

Photoinduced Metal-Free Atom Transfer Radical Polymerization of Biomass-Based Monomers

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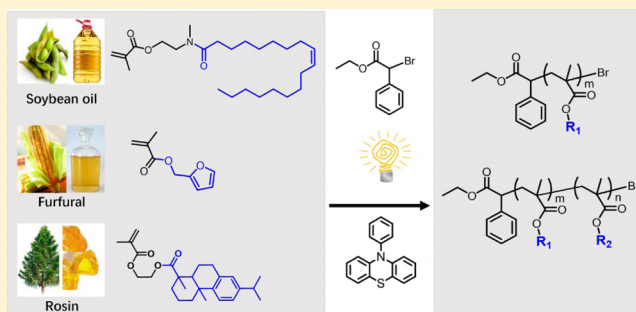
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S Supporting Information

ABSTRACT: Well-defined polymers derived from biomass feedstock (e.g., soybean oil, rosin acid, and furfural) were successfully prepared by metal-free atom transfer radical polymerization (ATRP). In the presence of photoredox catalysts and UV irradiation, three biomass-based methacrylate monomers were efficiently polymerized with good control over molecular weight and dispersity. NMR and MALDI-TOF MS confirmed high fidelity of chain end groups originated from initiators. Furthermore, block copolymers from these monomers were also achieved through chain extension by metal-free ATRP.



INTRODUCTION

Polymers from renewable resources are receiving tremendous attention due to the increasing concerns on the depletion of fossil oils and deteriorated environments. On one hand, natural polymers including cellulose, hemicellulose, lignin, chitosan, starch, protein, and natural rubber have been widely used to manufacture novel polymeric materials.^{1–3} On the other hand, monomers from renewable biomass, including vegetable oils, fatty acids, rosin acids, furfural, turpentine, and lactic acid, are molecularly engineered into green polymers.^{4–12} Compared with natural polymers, materials obtained by polymerization of such monomers exhibit advantages in precision of macromolecular structures and control of properties.

Living polymerization is a powerful tool for the preparation of polymers from biomass-derived monomers.^{13–15} Controlled radical polymerization has been often used due to their applicability to a wide range of monomers.^{16–21} Atom transfer radical polymerization (ATRP) enables the synthesis of well-defined polymers through an equilibrium of alkyl radical/alkyl halide mediated by the ligand/metal complex.^{22,23} In recent years, a few groups have carried out research on the ATRP of monomers derived from biomass, including vegetable oils, fatty acids, rosin acids, terpenes, etc.^{24–34} With control over molecular structures, resultant polymers exhibit interesting properties (e.g., shape memory, thermoplastic elastomeric, antibacterial, UV-blocking).^{28,29,35,36} However, metal catalysts have been used in traditional ATRP process and could be a contamination source for many applications, although the catalyst loading can be reduced to parts per million (ppm).^{37,38}

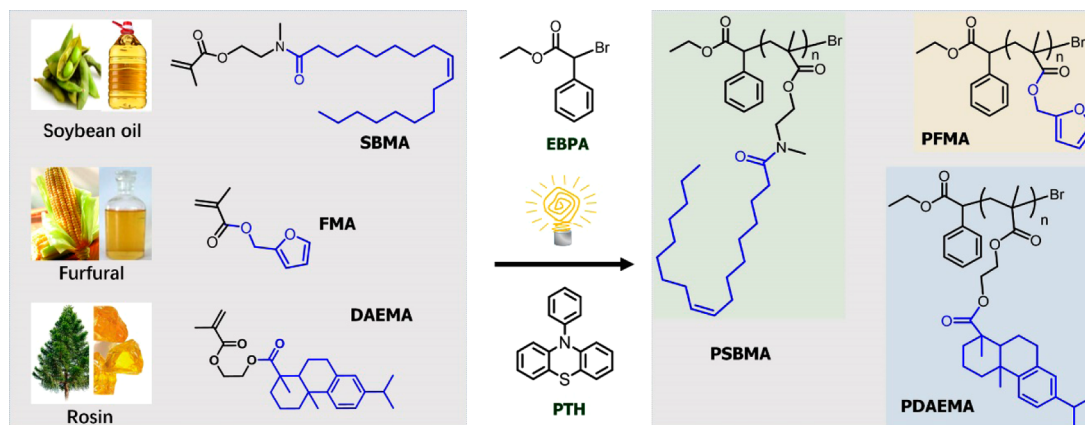
Very recently, metal-free ATRP was conceptualized by using photoredox catalysts to mediate the exchange between active and dormant species under light irradiation.^{39–43} Hawker and co-workers first developed phenylphenothiazine as an organic catalyst to perform metal-free ATRP of methyl methacrylate (MMA) and dimethylaminoethyl methacrylate.^{44,45} Matyjaszewski and co-workers expanded this catalyst for the polymerization of acrylonitrile and further elucidated the mechanism of metal-free ATRP.^{42,46} Miyake and co-workers used organic photoredox catalysts (perylene, diaryl dihydrophenazines) to mediate ATRP of MMA under visible light.^{47,48} Recently, Cheng and co-workers used fluorescein as an organic catalyst for controlled polymerization of MMA.⁴¹ Applications of metal-free ATRP have been observed in polymer–inorganic hybrid materials and functional surface modifications.^{40,49} However, polymerization of biomass-derived monomers through metal-free ATRP has not been explored.

