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ARTICLE

Synthesis of Well-defined Mechanochromic Polymers Based on a Radical-Type Mechanochromophore by RAFT Polymerization: Living Radical Polymerization from a Polymerization Inhibitor

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Mechanochromic polymers that contain a single radical-type mechanochromophore (RM) unit, which generates relatively stable colored radicals by mechanical stimuli, but works as a polymerization inhibitor, were prepared via a reversible addition-fragmentation chain transfer (RAFT) polymerization method. The RAFT polymerization of monomers such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-hydroxyethyl methacrylate, and styrene, in the presence of a diarylbibenzofuranone (DABBF)-based RAFT agent that consists of one unit of the typical RM DABBF and two RAFT agent units successfully proceeded in a living manner to give the corresponding well-defined DABBF-centered polymers (M_n 3000–47800, PDI 1.12–1.24). Furthermore, a triblock copolymer with RM at the center of polymer chain was also synthesized by using the DABBF-centered polymer as a macro-RAFT agent. The resulting polymers exhibit mechanochromic properties via the cleavage of the central carbon–carbon bond of DABBF, which was confirmed by solid-state UV-Vis absorption and EPR spectroscopy.

Introduction

Mechanochromic polymers,[1-16] which change color upon exposure to mechanical stress, have attracted great attention in the field of materials science due to their potential applications as probes to detect stress in materials and provide insight into fracture mechanisms. Mechanochromic polymers based on chemical reactions were initially reported by Moore and co-workers,[1] who indicated that one promising strategy for the design of mechanochromic polymers is the incorporation of mechanochromic molecules, which are also referred to as mechanophores or mechanochromophores, into polymer chains. Furthermore, they discovered that the mechanochemical reactions of mechanochromophores can be accelerated when they are located in the middle of the polymer chain. This report paved the way for mechanochemical reactions, and since then, substantial effort has been directed toward the synthesis of novel mechanochromophores.[15, 17-24] Among these, radical-type mechanochromophores (RMs), which generate relatively stable colored radicals in response to mechanical stress, are particularly interesting.[10, 25-31] The most outstanding advantageous feature of RMs is that the generated radicals can be evaluated quantitatively both in solution and in the bulk using electron paramagnetic resonance (EPR) spectroscopy.

We have previously developed and characterized several mechanochromic polymers based on RMs. However, the application range of RMs is limited due to the equilibrium between the RMs and the corresponding radicals, which act as polymerization inhibitors (Figure 1a).[32] Therefore, most RMs cannot be used in radical polymerizations, a technique that usually allows the easy introduction of mechanochromophores into polymer chains using a wide range of available monomers. One strategy to overcome this problem is the development of novel RMs with high thermal resistance in order to restrict the amount of radicals formed upon heating, which could enable the radical polymerization of RMs under mild conditions.[31] However, examples of such mechanochromophores remain scarce. If a polymerization system could be developed that prevents the deactivation of the mechanochromophores and promotes the propagation reaction between the radical propagating center and the monomers, it would be possible to easily synthesize mechanochromic polymers via radical polymerization using existing RMs. For this purpose, we focused on reversible addition-fragmentation chain transfer (RAFT) polymerization, which has proven to be the most versatile of the living conventional radical polymerization techniques.[33-43] The RAFT process makes use of thiocarbonylthio compounds as reversible chain transfer agents (CTA), which react with the growing polymer chains. We envisioned that in RAFT polymerization, the CTA would react faster with the propagating radical than with the RM, thus achieving living polymerization without deactivation by the RM (Figure 1b). Ideally, a polymerization system mediated by RM-containing CTA would enable the easy synthesis of mechanochromic polymers with an RM unit at the center of the polymer chain (Figure 1c).

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Diarylbibenzofuranone (DABBF), whose central carbon–carbon bond can be cleaved to generate blue arylbenzofuranone (ABF) radicals upon exposure to mechanical stimuli (Figure 1a), was used as the RM in this study. This compound was chosen for its easy, straightforward synthesis from commercially available products and the molar attenuation coefficient of the ABF radical, which is relatively high compared to other RMs.[25] In this paper, we report the synthesis and characterization of well-defined polymers with a DABBF unit at the center of each polymer chain via RAFT polymerization using a DABBF-based RAFT agent.

