sup>\*</sup>, and Zhen-Ping Cheng<sup>\*</sup>

State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

## Electronic Supplementary Information

**Abstract** Dispersity ( $\mathcal{D}$ ) of polymers has a great effect on the properties of polymeric materials, and therefore how to control  $\mathcal{D}$  is very important but still a huge challenge in polymer synthesis, especially for reversible-deactivation radical polymerization (RDRP) strategy. Herein, we successfully developed a novel strategy to adjust  $\mathcal{D}$  of polymers by visible light-controlled reversible complexation mediated living radical polymerization (RCMP) and combination of single-electron transfer-degenerative chain transfer living radical polymerization (SET-DTLRP) at room temperature. In RCMP system, 2-iodo-2-methylpropionitrile (CP-I) and ethyl 2-iodo-2-phenylacetate (EIPA) were used as alkyl iodide initiators, by using methyl methacrylate (MMA) as the model monomer and *n*-butylacrylate (BA) as the end-capping reagent to regulate  $\mathcal{D}$  of polymers. Subsequently, we successfully prepared the block copolymer PMMA-*b*-PBA with adjustable  $\mathcal{D}$  by reactivating the polymer end-chains via SET-DTLRP in the presence of copper wire, fully demonstrating that it is a promising strategy that can keep the "living" feature of polymers while regulating their molar mass dispersities easily.

**Keywords** Dispersity control; Iodine-mediated reversible-deactivation radical polymerization (RDRP); Visible light-controlled polymerization; Reversible complexation mediated living radical polymerization (RCMP); Single-electron transfer-degenerative chain transfer living radical polymerization (SET-DTLRP)

**Citation:** Wang, J. Y.; Ni, Y. Y.; Cheng, J. N.; Zhang, L. F.; Cheng, Z. P. Molar mass dispersity control by iodine-mediated reversible-deactivation radical polymerization. *Chinese J. Polym. Sci.* 2021, 39, 1155–1160.

## INTRODUCTION

Reversible-deactivation radical polymerization (RDRP),<sup>[1–8]</sup> such as atom transfer radical polymerization (ATRP),<sup>[9–12]</sup> reversible addition-fragmentation chain transfer (RAFT)<sup>[13–16]</sup> and iodine transfer polymerization (ITP),<sup>[17–19]</sup> has unique advantages in preparing polymers with wide range of available monomers, mild polymerization conditions, controlled molar mass, high fidelity of terminal functionalization and designable molecular structure. These features greatly facilitate RDRP to precisely synthesize polymers with different topologies.<sup>[20–25]</sup> The polymer materials prepared by the RDRP methods usually have a relatively narrow molar mass dispersity ( $\mathcal{D}$ ). However, the materials required for different occasions in practical applications do not blindly pursue the narrow  $\mathcal{D}$ , sometimes it is much preferable for the polymers with adjustable  $\mathcal{D}$  values. Therefore, how to regulate  $\mathcal{D}$  has become a challenging topic in

the research field of RDRP. At present, there are relatively few reports on the strategy of adjusting polymer  $\mathcal{D}$ . Blending polymers with different molar mass<sup>[26]</sup> is a convenient way to obtain polymers with adjustable  $\mathcal{D}$ , but this method requires multiple independent preparations of the polymers, and the  $\mathcal{D}$  curve of the resulting blended polymers usually has multiple peak distribution. In the RDRP methods, changing some polymerization conditions,<sup>[27]</sup> such as the catalyst loading, reaction temperature and other chain transfer agents,<sup>[28]</sup> can also adjust  $\mathcal{D}$  of the resultant polymers to some certain extent (1.1–2.0). However, the crude adjusting strategy usually comes at the expense of the end functionalization of the resultant polymers, and it is almost impossible to carry out further chain extension reactions,<sup>[29–32]</sup> also impossible to be used for designing the polymers with complex structure.

Recently, Fors *et al.* used a feed pump to intermittently add initiator in polymerization mixture to control the reaction time, cleverly changed  $\mathcal{D}$  values and the "shape" of the  $\mathcal{D}$ .<sup>[33–36]</sup> Boyer and colleagues controlled the addition of macro initiator in light-controlled RAFT polymerization, and successfully obtained a block copolymer with a controllable  $\mathcal{D}$ . In addition, they also changed light-induced continuous RAFT polymerization factors such as the flow rate (residence time) of the reactants, the wavelength of the light source, and

<sup>\*</sup> Corresponding authors, E-mail: zhanglifan@suda.edu.cn (L.F.Z.)  
E-mail: chengzhenping@suda.edu.cn (Z.P.C.)

<sup>†</sup> These authors contributed equally to this work.