Herein we report metal-free ATRP of biomass-derived monomers and its application in making block copolymers. Three monomers from different classes of biomass are targeted: soybean oil methacrylate (SBMA), furfuryl methacrylate (FMA), and dehydroabiatic ethyl methacrylate (DAEMA) (Scheme 1). SBMA is derived from soybean oil, and its long alkyl chain can decrease glass transition temperature (T_g) of

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Scheme 1. Metal-Free ATRP of Biomass-Based Monomers^a

^aThe blue parts are originally from biomass.

incorporated copolymers.^{50,51} FMA is a monomer derived from furfural, a biomass based feedstock prepared readily and economically from a vast array of agricultural or forestry waste.⁵² The furan group could be used as a reactive moiety for post-polymerization modifications such as Diels–Alder reaction.⁵³ DAEMA is a monomer with bulky hydrophenanthrene group derived from rosin, a renewable and abundant natural resource obtained from pine and conifer trees. Both DAEMA and FMA could help increase T_g of polymers incorporated.^{25,26,54–56} In this work, we first studied metal-free ATRP of SBMA, FMA, and DAEMA. Subsequently, metal-free ATRP was employed to conduct respective chain extension of PSBMA with FMA or DAEMA, PFMA with SBMA, and PDAEMA with SBMA, targeting diblock copolymers containing both hard and soft segments.

EXPERIMENTAL SECTION

Materials. Soybean oil methacrylate (SBMA) and dehydroabietic ethyl methacrylate (DAEMA) were prepared according to our previous work.^{25,50} 10-Phenylphenothiazine (PTH) was synthesized according to published procedures.^{44,46} Furfuryl methacrylate (FMA), ethyl α -bromophenylacetate (EBPA, 97%), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were purchased from Aldrich. All other reagents were used as received. LED strips (380 nm) were purchased from Ledlightinghut LTD. A UVA/B light meter 850009 was purchased from Sper Scientific.

Metal-Free ATRP of Biomass-Based Monomers. Metal-free ATRP of SBMA was used as an example: 2.02 g of SBMA (5 mmol, 50 equiv), 0.025 g of EBPA (0.1 mmol, 1 equiv), 2.75 mg of PTH (0.01 mmol, 0.1 equiv), and 4 mL of tetrahydrofuran (THF) were charged into a Schlenk flask. The flask was bubbled with nitrogen for 15 min to remove oxygen. The polymerization of SBMA was then initiated by placing the flask under UV light irradiation. The conversion of SBMA to polymer was determined by ¹H NMR. The solution was precipitated into methanol to yield poly(soybean oil methacrylate) (PSBMA).

Preparation of Diblock Copolymers by Chain Extension with Metal-Free ATRP. Chain extension of PSBMA with FMA by photoinduced metal-free ATRP was used as an example: The PSBMA with –Br end group (1.0 g, 1 equiv) was used as a macroinitiator; FMA (1.48 g, 100 equiv), PTH (4.9 mg, 0.2 equiv), and 2.0 mL of THF were charged to a Schlenk flask. The flask was bubbled with nitrogen for 15 min to remove oxygen. The polymerization was initiated by placing the solution under UV light irradiation. The conversion of FMA to block copolymer was determined by ¹H NMR. The solution was precipitated into methanol to yield poly(soybean oil methacrylate)-*b*-poly(furfuryl methacrylate) (PSBMA-*b*-PFMA). Similarly, block copolymers

Table 1. Optimization of Photoinduced ATRP of SBMA^a

entry	[SBMA]:[EBPA]: [catalyst]	conv (%)	M_n (theory ^c) (kg/mol)	M_n (GPC) (kg/mol)	\bar{D}
1 ^b	100:0:0	35	N/A	27.2	1.58
2	100:0:0	0	N/A	N/A	N/A
3	100:1:0.1	41	16.8	8.1	1.32
4	50:1:0.1	45	9.5	4.2	1.13
5	20:1:0.1	32	3.2	2.5	1.12
6 ^d	50:0:0	0	N/A	N/A	N/A
7 ^d	50:1:0.1	32	6.7	3.1	1.15
8 ^e	50:1:0.1	73	15.2	7.2	1.41

^aReaction conditions: SBMA (20, 50, or 100 equiv), EBPA (1 equiv), PTH (0.1 equiv), SBMA/THF = 1:2 (v/v), room temperature, 4 h, UV light (380 nm, 0.05 mW/cm² for entries 2, 3, 4, and 5). ^bUV irradiation by 2.2 mW/cm². ^cCalculation based on conversion obtained by ¹H NMR. ^dIrradiation by visible light (0.07 mW/cm² determined by UVA/B light meter 850009). ^ePolymerization in the presence of air for 20 h.

PSBMA-*b*-PDAEMA, PFMA-*b*-PSBMA, and PDAEMA-*b*-PSBMA were prepared.