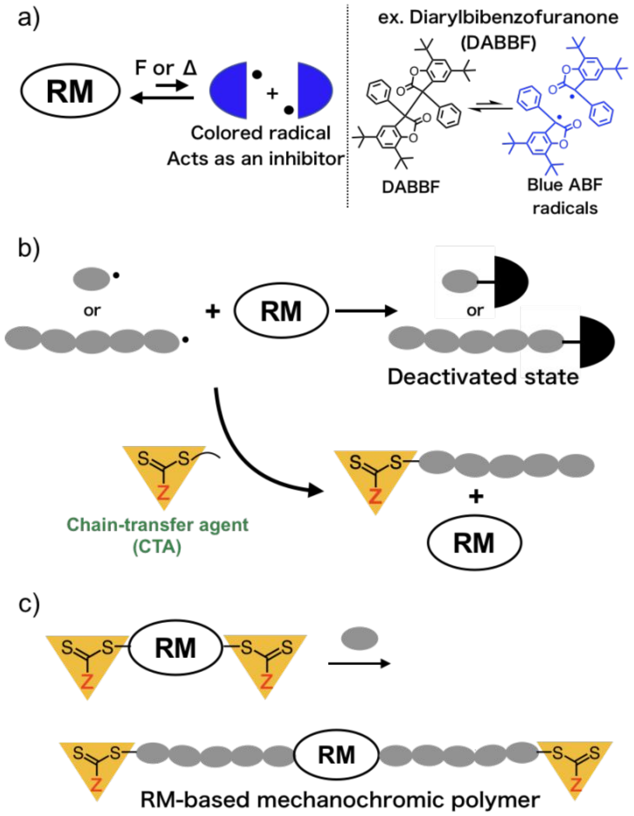


Figure 1. (a) Equilibrium between a radical-type mechanochromophore (RM) and its corresponding colored radicals. (b) Polymerization system combining an RM and a RAFT agent. (c) Synthesis of a mechanochromic polymer with an RM unit at the center of the polymer chain via RM-based CTA.

Results and discussion

To demonstrate that DABBF acts as a polymerization inhibitor, the conventional radical polymerization of methyl methacrylate (MMA) was carried out in the presence of a diol derivative of DABBF (**DABBF-diol**) and azobisisobutyronitrile (AIBN) as a radical source (Scheme 1a). When MMA was polymerized in the absence of **DABBF-diol** (Scheme 1, condition 1), poly(methyl methacrylate) (PMMA; $M_n = 64{,}000$, $M_w/M_n = 2.5$) was obtained after 3 h (Figure 2a). On the other hand, when **DABBF-diol** was included in the polymerization system (Scheme 1, condition 2), a 6 h induction period, i.e., inhibition of the polymerization, was observed (Figure 2b), and the polymer obtained after 8 h exhibited a higher molar mass ($M_n = 177{,}000$, $M_w/M_n = 2.3$) than that obtained without **DABBF-diol** (Figure 2c). These results demonstrate that **DABBF** acts as an inhibitor in radical polymerization. Subsequently, both the CTA 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid and **DABBF-diol** were added to the polymerization system to investigate the effect of adding a RAFT agent (Scheme 1, condition 3). The resulting polymer exhibited narrow polydispersity ($M_n = 19{,}000$, $M_w/M_n = 1.1$) (Figure 2d), indicating that the polymerization could be controlled by the RAFT agent even in the presence of **DABBF-diol**. Notably, the gel permeation chromatography (GPC) peak corresponding to **DABBF-diol** in the low-molar-mass region was observed at the same position after the polymerization with the RAFT agent (Figure 2f with CTA), while this peak was shifted to higher molar mass when the RAFT agent was not used (Figure 2f without CTA). These results suggest that **DABBF-diol** remained unreacted in the system with CTA, but underwent reaction in the system without the RAFT agent.