Special Topic: Reversible Deactivation Radical Polymerization

Received March 31, 2021; Accepted May 4, 2021; Published online July 20, 2021

the intensity of the light, so as to obtain a polymer with a specific  $\bar{D}$ .<sup>[37,38]</sup> However, these methods are inseparable from metering pump-assisted sampling, and are not suitable for heterogeneous systems (synthesis of polymer brushes on solid substrates, etc.), which limits the application of these methods to a certain extent. Goto *et al.* used the temperature selectivity characteristics of the reversible complexation mediated living radical polymerization (RCMP) system for two different types of monomers (methacrylates and acrylates),<sup>[39]</sup> added a certain amount of acrylate monomers at low temperature (70 °C, it is noted that acrylates cannot be polymerized at the low temperature due to the high dissociation energy of the secondary carbon-iodine bond formed ( $\approx 174.0$  kJ/mol)) to randomly terminate the polymerization so as to obtain polymers with wide dispersities ( $\bar{D}=1.11\text{--}1.50$ ), and then performed polymerization of acrylate monomers at high temperature (110 °C), and successfully obtained block polymers of poly(methacrylates) and poly(acrylates) with various topologies. The significant advantage of this method is that the dispersity can be adjusted in any segment of multi-block, star and brush polymers, and it is also suitable for preparing polymer brushes with adjustable  $\bar{D}$  on the surface of silicon wafers. All in all, mastering the method of adjusting and controlling the dispersity of polymers and the influence of the width and "shape" of the  $\bar{D}$  on the properties of materials is of great value for promoting the industrial application of polymer materials.

In our previous work, we found that only methacrylates could be polymerized by visible light-controlled RCMP.<sup>[40]</sup> On the other hand, the single-electron transfer-degenerative chain transfer living radical polymerization (SET-DTLRP)<sup>[41–43]</sup> method with the participation of alkyl iodides can be carried out with a wide range of monomers including methacrylates and acrylates at room temperature. At the same time, it has the advantages of fast polymerization rate and less catalyst residue. In this work, we successfully developed a novel iodine-mediated RDRP strategy to control dispersity while maintaining the "living" feature of the polymers at room temperature, by visible light-controlled RCMP and by combination with SET-DTLRP with methyl methacrylate (MMA) and butyl acrylate (BA) as the model methacrylates and acrylates monomers. PMMAs with controllable dispersities ( $\bar{D}=1.21\text{--}1.53$ ) were obtained. Subsequently, a model block polymer PMMA-*b*-PBA ( $\bar{D}=1.55$ ) was obtained by using PMMA with  $\bar{D}$  of 1.63 as the macroinitiator *via* chain extension through the SET-DTLRP process to confirm the "living" feature of the resultant PMMAs with adjustable  $\bar{D}$ .

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA, 99%, J&K China Chemical Ltd.), benzyl methacrylate (BnMA, 98%, J&K China Chemical Ltd.), 2-hydroxyethyl methacrylate (HEMA, 99%, Sigma-Aldrich), 2-hydroxypropyl methacrylate (HPMA, 99%, Sigma-Aldrich), butyl acrylate (BA, 99%, TCI), *N*-vinylpyrrolidone (NVP, 98%, J&K China Chemical Ltd.) and polyethylene glycol monomethyl ether acrylate (PEGA, average molar mass 480 Da, 98%, Sigma-Aldrich) were passed through a neutral alumina column before use. Ethyl 2-iodo-2-phenylacetate (EIPA, 98%), 2-iodo-2-methyl-

propionitrile (CP-I, 99%) and 1,3-dimethyl-2-imidazolinone (DMI, analytical reagent) were purchased from TCI and used as received. Dimethyl sulfoxide (DMSO, analytical reagent) was purchased from Shanghai Chemical Reagents Co. Ltd. and used as received. Tris(2-dimethylaminoethyl)amine ( $\text{Me}_6\text{TREN}$ , 98%) and tris(2-pyridylmethyl)amine (TPMA, 98%) were purchased from J&K China Chemical Ltd. and used as received. High purity copper wire (J&K China Chemical Ltd.) was polished with sandpaper to remove the surface oxide film before use. All other chemicals were obtained from Shanghai Chemical Reagents Co. Ltd. and were used as received unless otherwise mentioned.

### General Procedure for Visible Light-controlled RCMP

Polymerizations were carried out under irradiation with blue light-emitting diode (LED) light ( $\lambda_{\text{max}}=460$  nm, 18.6 mW/cm<sup>2</sup>) in an ampoule under an argon atmosphere. A typical polymerization procedure with the feed molar ratio of  $[\text{MMA}]_0/[\text{BA}]_0/[\text{CP-I}]_0=90/10/1$  is shown as follows. A reaction mixture consisting of MMA (0.45 mL, 4.24 mmol), BA (68.0  $\mu\text{L}$ , 0.47 mmol), CP-I (5.3  $\mu\text{L}$ , 0.047 mmol), and DMI (0.5 mL) was prepared in a 5 mL ampoule with a magnetic stir bar. The reaction mixture was degassed by at least three freeze-pump-thaw cycles to remove oxygen, and the ampoule was flame-sealed at argon atmosphere. Subsequently, the ampoule was placed in device, and the distance between the polymerization ampoule and the light source was about 1.5 cm. The mixture was then transferred into blue LED light source to conduct polymerization under vigorous magnetic stirring while cooling with a circulating water-cooled aluminum plate to remove the heat of light strips from the test ampoules and maintain the room temperature (25 °C). After the desired polymerization time, the ampoule was transferred into the dark. Then the reaction mixture was dissolved in THF ( $\sim 2.0$  mL), followed by precipitation into 250 mL of petroleum ether. The polymer was collected by filtration and dried under vacuum at 30 °C to a constant weight.