Characterization. The 300 MHz ¹H NMR analysis was carried out on a Bruker AVANCE 300 NMR spectrometer with CDCl₃ or acetone-*d*₆ as solvent. Gel permeation chromatography (GPC) was performed at 30 °C on a Waters gel permeation chromatography (GPC) system equipped with a 1525 binary pump and a 2414 refractive index detector. The columns were styragel columns (HR 1, HR 3, and HR SE in the range of molecular weight 100–5000, 500–30 000, and 2000–4 000 000 g/mol, respectively). HPLC grade THF was the eluent at a flow rate of 1.0 mL min⁻¹. Monodispersed polystyrene (PSt) was used as the standard to generate the calibration curve. Polymer samples were filtered through a microfilter with a pore size of 0.2 μ m (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). Differential scanning calorimetry (DSC) was run on TA Q2000 DSC (TA Instruments) under a nitrogen atmosphere. The temperature was increased from –50 to 120 °C at a rate of 10 °C/min and decreased at the same rate. The results were collected from the second heating scan for measuring the glass transition temperature (T_g). MALDI-TOF MS spectra were taken on a Bruker Ultra Flex extreme equipped with a 337 nm nitrogen laser. An accelerating voltage of 23 kV was applied, acquiring 200 shots for each sample. Samples were prepared using trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene]-malonitrile (DCTB) as the matrix (10 mg mL⁻¹ in THF) and sodium trifluoroacetate as the cationization agent (10 mg mL⁻¹ in THF). Samples were dissolved in THF (5 mg mL⁻¹). Solutions of matrix, salt, and polymer were mixed with a ratio of volume at 4:1:1. The mixed solutions (0.5 μ L) were hand-spotted on a stainless steel MALDI target and allowed to dry completely. All spectra were recorded in the reflectron mode.

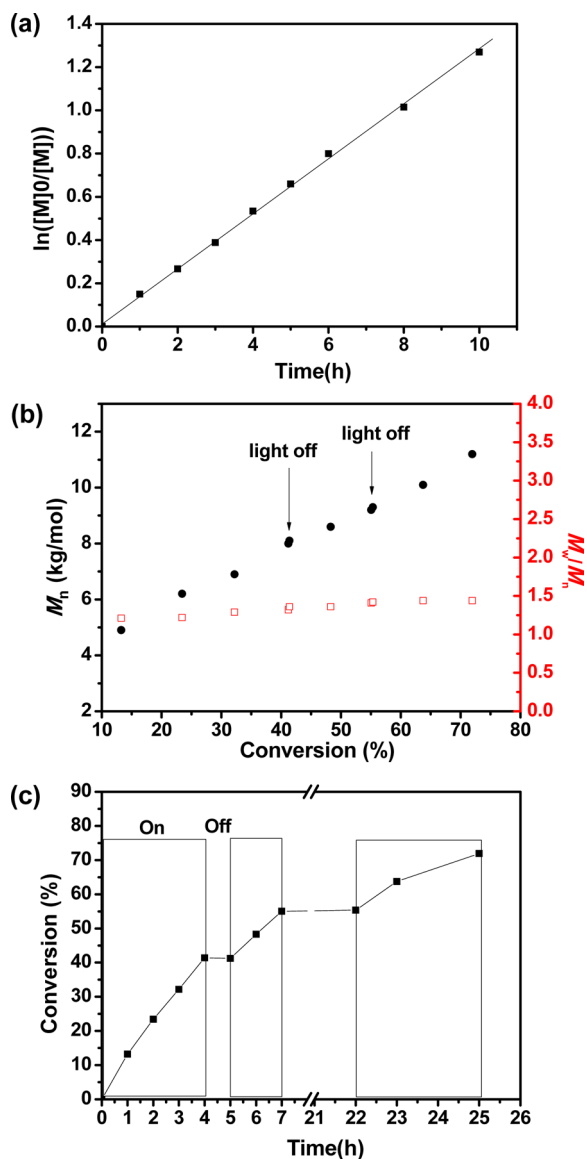


Figure 1. Kinetic study of the metal-free ATRP of SBMA (Table 2, entry 1): (a) semilogarithmic kinetic plot; (b) number-average molecular weight (M_n) and dispersity (\bar{M}_w/\bar{M}_n) vs conversion with repeated “on–off” of light and (c) conversion vs time with repeated “on–off” of light.

RESULTS AND DISCUSSION

Homopolymers by Metal-Free ATRP of Biomass-Based Monomers. According to the pioneer work of Hawker, Matyjaszewski, and Miyake, we carried out the following process for metal-free ATRP: 10-phenylphenothiazine (PTH) is used as

the organic photocatalyst. Under UV irradiation, PTH is excited to form a reductant PTH^* , which activates ethyl α -bromophenylacetate (EBPA) and generates a radical. The radical generated can add to methacrylate monomers (SBMA, FMA, and DAEMA) to form alkyl radicals, which are deactivated by the oxidized radical cation $PTH^{\bullet+}$ to regenerate the ground state of PTH (Scheme S1).⁴²

We started from the polymerization of SBMA under metal-free ATRP conditions. The intensity of UV light is an important parameter for controlled polymerization. SBMA was first exposed to UV light with an intensity of 2.2 and 0.05 mW/m² respectively for 4 h without catalysts and initiators (Table 1, entries 1 and 2). It was found that the higher intensity of UV light (Table 1, entry 1) induced the polymerization of SBMA, while no conversion was detected under the low intensity UV light (Table 1, entry 2). A similar phenomenon was observed for monomer FMA (Table S1). The high molecular weight and high dispersity (\bar{M}_w/\bar{M}_n) of PSBMA and PFMA from higher intensity of UV irradiation could be explained by a mechanism of conventional free radical polymerization. Therefore, low intensity UV light (0.05 mW/cm²) was used to perform the metal-free ATRP in the initial study.