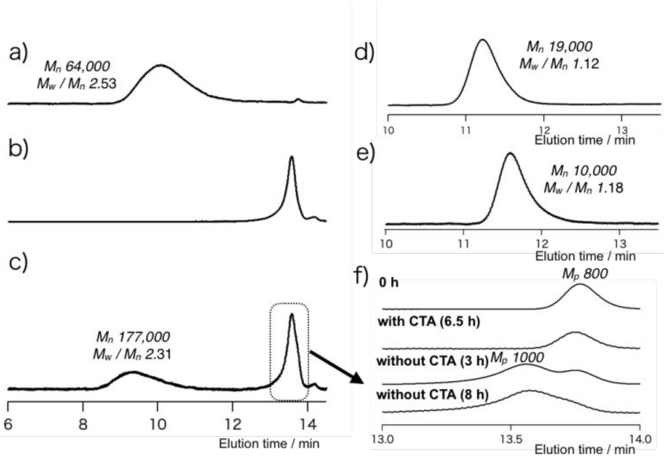
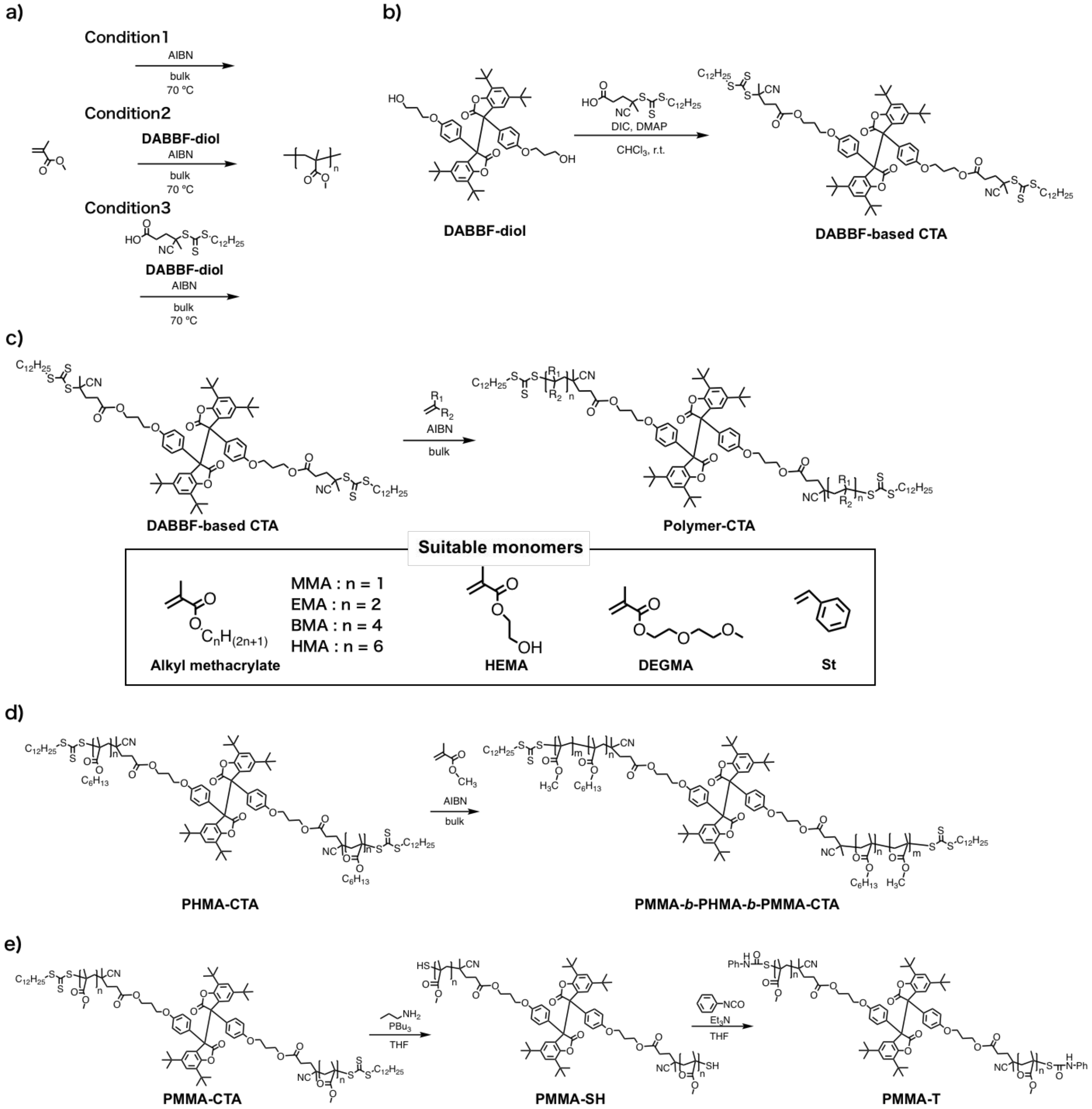