### Chain Extension Using PMMA as a Macroinitiator

The PMMA macroinitiator was synthesized with the molar ratio of  $[\text{MMA}]_0/[\text{BA}]_0/[\text{CP-I}]_0/[\text{TPMA}]_0=45/5/1/1$  for 18 h ( $M_{n,\text{GPC}}=3400$  g/mol,  $\bar{D}=1.62$ ). Namely, MMA (0.45 mL, 4.24 mmol), BA (68.0  $\mu\text{L}$ , 0.47 mmol), CP-I (5.3  $\mu\text{L}$ , 0.047 mmol), TPMA (13.6 mg, 0.047 mmol) and 0.5 mL of DMI were prepared in a 5 mL dried ampoule; after polymerization under irradiation with a blue LED light ( $\lambda_{\text{max}}=460$  nm, 18.6 mW/cm<sup>2</sup>) at room temperature, the resultant PMMA was directly used as the macroinitiator for chain extension *via* SET-DTLRP in polymerization solution without purification process. After the ampoule was broken, BA (0.3 mL, 2.08 mmol) and DMI (0.5 mL) were added into the ampoule directly, and then transferred the polymerization mixture to a new ampoule with a magnetic stir bar wrapped with 10 cm copper wire. After three freeze-pump-thaw cycles to remove oxygen, the ampoule was flame-sealed at argon atmosphere, and performed the chain extension in a water bath at 25 °C. After the desired polymerization time, the ampoule was transferred into the dark. Then the reaction mixture was dissolved in THF ( $\sim 2.0$  mL) followed by precipitation into 250 mL of petroleum ether. The resultant block copolymer was collected by filtration and dried under vacuum at 30 °C to a constant weight.

## Characterizations

The number average molar mass ( $M_{n, \text{GPC}}$ ) and  $\bar{D}$  values of the resultant polymers were determined using a TOSOH-HLC-8320 gel permeation chromatograph (GPC) equipped with a refractive index detector (Waters 2414) using TSK gel Super AWM-H columns (4.6 mm I.D.  $\times$  15 cm  $\times$  2) with measurable molar mass ranging from  $5 \times 10^2$  g/mol to  $5 \times 10^5$  g/mol. THF was used as the eluent with a flow rate of 0.35 mL/min at 40 °C. The GPC samples were injected using a TOSOH plus autosampler and calibrated with PMMA standards obtained from TOSOH.

## RESULTS AND DISCUSSION

As discussed above, herein, we aimed to develop a novel strategy to control  $\bar{D}$  of the resultant polymers, namely, visible light-controlled RCMP method for homopolymers and one-pot-two-step method by combination of RCMP and SET-DTLRP for block copolymers at room temperature. Therefore, it is very important to find a solvent suitable for both the different polymerization processes. As we all know, water, DMI and DMSO are good solvents for SET-DTLRP. However, considering the solubility of MMA and BA in the SET-DTLRP process, organic solvents not water were selected to optimize the polymerization conditions although we have proved that oxygen atoms in water molecules can form oxygen-iodine halogen bonds and act as a catalyst in visible light-controlled RCMP process.<sup>[33]</sup> As shown in Table S1 (in the electronic supplementary information, ESI), MMA and BA were respectively used as model monomers and the effects of DMI and DMSO on visible light-controlled-RCMP and SET-DTLRP were investigated. It can be seen that PMMA prepared with DMSO as the solvent had a broader dispersity ( $\bar{D}$ =1.35) (Table S1, entry 1 in ESI) as compared with that ( $\bar{D}$ =1.17) obtained in DMI (Table S1, entry 2 in ESI), and similar results were also available for PBAs obtained by SET-DTLRP. Therefore, DMI was considered as the optimal solvent for our polymerization system.

Subsequently, the visible light-controlled RCMP polymerization kinetics was first investigated to confirm the polymerization behavior of MMA in DMI. As shown in Table S2 (in ESI), the dispersities of PMMA homopolymer were maintained below 1.30. According to the previous discussion, acrylate monomers can be used as end-capping agents in the visible light-controlled RCMP of methacrylates, and further to achieve adjusting dispersity while maintaining the "living" feature of the resultant polymers. Therefore, we added different amounts of BA as a capping agent to the MMA polymerization system to investigate the effect of the amount of BA on the dispersities of the resultant PMMAs, and the results were shown in Table 1 (GPC traces were shown in Fig. S1 in ESI). It can be seen that the addition of BA could indeed play a key role in regulating  $\bar{D}$  of the polymers. As the amount of BA increased, the monomer conversion decreased, and the  $\bar{D}$  values of the resultant polymers became broad gradually. This phenomenon was in line with our hypothesis. During the polymerization process, the dormant species PMMA-BA-I can be gradually formed by the addition of some of propagating radicals PMMA $\cdot$  and BA monomer, which could not be react-

ated to generate propagating radical PMMA-BA $\cdot$  under visible light irradiation. At the same time, another parts of propagating radicals PMMA $\cdot$  were still growing gradually. Therefore, the dispersity of the resultant polymers broadened accordingly. For example, when the initial molar ratio of MMA/BA was 90/10, the corresponding  $\bar{D}$  reached the maximum value of 1.53 (Table 1, entry 4) from 1.21 (Table 1, entry 1). Therefore, we actually adjust  $\bar{D}$  of the resultant polymers by adding the amount of BA to the visible light-controlled RCMP of MMA.