As summarized in Table 1 (entries 3–5), PSBMA with low \bar{M}_w/\bar{M}_n and predictable molecular weight could be achieved in the presence of initiator and organic catalyst under UV irradiation. The linear semilogarithmic plots (Figure 1a and Figure S1) confirmed the controlled radical polymerization process. PFMA with predictable molecular weight and low \bar{M}_w/\bar{M}_n was also prepared under the same conditions (Table S1), and the living radical polymerization behavior was confirmed via the kinetic studies (Figure S2).

To further explore the conditions for metal-free ATRP of biomass-based monomers in the presence of EPBA and PTH, the respective polymerization of SBMA and FMA (entry 7 in Table 1 and entry S4 in Table S1) was performed under visible light (with 0.07 mW/cm² UV light intensity). Both SBMA and FMA were polymerized by metal-free ATRP under visible light irradiation, although their polymerization was slower than that induced directly under UV light. Surprisingly, SBMA could also be polymerized under visible light irradiation with exposure to the air (entry 8 in Table 1). The UV intensity on a sunny day is about 0.17 mW/cm², whereas it is around 0.07 mW/cm² on a cloudy day (in Columbia, SC), which may result in different polymerization rates on the course of photoinduced metal-free ATRP. As control studies, no conversion was observed (entry 6 in Table 1 and entry S2 in Table S1) in the absence of EPBA and PTH. These results confirmed that visible light could be used as a choice of LED strips for the metal-free ATRP of SBMA and FMA.

The initial evaluation of SBMA and FMA (Table 1 and Table S1) for metal-free ATRP was carried out for only 4 h under the irradiation of UV LED strips (0.05 mW/cm UV light intensity).

Table 2. Photoinduced ATRP of Biomass-Based Monomers^a

entry	monomer ^b	time (h)	conv (%)	M_n (theory)(kg/mol)	M_n (NMR) (kg/mol)	M_n (GPC) (kg/mol)	\bar{M}_w/\bar{M}_n
1	SBMA100	10	72	29.3	24.9	11.2	1.37
2	SBMA50	7	64	13.1	11.2	6.1	1.20
3	FMA50	12	66	5.7	6.2	6.1	1.41
4	FMA20	15	73	2.7	2.1	2.9	1.35
5	DAEMA50	6.5	70	14.4	11.0	6.5	1.28
6	DAEMA20	5	52	4.4	4.2	3.8	1.25

^aReaction conditions: $[M]:[EBPA]:[catalyst] = 100, 50, \text{ or } 20:1:0.1$, at room temperature with irradiation by 380 nm UV light (LED strips with 0.05 mW/cm UV light intensity). ^bThe number following SBMA, FMA, or DAEMA represents the molar ratio to [EBPA].