Figure 2. GPC profiles (in THF; RI) for (a) PMMA synthesized by conventional radical polymerization (Scheme 1, condition 1), (b) PMMA synthesized in the presence of **DABBF-diol** after 6 h and (c) 8 h (Scheme 1, condition 2), (d) PMMA synthesized by RAFT polymerization in the presence of **DABBF-diol** (Scheme 1, condition 3), (e) PMMA synthesized by **DABBF-based CTA**, and (f) an expansion of the low-molar-mass region of the polymerization of PMMA in the presence of **DABBF-diol** with and without the RAFT agent.

Based on the above investigation, we expected that RAFT polymerization of monomers using a DABBF-based RAFT agent could enable the synthesis of well-defined mechanochromic polymers with a DABBF unit at the center of the polymer chain via living radical polymerization (Figure 1c). The DABBF-based RAFT agent **DABBF-based CTA** (Scheme 1b) was designed and synthesized via the condensation reaction between **DABBF-diol** and 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanylpentanoic acid. The chemical structure of the obtained product was fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy as well as FAB mass spectrometry (Figures S1 and S2), which all indicated the successful synthesis of **DABBF-based CTA**.



Scheme 1. (a) Polymerization of MMA. (b) Synthesis of **DABBF-based CTA**. (c) RAFT polymerization using **DABBF-based CTA**, and the chemical structures of the applied monomers. (d) Synthesis of a DABBF-containing triblock copolymer. (e) End-group transformation of **PMMA-CTA**.

Then, the RAFT polymerization of MMA in the bulk with **DABBF-based CTA** was carried out at 70 °C in the presence of AIBN, using various MMA:CTA:AIBN ratios and reaction times, which afforded PMMA polymers with narrow polydispersity (Table 1, entries 1–5) (Figure 2e).

A PMMA polymer with a relatively low molar mass (M_n = 3,400, M_w/M_n = 1.2; entry 2 in Table 1) was synthesized in order to facilitate the characterization; however, its GPC profile was not unimodal due to a shoulder peak in the low-molar-mass region. The samples were fully analyzed using ^{1}H NMR spectroscopy (Figure 3a), diffusion-ordered NMR spectroscopy (DOSY) (Figure S5), and MALDI-TOF mass spectrometry (Figure S6).

As shown in Figure 3a, the ^{1}H NMR spectrum of **PMMA3-CTA** (M_n = 14,300) showed signals corresponding to the polymer units (H_a-H_c) and the **DABBF-CTA** moiety, i.e., the signals in the aromatic region (aryl) and aliphatic signals at 4.3 ppm (H_x) and 4.0 ppm (H_y). The DOSY spectrum (Figure S5) showed that the diffusion coefficients (Y axis) of all signals that originate from the polymer units and the **DABBF-based CTA** moiety fell on the same horizontal line, suggesting that the **DABBF** moiety is covalently incorporated into the polymer chain. Additionally, the MALDI-TOF mass spectrum in Figure S6 shows a series of peaks that correspond to the molar mass of PMMA with an ABF moiety. This provided direct evidence that the RAFT polymerization proceeded while maintaining the **DABBF-based CTA** structure, given that the central C–C bond of **DABBF-based CTA** is cleaved to afford two ABF moieties during the MALDI-TOF-MS measurement. Overall, these results clearly demonstrate the successful synthesis of a well-defined polymer with a DABBF unit at the center of the polymer chain via the polymerization of MMA with **DABBF-based CTA**.

[a]Determined by GPC (eluent: THF; calibration: polystyrene standards). [b]Determined by GPC (eluent: DMF; calibration: polystyrene standards). [c]A shoulder peak was observed in the GPC curve. [d]High-molar-mass polymers were not obtained.