**Table 1** Effect of amount of BA on visible light-controlled RCMP of MMA.<sup>a</sup>

| Entry | R       | Conv. <sup>b</sup><br>(%) | $M_{n, \text{th}}$ <sup>c</sup><br>(Da) | $M_{n, \text{GPC}}$ <sup>d</sup><br>(Da) | $\bar{D}$ <sup>d</sup> |
|-------|---------|---------------------------|-----------------------------------------|------------------------------------------|------------------------|
| 1     | 100/0/1 | 72.0                      | 7400                                    | 10700                                    | 1.21                   |
| 2     | 98/2/1  | 66.9                      | 6900                                    | 9500                                     | 1.36                   |
| 3     | 95/5/1  | 44.9                      | 4600                                    | 6100                                     | 1.49                   |
| 4     | 90/10/1 | 41.9                      | 4100                                    | 5200                                     | 1.53                   |
| 5     | 80/20/1 | 40.6                      | 3600                                    | 4200                                     | 1.44                   |
| 6     | 75/25/1 | 17.0                      | 1600                                    | 2700                                     | 1.36                   |

<sup>a</sup> Polymerization conditions: R = [MMA]<sub>0</sub>/[BA]<sub>0</sub>/[CP-I]<sub>0</sub>,  $V_{\text{CP-I}}$ =5.4  $\mu$ L,  $V_{\text{DMI}}$ =0.5 mL, time=18 h, under irradiation with blue LED light ( $\lambda_{\text{max}}$ =460 nm, 18.6 mW/cm<sup>2</sup>) at room temperature. <sup>b</sup> Determined by gravimetry. <sup>c</sup>  $M_{n, \text{th}}$  = [MMA]<sub>0</sub>/[CP-I]<sub>0</sub>  $\times$   $M_{\text{MMA}}$   $\times$  conv.% +  $M_{\text{CP-I}}$  when [BA]<sub>0</sub> is equal to 0,  $M_{n, \text{th}}$  = [MMA]<sub>0</sub>/[CP-I]<sub>0</sub>  $\times$   $M_{\text{MMA}}$   $\times$  conv.% +  $M_{\text{BA}}$  +  $M_{\text{CP-I}}$  when [BA]<sub>0</sub> is not equal to 0. <sup>d</sup> Molar mass and molar mass dispersity were determined by GPC using linear PMMA as calibration.

Subsequently, we fixed the feed molar ratio of [MMA]<sub>0</sub>/[BA]<sub>0</sub>/[CP-I]<sub>0</sub>=90/10/1 as an example to investigate the polymerization kinetics in the presence of BA, and the results were shown in Fig. 1 and Table S3 (in ESI). Under this ratio, the adjustable range of dispersity of the resultant polymers was between 1.28–1.53. Beside CP-I, we also used EIPA as the initiator to conduct the control experiments. The polymerization results listed in Table S4 (in ESI) showed that the addition of BA could also be used to regulate the dispersities ( $\bar{D}$ =1.31–1.62) of the homopolymers. In addition, all the results mentioned above were based the two model monomers MMA and BA. In order to investigate the universality of this novel strategy for adjusting polymer dispersity, other methacrylates such as BnMA, HEMA and HPMA were also studied with BA as the end-capping agent. The results were shown in Table 2 (GPC traces were shown in Fig. S2 in ESI), adjustable  $\bar{D}$  values for other methacrylates polymers such as PBnMA can also be available by this visible light-controlled RCMP strategy. In addition, we also used other monomers, such as PEGA and NVP, as the end-capping agents to regulate the polymerization of MMA, and the results were shown in Table S5 (in ESI). It is found that both PEGA and NVP can efficiently regulate  $\bar{D}$  of the resultant polymers, which indicated that both PEGA and NVP are also good end-capping agents for our polymerization system.

On the other hand, in the SET-DTLRP process, in order to increase the solubility of catalyst copper and reduce its redox potential, ligand is essential. The more commonly used ligands reported in the literature are Me<sub>6</sub>TREN and TPMA. Therefore, we also investigated the effect of additives ligand on the visible light-controlled RCMP (it should be noted that ligand