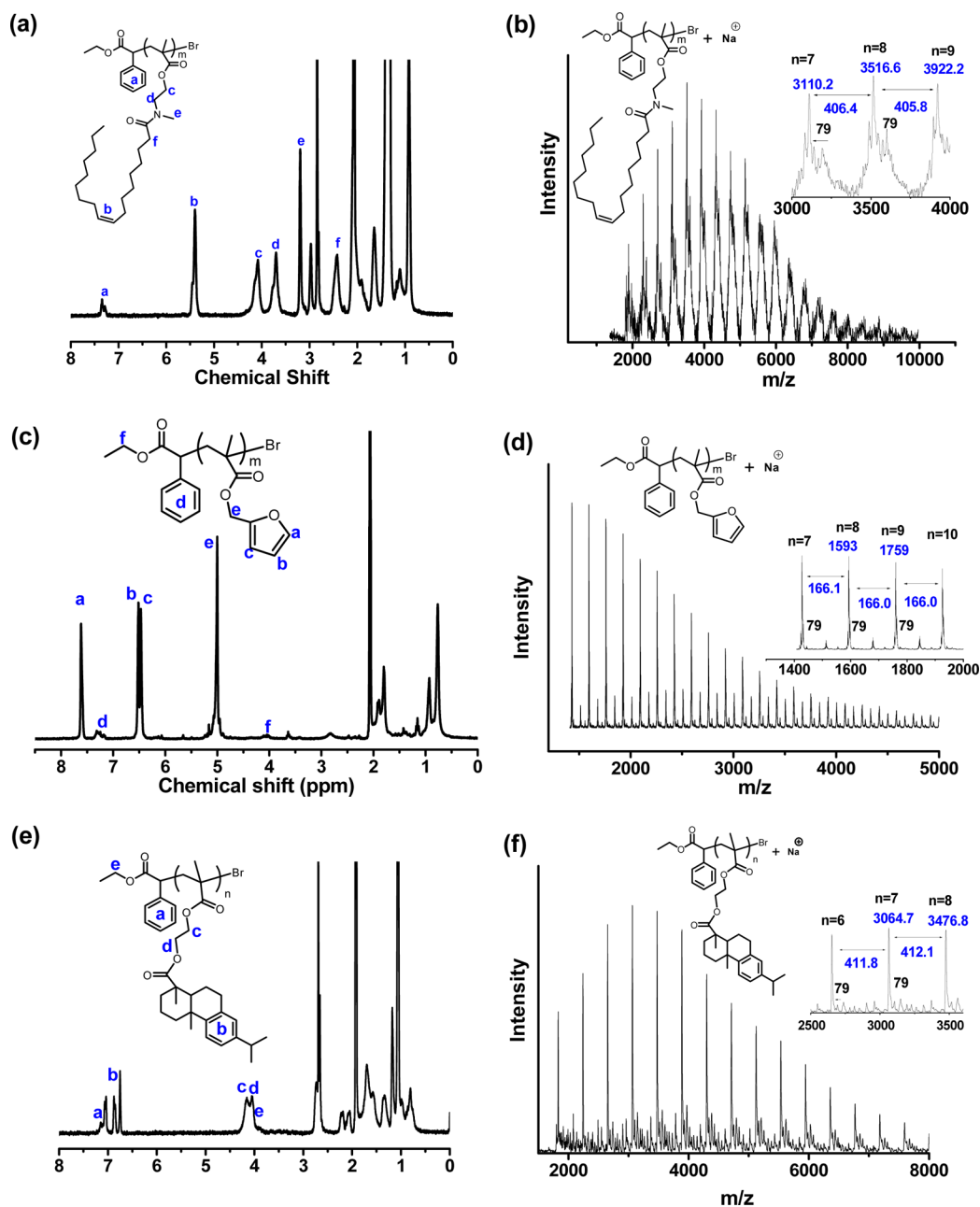


Figure 2. ^1H NMR spectra of (a) PSBMA, (c) PFMA, and (e) PDAEMA. MALDI-TOF MS spectra of (b) PSBMA, (d) PFMA, and (f) PDAEMA.

Low to medium conversions (17%–45%) were achieved after the polymerization. Higher conversions (52%–73%) of the chosen three monomers could be reached by increasing the polymerization time (Table 2). The controlled polymerization of DAEMA was also validated through the linear plot of $\ln([M]_0/[M])$ versus polymerization time (Figure S4). The molecular weight of polymers (Table 2) matched well between theoretical values as calculated from monomer conversion and values from the end-group analysis of NMR spectra. The deviation of GPC molecular weight from the theoretical values might be explained by the different hydrodynamic behaviors between the PSt standard and the biomass-derived polymers.

The controlled nature of these polymerizations was subsequently corroborated by their activation and deactivation behavior. The polymerization was performed under alternating light “ON” and “OFF” environments. As shown in Figures 1b and 1c, no further conversion of SBMA was observed when the light was “OFF”.

Table 3. Molecular Weight and Dispersity (\mathcal{D}) of Block Copolymers Prepared by Metal-Free ATRP Using PSBMA, PFMA, and PDAEMA as Macroinitiators^a

entry	diblock copolymer ^b	time (h)	conv (%)	M_n (theory) ^c (kg/mol)	M_n (GPC) (kg/mol)	\mathcal{D}
1 ^c	PSBMA ₂₇ - <i>b</i> -PFMA ₄₁	9.5	59	21.0	11.2	1.92
2 ^c	PSBMA ₂₇ - <i>b</i> -DAEMA ₉₈	24	89	47.9	16.5	2.10
3 ^d	PFMA ₃₆ - <i>b</i> -PSBMA ₁₁	15	53	10.7	13.1	1.67
4 ^e	PDAEMA ₁₀ - <i>b</i> -PSBMA ₃₅	16	90	18.7	15.8	1.78

^aThe reactions were carried out in THF at room temperature irradiated by 380 nm UV light (LED strip with 0.05 mW/cm UV light intensity).

^bThe number following SBMA, FMA, or DAEMA represents the number of repeat unit. ^c[Monomer]:[macroinitiator PSBMA]:[catalyst] = 100:1:0.1. ^d[SBMA]:[macroinitiator PFMA]:[catalyst] = 20:1:0.1. ^e[SBMA]:[macroinitiator PDAEMA]:[catalyst] = 40:1:0.1.