The living character[33] of the current process was corroborated by (I) the narrow polydispersity of the products (Table 1), (II) the linear molar mass-conversion profile (Figure 3b), (III) the predictability of the molar mass based on the ratio of consumed monomer to transfer agent (Table 1 and Figure 3), and (IV) the ability to produce block copolymers or higher-molar-mass polymers by further monomer addition (Scheme 1d; *vide infra*). Various polymers were then synthesized via the RAFT polymerization of common monomers using **DABBF-based CTA** (Scheme 1c). Alkyl methacrylates, di(ethylene glycol) methacrylate (DEGMA), and 2-hydroxyethyl methacrylate (HEMA), as well as styrene, which cannot be polymerized via atom transfer radical polymerization (ATRP) with RMs that have high thermal resistance,[31] were suitable for the present method, resulting in products with controlled molar mass and narrow polydispersity (Table 1, entries 1–12). However, acrylate monomers were not applicable, i.e., methyl acrylate (MA) and *N*-isopropylacrylamide (NIPAM) with well-controlled molar mass and narrow polydispersity were not achieved (Table 1, entries 13–15; Figure S4). The failure of these reactions might be rationalized in terms of the higher reactivity of the propagating polyacrylate radical relative to that of methacrylate or styrene, which would lead to a deactivation of DABBF during polymerization. It should be noted that all the reactions were stopped before the conversion reached 100% and purified by reprecipitation.

Subsequently, we investigated the possibility to produce block copolymers using a macromonomer obtained via the current method. **PHMA1-CTA** (Table 1, Entry 8) was used as a macro-RAFT agent. RAFT polymerization using MMA as the second monomer was conducted in the presence of **PHMA1-CTA** (Scheme 1d). The polymerization was stopped when GPC measurements confirmed that the molar mass had reached a plateau. After precipitation in methanol, the obtained ABA-type triblock copolymer (**PMMA-*b*-PHMA-*b*-PMMA-CTA**) was analyzed by ^{1}H NMR and GPC measurements (Figure S9). The ^{1}H NMR spectrum of **PMMA-*b*-PHMA-*b*-PMMA-CTA** indicated the presence of both poly(hexyl methacrylate) (PHMA) and PMMA blocks.

The DOSY spectrum (Figure S10) of **PMMA-*b*-PHMA-*b*-PMMA-CTA** showed that the diffusion coefficients (Y axis) of both polymer blocks fell along the same horizontal line, confirming the successful synthesis of the triblock copolymer. The composition of the triblock copolymer was estimated to be HMA:MMA = 1:28 based on the ^{1}H NMR integration of the signals associated with the MMA units (H_{MMA}) and HMA units (H_{HMA}), and this value is reasonable. These results demonstrate that the current method is applicable to the synthesis of well-defined block copolymers.

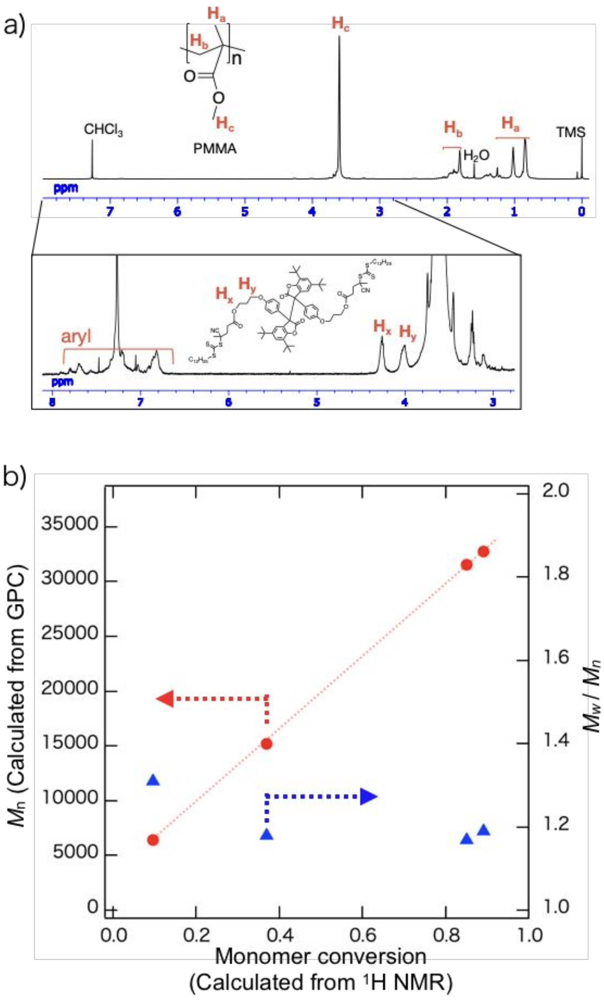


Figure 3. (a) ^{1}H NMR spectrum of **PMMA3-CTA** (M_n = 14 300), and an expansion of the chemical shift range from 2.8 to 8.0 ppm. (b) Evolution of the molar mass and polydispersity as a function of the conversion during the polymerization of MMA in the presence of **DABBF-based CTA** and AIBN.