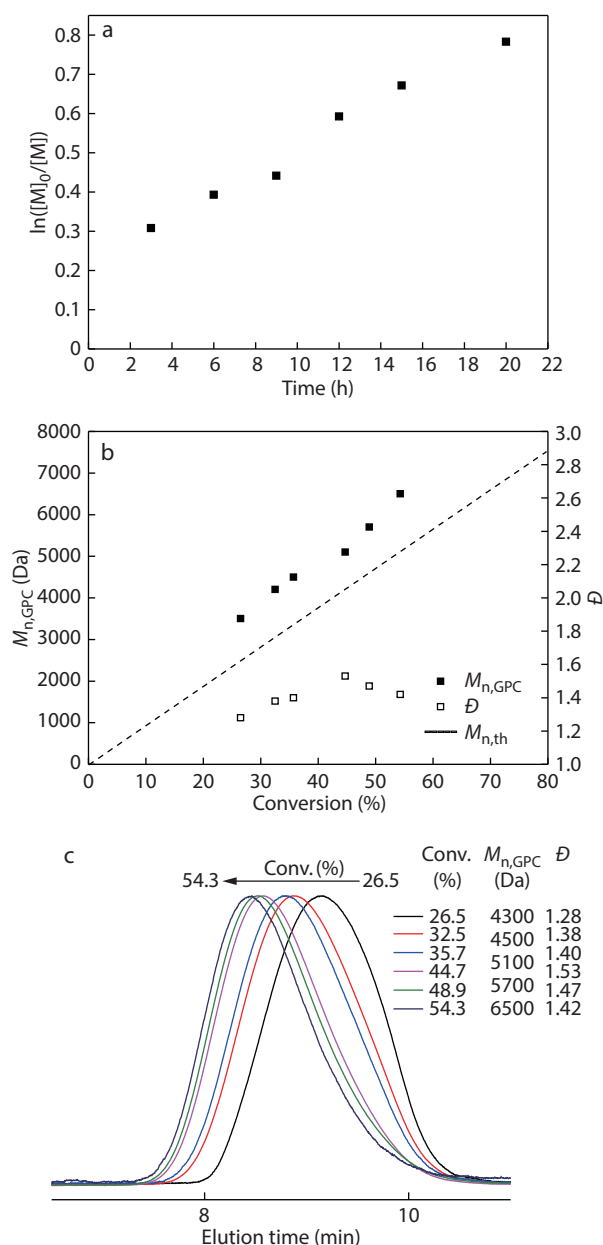


**Fig. 1**  $\ln([M]_0/[M])$  as a function of time (a) and number-average molecular weight ( $M_{n,GPC}$ ) and molecular weight distribution ( $M_w/M_n$ ) versus monomer conversion (b) and GPC traces (c) of PMMA for visible light induced iodine-mediated RCMP of MMA. Polymerization conditions:  $[MMA]_0/[BA]_0/[CP-I]_0=90/10/1$ ,  $V_{MMA}=0.45$  mL,  $V_{DMI}=0.5$  mL, under the irradiation with blue LED ( $\lambda_{max}=464$  nm, 15.0 mW/cm<sup>2</sup>) at room temperature.

**Table 2** Polymerizations of different methacrylates in the presence of BA.<sup>a</sup>

| Entry | M    | R         | Time (h) | Conv. <sup>b</sup> (%) | $M_{n,th}$ <sup>c</sup> (Da) | $M_{n,GPC}$ <sup>d</sup> (Da) | $\bar{D}$ <sup>d</sup> |
|-------|------|-----------|----------|------------------------|------------------------------|-------------------------------|------------------------|
| 1     | MMA  | 90/10/1/1 | 18       | 57.2                   | 5600                         | 6500                          | 1.58                   |
| 2     | BnMA | 90/10/1/1 | 18       | 58.3                   | 9700                         | 11600                         | 1.47                   |
| 3     | HEMA | 90/10/1/1 | 18       | 77.7                   | 9500                         | 5000                          | 1.23                   |
| 4     | HPMA | 90/10/1/1 | 18       | 75.7                   | 10200                        | 17200                         | 1.20                   |

<sup>a</sup> Polymerization conditions: R =  $[M]_0/[BA]_0/[EIPA]_0/[TPMA]_0$ ,  $V_{EIPA}=8.7$   $\mu$ L,  $V_{DMI}=0.5$  mL, under irradiation with blue LED light ( $\lambda_{max}=460$  nm, 18.6 mW/cm<sup>2</sup>) at room temperature. <sup>b</sup> Determined by gravimetry. <sup>c</sup>  $M_{n,th} = [M]_0/[EIPA]_0 \times M_M \times \text{conv.}\% + M_{BA} + M_{EIPA}$ . <sup>d</sup> Molar mass and molar mass dispersity were determined by GPC using linear PMMA as calibration standard in THF.

is not a necessary component for RCMP) and subsequently screened the suitable ligand for our polymerization system. As shown in Table S6 (in ESI), the presence of TPMA did not have negative effect on the RCMP process (Table S6, entries 2–4, in ESI). However, the presence of Me<sub>6</sub>TREN resulted in poor polymerization control (Table S6, entries 5–6, in ESI). Therefore, TPMA is a better ligand than Me<sub>6</sub>TREN for the subsequent SET-DTLRP process (Table S6, entry 1, in ESI). Based on the results above, we can conclude that the visible light-controlled RCMP can also be conducted smoothly in the presence of additives ligand TPMA, which was further confirmed by the results of MMA polymerization in the presence of BA and TPMA (Table S7 in ESI). This feature will help to simplify the feeding steps of the subsequent SET-DTLRP and it is conducive to the preparation of block copolymers with adjustable  $\bar{D}$  by cascade reaction method. In order to confirm this issue, the cascade reaction strategy was used by the combination of visible light-controlled RCMP in the presence of BA and TPMA with SET-DTLRP of BA at room temperature, and the polymerization results were shown in Table 3. It can be seen that a homopolymer PMMA end-capped with BA (<sup>1</sup>H-NMR spectrum of the resultant PMMA in Table 3 was shown in Fig. S3 in ESI) with  $\bar{D}=1.63$  was first obtained with the molar ratio of  $[MMA]_0/[BA]_0/[EIPA]_0/[TPMA]_0=45/5/1/1$  by RCMP process in the presence of BA and TPMA, and subsequently a block copolymer PMMA-*b*-PBA (<sup>1</sup>H-NMR spectrum of the resultant PMMA-*b*-PBA in Table 3 were shown in Fig. S4 in ESI) with  $\bar{D}=1.55$  was obtained by SET-DTLRP after addition of second monomer (BA). From the GPC traces (shown in Fig. 2) of corresponding PMMA and PMMA-*b*-PBA, an obvious peak shift can be observed from low molar mass (PMMA, 2600 Da) to the high one (PMMA-*b*-PBA, 17700 Da), indicating the successful chain extension by the cascade reaction method. The corresponding possible polymerization mechanism of RCMP and SET-DTLRP was shown in Schemes 1 and 2, respectively.