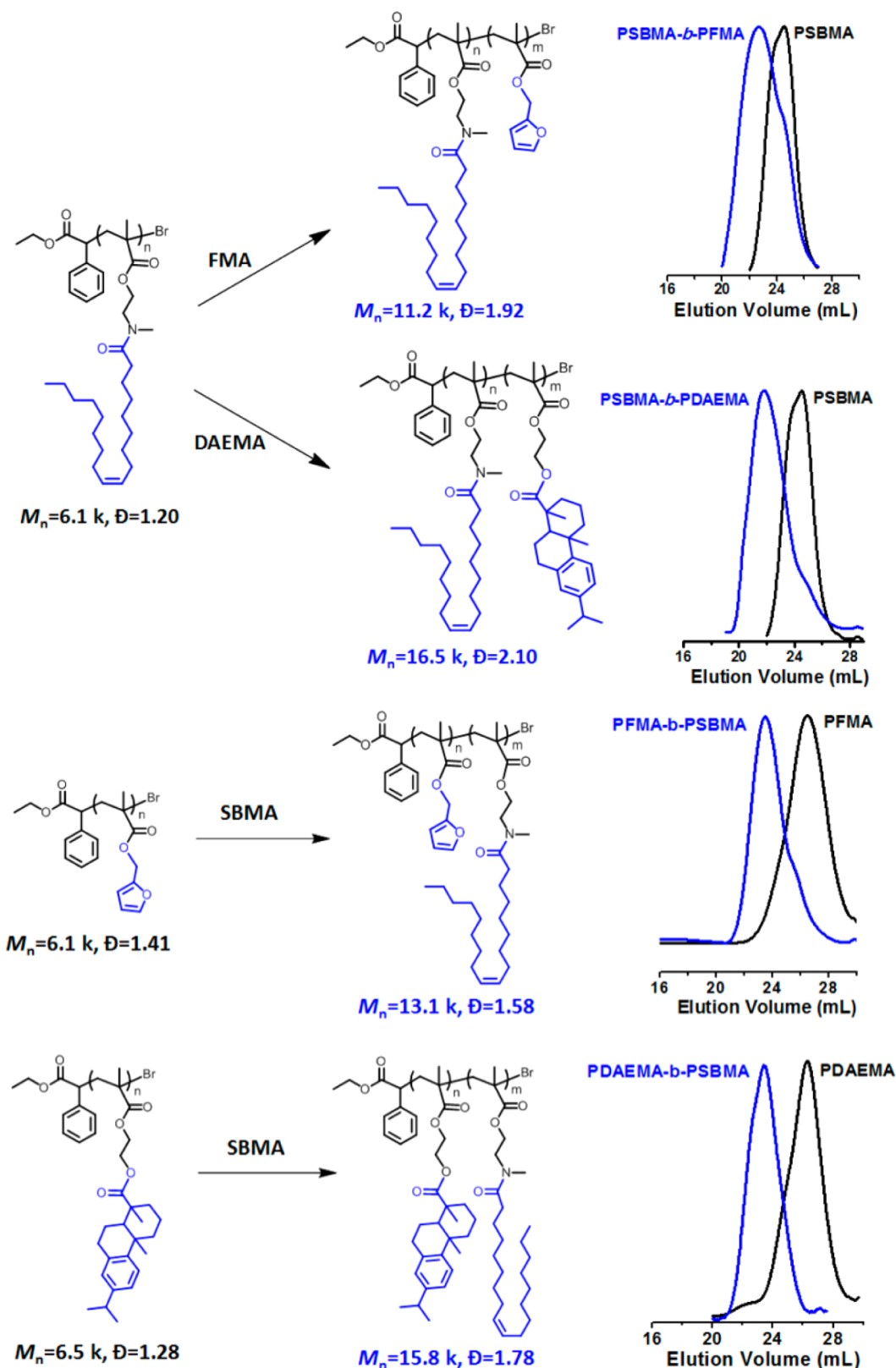


Figure 3. Preparation of diblock copolymers using PSBMA, PFMA, and PDAEMA as macroinitiators with GPC traces of polymers before and after the chain extension.

When the light was switched to “ON”, the polymerization resumed as expected. This polymerization could be restarted even after 15 h “light off”, demonstrating an efficient control over the activation and deactivation of the polymerization process. Importantly, the polymerization with multiple “on–off” light

switching cycles (Figure 1b) still gave a linear relationship in molecular weight versus conversion and exhibited first-order kinetics throughout the course of polymerization (Figure 1a). The light “on–off” metal-free ATRP of FMA and DAEMA was also carried out (Figures S3 and S5). It was also observed that the

monomer conversion increased with the exposure time to UV irradiation. These data showed that the polymer radical chains were oxidized to the stable and dormant alkyl bromides when the light was turned to "OFF", and the dormant chain ends could be efficiently and reversibly reduced into propagating radicals upon light irradiation.

Overall the polymerization of SBMA, FMA, and DAEMA could be well controlled under optimal conditions. A slightly broader molecular distribution ($\mathcal{D} = 1.2\text{--}1.4$) at higher molecular weight could be explained by (1) the complexity of fatty chains of SBMA (more than one type of fatty chain), (2) the possible H-abstraction of the methylene group next to the furan unit by propagating radicals, and (3) the steric effect from the fused-ring structure of the rosin group.

Characterizations of PSBMA, PFMA, and PDAEMA.