Having confirmed the living nature of the current RAFT polymerization with **DABBF-based CTA** and the well-defined structure of the obtained DABBF-based polymers, the mechanochromic properties of the obtained polymers were investigated. Generally, polymers synthesized by RAFT polymerization exhibit a yellowish color derived from their trithiocarbonate groups. While the yellowish color of the obtained polymers demonstrates the successful synthesis of well-defined polymers with trithiocarbonate moieties at the polymer chain ends via the RAFT process, the color might also interferes with the observation of the mechanically induced coloration that originates from the DABBF moiety. Therefore, the obtained poly(methyl methacrylate) (**PMMA5-CTA**), which was expected to be a good mechanochromic polymer due to its high glass-transition temperature, was treated with hexylamine to obtain thiol-terminated PMMA (**PMMA-SH**) as a white powder (Scheme 1e). If the molar mass of **PMMA-SH** is relatively small, the change in ^{1}H NMR spectrum can be confirmed. The ^{1}H NMR spectrum of **PMMA-SH** (Figure S11a) did not exhibit the characteristic signal for the methylene protons adjacent to the trithiocarbonate moieties at 3.2 ppm (H_d), indicating that the trithiocarbonate groups were quantitatively converted to thiol groups. This conversion was clearly confirmed by UV-vis absorption spectroscopy measurements of **PMMA-CTA** and **PMMA-SH** in chloroform, which clearly revealed that the characteristic absorbance of the trithiocarbonate groups at 310 nm disappeared after the aminolysis (Figure S11b).

As we had concerns regarding the possible reaction of the DABBF moiety with the thiol groups at the polymer ends, the thiol groups were further converted to more stable thiocarbamate groups. Namely, **PMMA-SH** was treated with phenyl isocyanate to afford thiocarbamate-terminated PMMA (**PMMA-T**), which was deemed an appropriate candidate for studying the mechanochromic properties (Scheme 1e). The ^{1}H NMR spectrum of **PMMA-T** (Figure S12) showed signals characteristic of the phenyl protons at 7.5 ppm (H_{Ph}), indicating that the thiol groups were quantitatively converted to thiocarbamate groups. However, chain end fidelity cannot be determined with high accuracy in this case since NMR peaks are broad when the polymer with high molar mass is applied.

The mechanochromic behavior of **PMMA-T** was evaluated via a grinding test. Upon grinding, **PMMA-T** changed from colorless to blue (Figure 4a). Its mechanochromism was also supported by solid-state UV-Vis absorption measurements, in which absorption peaks derived from ABF radicals were observed at approximately 580 nm after grinding (Figure 4b).[30] **PMMA-T** changed immediately from blue to colorless when THF was added (Figure S14) due to the recombination of the generated carbon-centered radicals.

To further analyze the mechanochromic behavior based on the generation of radicals, EPR measurements were carried out after grinding the polymer in a ball mill (30 Hz, 10 min). Figure 4c shows the EPR spectra of **PMMA-T** before and after grinding, indicating that the radical content increased after grinding in a similar fashion to that of ground **DABBT-diol**. These results confirm that this color change is due to the dissociation of the **DABBF** moiety at the center of **PMMA-T**. Additionally, the EPR spectrum of **PMMA-SH** was measured after grinding in a manner similar to **PMMA-T** (30 Hz, 10 min). This spectrum also showed a radical peak derived from the cleavage of the DABBF moiety, and the dissociation ratio of the DABBF moiety was almost identical to that of **PMMA-T** (Figure S15 and S16). To confirm the chemical structure of triblock copolymer **PMMA-*b*-PHMA-*b*-PMMA-CTA**, i.e., whether or not it contained a DABBF moiety, EPR measurements of its thiocarbamate derivative, **PMMA-*b*-PHMA-*b*-PMMA-T**, were carried out before and after grinding. The EPR spectrum of **PMMA-*b*-PHMA-*b*-PMMA-T** after grinding showed a peak derived from the DABBF radical, demonstrating the presence and cleavage of the DABBF moiety in the triblock copolymer chain (Figure S18).