**Table 3** Synthesis of PMMA-*b*-PBA by cascade reaction method. <sup>a</sup>

| Entry          | Block               | Method    | R        | Time (h) | Conv. <sup>b</sup> (%) | $M_{n,th}$ <sup>c</sup> (Da) | $M_{n,GPC}$ <sup>d</sup> (Da) | $\bar{D}$ <sup>d</sup> |
|----------------|---------------------|-----------|----------|----------|------------------------|------------------------------|-------------------------------|------------------------|
| 1 <sup>e</sup> | PMMA                | RCMP      | 45/5/1/1 | 18       | 37.2                   | 2100                         | 2600                          | 1.63                   |
| 2 <sup>f</sup> | PMMA- <i>b</i> -PBA | SET-DTLRP | –        | 9        | 95.7                   | 9500                         | 17700                         | 1.55                   |

<sup>a</sup> Polymerization conditions: R =  $[MMA]_0/[BA]_0/[EIPA]_0/[TPMA]_0$ ,  $V_{MMA}=0.225$  mL,  $V_{DMI}=0.5$  mL,  $T=25$  °C. <sup>b</sup> Determined by gravimetry. <sup>c</sup> For entry 1,  $M_{n,th} = [MMA]_0/[EIPA]_0 \times M_{MMA} \times \text{conv.}\% + M_{BA} + M_{EIPA}$ . For entry 2,  $M_{n,th} = M_{n,PMMA} + [BA]_0/[PMMA]_0 \times M_{BA} \times \text{conv.}\%$ . <sup>d</sup> Molar mass and molar mass dispersity were determined by GPC using linear PMMA as calibration standard in THF. <sup>e</sup> Under irradiation with blue LED light ( $\lambda_{max}=460$  nm, 18.6 mW/cm<sup>2</sup>) at room temperature. <sup>f</sup> 0.3 mL of BA and 0.5 mL of DMI were added, copper wire (10 cm) wrapped around the stir bar.

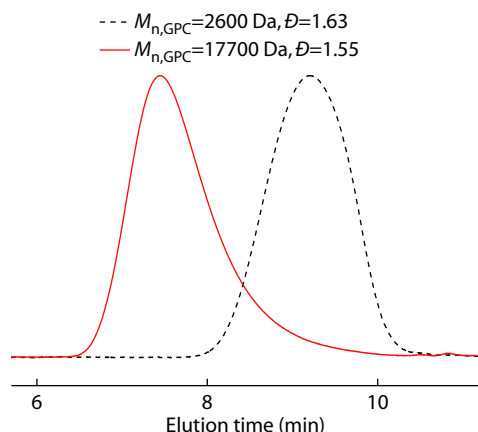
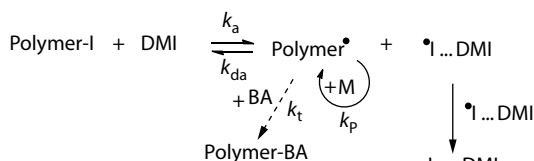
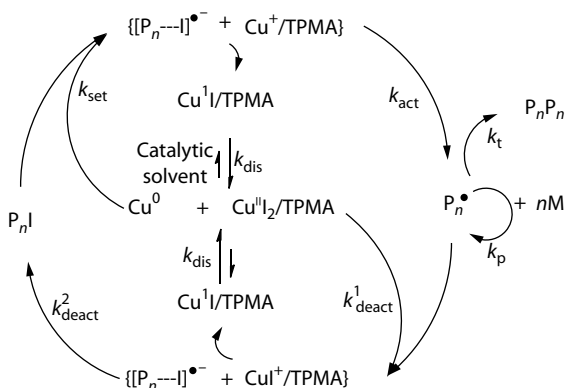


**Fig. 2** GPC traces of PMMA (black line) and PMMA-*b*-PBA (red line).



**Scheme 1** Proposed polymerization mechanism of RCMP in this work.



**Scheme 2** Proposed polymerization mechanism of SET-DTLRP in this work.

## CONCLUSIONS

In summary, we have developed a novel iodine-mediated RDRP method in regulation of polymer dispersity while maintaining the "living" features of the resultant polymers. The key point is based on the selection of methacrylates monomers (e.g., MMA, BnMA) for visible light-controlled RCMP. Therefore, acrylates monomer (e.g., BA) just acted as end-capping agent during the visible light-controlled RCMP. In addition, we can also regulate the dispersity of the resultant block copolymers by combination of visible light-controlled RCMP and iodine-mediated SET-DTLRP with copper wire as the catalyst at room temperature.

## Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of

charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2602-3>.

## ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 22071168 and 21774082) and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

## REFERENCES

- Jenkins, A. D.; Jones, R. G.; Moad, G. Terminology for reversible-deactivation radical polymerization previously called "controlled" radical or "living" radical polymerization (IUPAC Recommendations, 2010). *Pure Appl. Chem.* **2009**, *82*, 483–491.
- Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanically-induced chemical changes in polymeric materials. *Chem. Rev.* **2009**, *109*, 5755–5798.
- Magenau, A. J.; Strandwitz, N. C.; Gennaro, A.; Matyjaszewski, K. Electrochemically mediated atom transfer radical polymerization. *Science* **2011**, *332*, 81–84.
- Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L. Redox control of a ring-opening polymerization catalyst. *J. Am. Chem. Soc.* **2011**, *133*, 9278–9281.
- Miao, Y. P.; Lyu, J.; Yong, H. Y.; Sigen, A.; Gao, Y. S.; Wang, W. X. Controlled polymerization of methyl methacrylate and styrene via Cu(0)-mediated RDRP by selecting the optimal reaction conditions. *Chinese J. Polym. Sci.* **2019**, *37*, 591–597.
- Destarac, M. Industrial development of reversible-deactivation radical polymerization: is the induction period over? *Polym Chem.* **2018**, *9*, 4947–4967.
- Ni, Y. Y.; Zhang, L. F.; Cheng, Z. P.; Zhu, X. L. Iodine-mediated reversible-deactivation radical polymerization: a powerful strategy for polymer synthesis. *Polym. Chem.* **2019**, *10*, 2504–2515.
- Corrigan, N.; Jung, K.; Moad, G.; Hawker, C. J.; Matyjaszewski, K.; Boyer, C. Reversible-deactivation radical polymerization (controlled/living radical polymerization): from discovery to materials design and applications. *Prog. Polym. Sci.* **2020**, *111*, 101311.
- Wang, J. S.; Matyjaszewski, K. Controlled/"living" radical polymerization Halogen atom transfer radical polymerization promoted by a Cu(I)/Cu(II) redox process. *Macromolecules* **1995**, *28*, 7901–7910.
- Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. Atom transfer radical polymerization of methyl methacrylate initiated by alkyl bromide and 2-pyridinecarbaldehyde imine copper (I) complexes. *Macromolecules* **1997**, *30*, 2190–2193.
- Matyjaszewski, K. Transition metal catalysis in controlled radical polymerization: atom transfer radical polymerization. *Chem. Eur. J.* **1999**, *5*, 3095–3102.
- Huang, G. C.; Ji, S. X. Effect of Halogen Chain End Fidelity on the Synthesis of Poly(methyl methacrylate-*b*-styrene) by ATRP. *Chinese J. Polym. Sci.* **2018**, *36*, 1217–1224.
- Chieffari, J.; Chong, Y.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T.; Meijs, G. F.; Moad, C. L.; Moad, G. Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process. *Macromolecules* **1998**, *31*, 5559–5562.
- Moad, G.; Chong, Y.; Postma, A.; Rizzardo, E.; Thang, S. H. Advances in RAFT polymerization: the synthesis of polymers with defined end-groups. *Polymer* **2005**, *46*, 8458–8468.