^1H NMR was used to characterize homopolymers (PSBMA, PFMA, and PDAEMA) synthesized by metal-free ATRP. As shown in Figure 2, a peak at 7.35 ppm corresponding to the aromatic protons of initiator EPBA was clearly observed, indicating the fidelity of end-group. Also, the characteristic peaks for the side groups of PSBMA, PFMA, and PDAEMA were clearly assigned. Through the comparison between the integral area of phenyl unit from EBPA and specific groups in the polymer side chain, the molecular weight of polymers could be obtained (Table 2).

The end-group fidelity was further confirmed by MALDI-TOF MS analysis of PSBMA, PFMA, and PDAEMA. Figure 2b shows the MALDI-TOF MS spectroscopy of PSBMA (Table 2, entry 1). It can be observed that a series of main peaks are separated by the mass of SBMA unit (405–407 mass units). The molecular weight values of these individual PSBMA oligomers by MALDI-TOF MS spectroscopy include the mass of initiating unit (ethyl 2-phenylacetate group) at one chain end, a bromine atom at the propagating chain end, and a sodium ion. The degree of polymerization (n) of individual PSBMA can be calculated by eq 1.

$$n = \frac{M_p - 243 - 23}{M} \quad (1)$$

where M_p is the molecular weight of individual PSBMA read by the MS spectrum, 243 the molecular weight of EBPA, 23 the molecular weight of sodium ion, and M the molecular mass of monomer. The representative values of n are shown in Figure 2. Figures 2d and 2f display the MALDI-TOF MS spectroscopy of PFMA and PDAEMA. The main peaks were also found to be separated by the mass of FMA unit (166 mass units) and DAEMA unit (412 mass units), respectively, demonstrating the existence of initiating ethyl 2-phenylacetate group and bromine atom at the propagating chain end. These data firmly proved that metal-free ATRP of biomass-based monomers has a control over the chain ends.⁴²

Preparation of Diblock Copolymers by Chain Extension.

To further study the end-group fidelity, chain extension of PSBMA, PFMA, and PDAEMA was carried out using renewable monomers to yield diblock copolymers. The polymerization results are summarized in Table 3. GPC results displayed clear increase of molecular weight after the chain extension (Figure 3). GPC traces of these four diblock copolymers showed that chain extension from PSBMA to FMA or DAEMA has a small shoulder on the lower molecular weight side, indicating that the efficiency is not 100%. On the other hand, the opposite chain extension (from PFMA or PDAEMA to SBMA) is much more clean. This is not surprising, as the carbon–bromine (C–Br) bond might have slightly different bond dissociation energy with monomers containing dramatically different side groups.⁵⁷

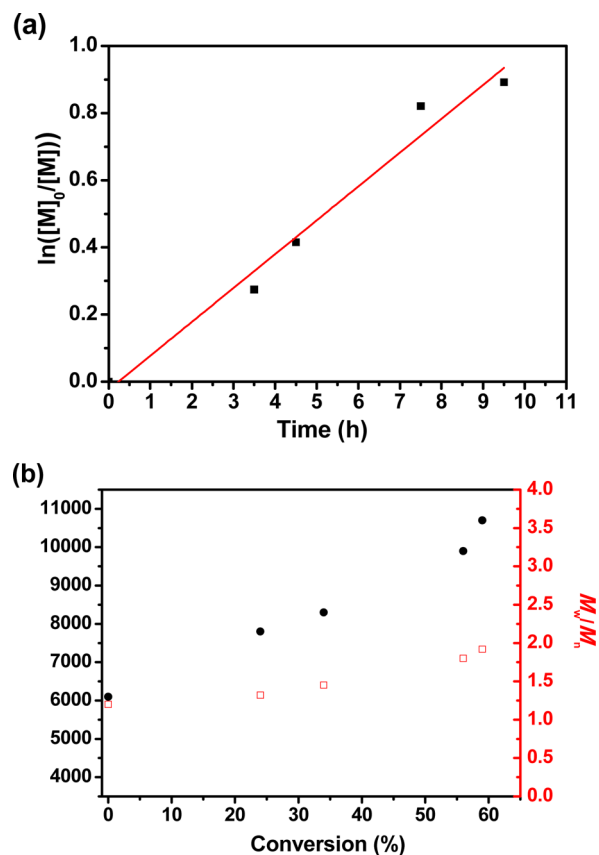


Figure 4. Preparation of PSBMA-*b*-PFMA diblock copolymer by the chain extension of PSBMA with FMA (Table 3, entry 1): (a) semi-logarithmic kinetic plot of polymerization; (b) number-average molecular weight and dispersity vs conversion.