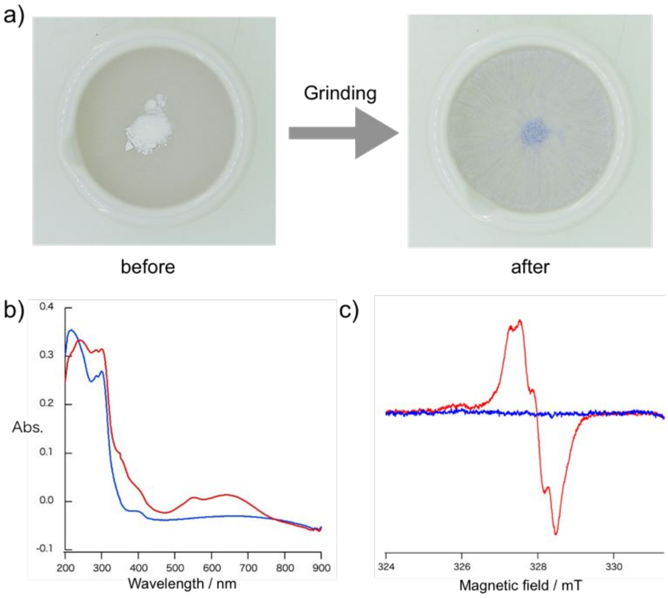


Figure 4. (a) Photographs of **PMMA5-T** before and after grinding. (b) UV-Vis spectra of **PMMA5-T** before (blue) and after (red) grinding, as well as (c) EPR spectra of **PMMA4-T** before (blue) and after (red) grinding.