- 15 Moad, G.; Rizzardo, E.; Thang, S. H. RAFT polymerization and some of its applications. *Chem. Asian J.* **2013**, *8*, 1634–1644.
- 16 Guang, N.; Liu, S.; Li, X.; Tian, L.; Mao, H. Micellization and gelation of the double thermoresponsive ABC-type triblock copolymer synthesized by RAFT. *Chinese J. Polym. Sci.* **2016**, *34*, 965–980.
- 17 Boyer, C.; Valade, D.; Lacroix-Desmazes, P.; Ameduri, B.; Boutevin, B. Kinetics of the iodine transfer polymerization of vinylidene fluoride. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5763–5777.
- 18 Wolpers, A.; Vana, P. UV light as external switch and boost of molar-mass control in iodine-mediated polymerization. *Macromolecules* **2014**, *47*, 954–963.
- 19 Tonnar, J.; Lacroix-Desmazes, P. Controlled radical polymerization of styrene by iodine transfer polymerization (ITP) in ab initio emulsion polymerization. *Polymer* **2016**, *106*, 267–274.
- 20 Tezuka, Y. *Topological Polymer Chemistry: Progress of Cyclic Polymers in Syntheses, Properties, and Functions*. World Scientific: **2013**.
- 21 Ionov, L.; Zdyrko, B.; Sidorenko, A.; Minko, S.; Klep, V.; Luzinov, I.; Stamm, M. Gradient polymer layers by “grafting to” approach. *Macromol. Rapid Commun.* **2004**, *25*, 360–365.
- 22 Lu, C.; Wang, C.; Yu, J.; Wang, J.; Chu, F. Metal-free ATRP “grafting from” technique for renewable cellulose graft copolymers. *Green Chem.* **2019**, *21*, 2759–2770.
- 23 Laurent, B. A.; Grayson, S. M. Synthetic approaches for the preparation of cyclic polymers. *Chem. Soc. Rev.* **2009**, *38*, 2202–2213.
- 24 Aksakal, R.; Resmini, M.; Becer, C. Pentablock star shaped polymers in less than 90 minutes via aqueous SET-LRP. *Polym. Chem.* **2016**, *7*, 171–175.
- 25 Matyjaszewski, K. Advanced materials by atom transfer radical polymerization. *Adv. Mater.* **2018**, *30*, 1706441.
- 26 Roy, D.; Giller, C.; Hogan, T.; Roland, C. The rheology and gelation of bidisperse 1,4-polybutadiene. *Polymer* **2015**, *81*, 111–118.
- 27 Yadav, V.; Hashmi, N.; Ding, W.; Li, T. H.; Mahanthappa, M. K.; Conrad, J. C.; Robertson, M. L. Dispersity control in atom transfer radical polymerizations through addition of phenylhydrazine. *Polym. Chem.* **2018**, *9*, 4332–4342.
- 28 Whitfield, R.; Parkatzidis, K.; Rolland, M.; Truong, N. P.; Anastasaki, A. Tuning dispersity by photoinduced atom transfer radical polymerisation: monomodal distributions with ppm copper concentration. *Angew. Chem. Int. Ed.* **2019**, *58*, 13323–13328.
- 29 Que, Y. R.; Liu, Y. J.; Tan, W.; Feng, C.; Shi, P.; Li, Y. J.; Huang, X. Y. Enhancing photodynamic therapy efficacy by using fluorinated nanoplatfrom. *ACS Macro Lett.* **2016**, *5*, 168–173.
- 30 Tao, D. L.; Feng, C.; Cui, Y. A.; Yang, X.; Manners, I.; Winnik, M. A.; Huang, X. Y. Monodisperse fiber-like micelles of controlled length and composition with an oligo(*p*-phenylenevinylene) core via “living” crystallization-driven self-assembly. *J. Am. Chem. Soc.* **2017**, *139*, 7136–7139.
- 31 Xu, B. B.; Feng, C.; Huang, X. Y. A versatile platform for precise synthesis of asymmetric molecular brush in one shot. *Nat. Commun.* **2017**, *8*, 333.
- 32 Feng, C.; Huang, X. Y. , Polymer brushes: efficient synthesis and applications. *Acc. Chem. Res.* **2018**, *51*, 2314–2323.
- 33 Gentekos, D. T.; Dupuis, L. N.; Fors, B. P. Beyond dispersity: deterministic control of polymer molecular weight distribution. *J. Am. Chem. Soc.* **2016**, *138*, 1848–1851.
- 34 Kottisch, V.; Gentekos, D. T.; Fors, B. P. “Shaping” the future of molecular weight distributions in anionic polymerization. *ACS Macro Lett.* **2016**, *5*, 796–800.
- 35 Gentekos, D. T.; Jia, J.; Tirado, E. S.; Barteau, K. P.; Smilgies, D. M.; DiStasio, R. A., Jr.; Fors, B. P. Exploiting molecular weight distribution shape to tune domain spacing in block copolymer thin films. *J. Am. Chem. Soc.* **2018**, *140*, 4639–4648.
- 36 Gentekos, D. T.; Fors, B. P. Molecular weight distribution shape as a versatile approach to tailoring block copolymer phase behavior. *ACS Macro Lett.* **2018**, *7*, 677–682.
- 37 Corrigan, N.; Almasri, A.; Taillades, W.; Xu, J.; Boyer, C. Controlling molecular weight distributions through photoinduced flow polymerization. *Macromolecules* **2017**, *50*, 8438–8448.
- 38 Corrigan, N.; Manahan, R.; Lew, Z. T.; Yeow, J.; Xu, J.; Boyer, C. Copolymers with controlled molecular weight distributions and compositional gradients through flow polymerization. *Macromolecules* **2018**, *51*, 4553–4563.
- 39 Liu, X.; Wang, C. G.; Goto, A. Polymer dispersity control by organocatalyzed living radical polymerization. *Angew. Chem.* **2019**, *131*, 5654–5659.
- 40 Ni, Y.; Tian, C.; Zhang, L.; Cheng, Z.; Zhu, X. Photocontrolled iodine-mediated green reversible-deactivation radical polymerization of methacrylates: effect of water in the polymerization system. *ACS Macro Lett.* **2019**, *8*, 1419–1425.
- 41 Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Weichold, O. Living radical polymerization of vinyl chloride initiated with iodoform and catalyzed by nascent CuO/tris(2-aminoethyl) amine or polyethyleneimine in water at 25 °C proceeds by a new competing pathways mechanism. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3283–3299.
- 42 Percec, V.; Guliasvili, T.; Ladislav, J. S.; Wistrand, A.; Stjern Dahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. Ultrafast synthesis of ultrahigh molar mass polymers by metal-catalyzed living radical polymerization of acrylates, methacrylates, and vinyl chloride mediated by SET at 25 °C. *J. Am. Chem. Soc.* **2006**, *128*, 14156–14165.
- 43 Kapishon, V.; Whitney, R. A.; Champagne, P.; Cunningham, M. F.; Neufeld, R. J. Polymerization induced self-assembly of alginate based amphiphilic graft copolymers synthesized by single electron transfer living radical polymerization. *Biomacromolecules* **2015**, *16*, 2040–2048.