Kinetic study of the chain extension of PSBMA with FMA was also performed. As shown in Figure 4, the monomer conversion as well as $\ln([M]_0/[M])$ increased with the exposure time to light, suggesting a controlled polymerization mechanism of chain extension, though there seemed to be an induction period. The diblock copolymers were then characterized by ^1H NMR. In the cases of PSBMA-*b*-PFMA and PFMA-*b*-PSBMA, the peaks at 5.40, 4.07, 3.69, 3.19, and 2.42 ppm correspond to the protons derived from PSBMA, while the peaks at 7.47, 6.35, and 4.88 ppm originate from PFMA, as presented in Figure 5a and Figure S6b. Particularly, the peak at 7.10–7.20 ppm corresponding to the protons of EPBA was also found in ^1H NMR after the chain extension. The ratio between degree of polymerization of PSBMA block and PFMA block (Table 3) was calculated by ^1H NMR. In the cases of PSBMA-*b*-PDAEMA and PDAEMA-*b*-PSBMA, the peaks at 6.8–7.2 ppm assigned to the aromatic protons in DAEMA and the characteristic peaks from PSBMA were also clearly observed (Figure 5b and Figure S6a). FT-IR spectra of the prepared diblock copolymers show the combination of characteristic absorption peak from each block. As shown in Figure S7, the diblock copolymers PSBMA-*b*-PFMA and PSBMA-*b*-PDAEMA have an increased intensity from the carbonyl group of ester at around 1730 cm^{-1} , in contrast to the peak at about 1647 cm^{-1} corresponding to the carbonyl group of amide from the PSBMA block.

Thermal Properties and Microphase Separation of Block Copolymers. Glass transition temperature (T_g) is a crucial physical parameter that could be used to investigate the

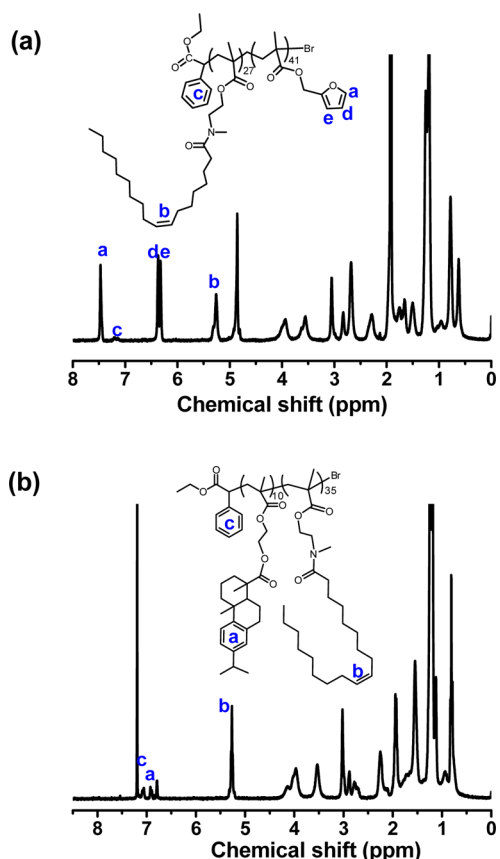


Figure 5. ^1H NMR spectra: (a) PSBMA₂₇-*b*-PFMA₄₁ (Table 3, entry 1) and (b) PDAEMA₁₀-*b*-PSBMA₃₅ (Table 3, entry 4).

segmental mobility and microphase separation of polymer chains. As shown in Figure S8, long alkyl side groups of PSBMA could significantly enhance the main chain mobility, resulting in a low T_g (-2°C). Because of the presence of the bulky furan group in the side chain of PFMA and hydrophenanthrene ring in the side chain of PDAEMA, higher T_g s were observed from both polymers (66°C for PFMA and 82°C for PDAEMA). DSC curves for the diblock copolymers unexceptionally gave two distinct T_g s, indicating the existence of microphase separation (Figure 6a). These T_g s corresponded

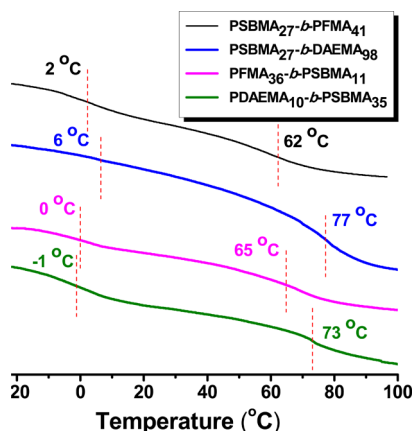


Figure 6. DSC curves of the synthesized diblock copolymers in Table 3.

nicely to each segment, further hinting the successful synthesis of block copolymers.

CONCLUSIONS

We demonstrated metal-free ATRP of biomass-based monomers under low intensity of UV LED light. Well-defined homopolymers with precise control over molecular weight, dispersity, and end-group fidelity were prepared from methacrylate monomers derived from renewable biomass (soybean oil, furfural, rosin). The polymerizations were initiated by EPBA with PTH as the catalyst under UV irradiation and could be carried out even under the condition of visible light irradiation and exposure to air. Activation and deactivation during the polymerization could be readily achieved by an “on–off” light switch. ^1H NMR and MALDI-TOF MS confirmed the fidelity of bromide chain ends of biomass-based homopolymers, which allow for the preparation of a variety of biomass-based block copolymers. These as-prepared biomass-based block copolymers demonstrated microphase separation as evidenced by DSC experiments. This study could open a new avenue for developing biomass-derived polymeric materials, such as multiblock thermoplastic elastomers, polymer–inorganic hybrids, and nanocomposites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b01997.

Semilogarithmic kinetic plots of polymerization of SBMA, FMA, and DAEMA; FTIR spectra and DSC curves of polymers (PDF)

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Notes

The authors declare no competing financial interest.

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