Conclusions

In summary, we have developed a new approach for the synthesis of RM-based mechanochromic polymers using RAFT polymerization. The polymerization of methacrylate and styrene monomers using the DABBF-containing RAFT agent to yield DABBF-centered polymers and a block copolymer was successful. The resulting PMMA polymers clearly exhibit mechanochromic properties based on the cleavage of the central carbon–carbon bond of the DABBF moiety, as supported by grinding tests, solid UV-Vis absorption and EPR spectroscopy measurements. We are convinced that this method will not only promote the development of RM-based mechanochromic polymers, but also provide a new concept to expand the applicability of RAFT polymerization in polymer chemistry, i.e., living radical polymerizations from polymerization inhibitors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
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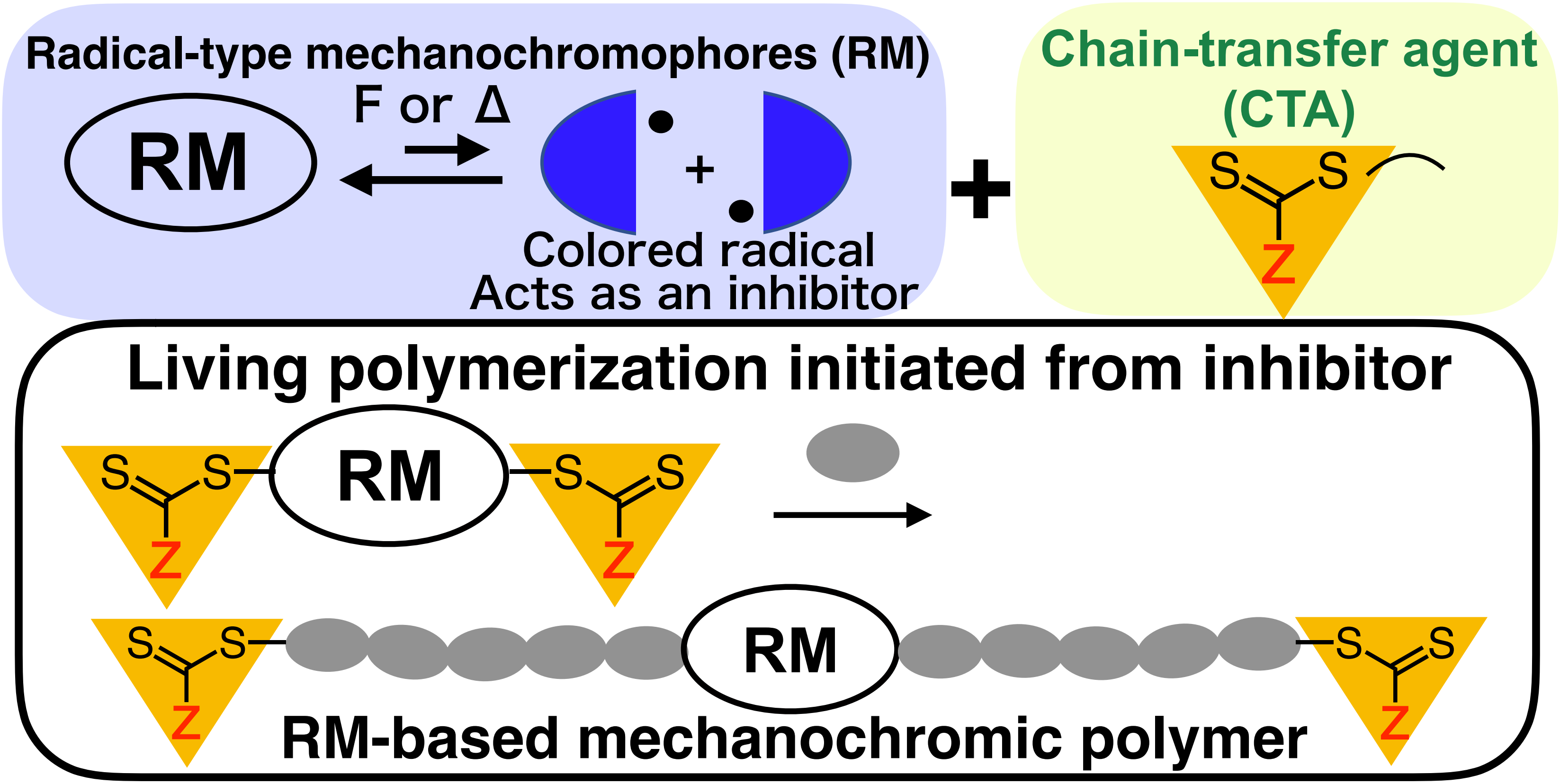
Table 1. RAFT polymerization of various monomers in the presence of **DABBF-based CTA**.

Entry	Monomer	Polymer	M_n[a]	M_n / M_n[a]	$[M]_0$:$[CTA]_0$:$[AIBN]_0$	Temp (ºC)	Time (h)
1	MMA	PMMA1-CTA	10,500	1.18	300:1:0.06	70	21
2	MMA	PMMA2-CTA	3,400	1.16	250:1:0.30	70	8
3	MMA	PMMA3-CTA	14,300	1.19	500:1:0.30	65	15
4	MMA	PMMA4-CTA	22,400	1.12	500:1:0.10	70	24
5	MMA	PMMA5-CTA	30,600	1.19	500:1:0.31	70	13
6	EMA	PEMA-CTA	47,800	1.14	500:1:0.33	70	20
7	BMA	PBMA-CTA	27,700	1.14	500:1:0.28	70	27
8	HMA	PHMA1-CTA	4,400	1.22	180:1:0.30	40	22
9	HMA	PHMA2-CTA	19,600	1.23	500:1:0.28	70	27
10	HEMA	PHEMA-CTA	99,200[b]	1.24[b]	1000:1:0.40	70	20
11	DEGMA	PDEGMA-CTA	10,700	1.47	500:1:0.28	60	20
12	St	PS-CTA	6,000	1.17	800:1:0.20	70	20
13	MA	MA-CTA	34,000	1.13[c]	800:1:0.27	70	13
14	MA	–[d]	–[d]	–[d]	800:1:0.30	70	23
15	NIPAM	–[d]	–[d]	–[d]	1000:1:0.10	r.t.	24



Synthesis of Mechanochromic Polymers Based on a Radical-Type Mechanochromophore by RAFT Polymerization: Living Radical Polymerization from a Polymerization Inhibitor