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Alternating Methyl Methacrylate/*n*-Butyl Acrylate Copolymer Prepared by Atom Transfer Radical Polymerization

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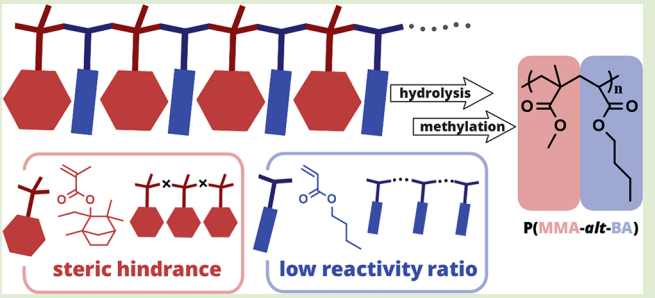
ABSTRACT: Poly(methyl methacrylate/*n*-butyl acrylate) [P(MMA/BA)] copolymer with an alternating structure was synthesized via an activator regenerated by electron transfer (ARGET) atom transfer radical (co)polymerization (ATRP) of 2-ethylfenchyl methacrylate (EFMA) and *n*-butyl acrylate (BA) with subsequent postpolymerization modifications (PPM). Due to the steric hindrance of the bulky pendant group of EFMA, as well as the low reactivity ratio of BA in copolymerization with methacrylates, copolymerization of EFMA and BA generated a copolymer with a high content of alternating dyads. A subsequent PPM procedure of the alternating EFMA/BA copolymer was comprised of the hydrolysis of a tertiary ester by trifluoroacetic acid and methylation by (trimethylsilyl)diazomethane. After the modifications, the architecture of the obtained alternating MMA/BA copolymers was compared with gradient and statistical copolymers with overall similar compositions, molecular weights, and dispersities. ^{13}C NMR indicated the absence of either MMA/MMA/MMA or BA/BA/BA sequences, in contrast to an abundance of homotriads in either the statistical or especially in the gradient copolymer. All three copolymers had similar glass transition temperatures, as measured by differential scanning calorimetry (DSC), but the alternating copolymer had the narrowest range of glass transition.



Macromolecular engineering provides new routes to (co)polymers with precisely controlled architectures in terms of composition, topology, and functionality.[1,2] Such (co)polymers have many intriguing properties, such as self-assembly, microphase separation, vibration or acoustic damping, self-healing, and shape memory.[3−10] Considering the compositional features, copolymers can be classified as block, gradient, periodic (the simplest case is alternating copolymer), and statistical (also termed random for Bernoullian statistics) copolymers. Even with an identical composition of comonomers, copolymers can exhibit significantly distinct properties if comonomer units arrange differently along the chain.[11] Recently, poly(methyl methacrylate/*n*-butyl acrylate) [P(MMA/BA)], synthesized by atom transfer radical polymerization (ATRP), at the feed ratio of both comonomers close to equimolar, were reported as excellent self-healing materials.[12−14] It was proposed that the pendant groups in the alternating MMA/BA sequences interdigitated, forming "key-and-lock" structures that facilitated efficient self-healing under ambient conditions. The long-term material persistence, superior self-healing endurance, and simple synthetic chemistry pointed out to the P(MMA/BA) copolymers as the next generation self-healing materials.[15]

(Co)polymers synthesized by ATRP have a predetermined molecular weight, low dispersity, and high chain-end fidelity, as well as controlled topology, functionality, and composition.[16−20] These features can lead to materials with new properties.[21−23] In radical copolymerization, MMA (M) is more reactive than BA (B), according to reported reactivity ratios (r_M = 1.79 and r_B = 0.30), meaning that at the equimolar initial monomer feed, MMA is consumed faster.[24] In ATRP, or any other reversible deactivation radical (co)polymerization (RDRP),[25,26] this difference in reactivity ratio will lead, at sufficiently high conversion, to a spontaneously generated gradient copolymer structure [P(MMA-*grad*-BA)].[24,27,28] At an equimolar initial feed ratio, MMA-rich segments will dominate at the beginning of every polymer chain, whereas BA-rich segments will dominate at chain ends. The Monte Carlo simulation of a model copolymerization of MMA with BA by ATRP indicated the formation of copolymers with the overall fraction of heterodyads F(MB) + F(BM) = 0.534 at around 90% conversion.[29] Moreover, this value could increase to 0.576 if copolymerization of MMA and BA started at a 30/70 initial feed ratio and was stopped at <10% conversion to

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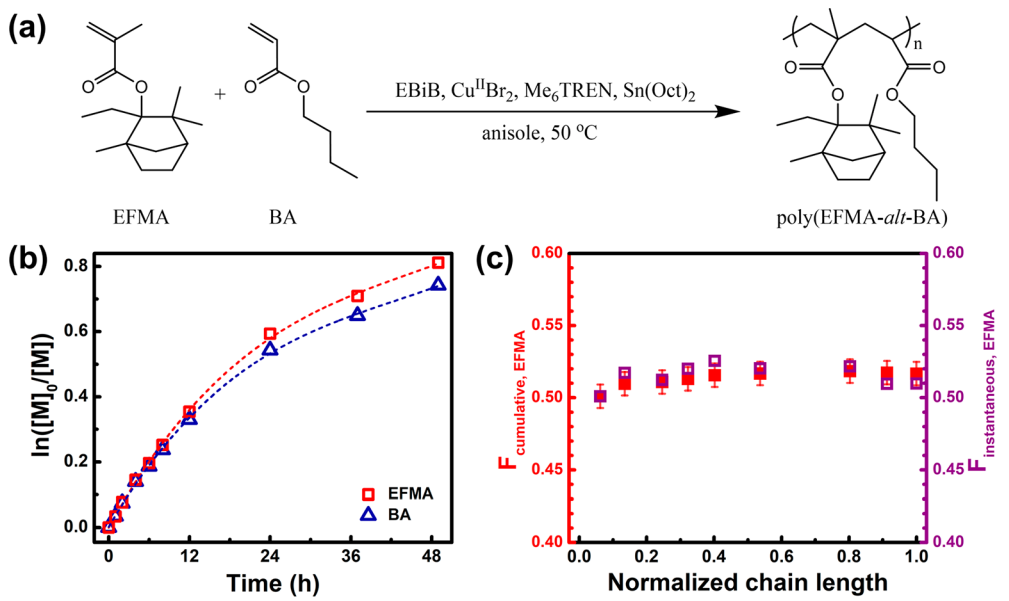

Figure 1. Alternating P(EFMA-*alt*-BA) by ARGET ATRP. (a) Reaction scheme, (b) kinetic plots of EFMA (red) and BA (blue) comonomers, and (c) cumulative (red, filled icons) and instantaneous (purple, empty icons) incorporation of EFMA into the copolymer. Around 2% ^{1}H NMR system error of comonomer conversion integration results was taken into consideration (illustrated as the error bars). Copolymerization conditions: BA 3 mL, BA and EFMA combined 50 vol % in anisole, $[EFMA]_0/[BA]_0/[EBiB]_0/[CuBr_2]_0$ = 500/500/1/0.3, $[CuBr_2]_0/[Me_6TREN]_0/[Sn(Oct)_2]_0$ = 1/3/5, 50 °C.

achieve an essentially statistical (nongradient) copolymer structure [P(MMA-*stat*-BA)] due to a small drift in monomer feed. Nevertheless, the synthesis of copolymers with an even higher alternating dyad fraction, to potentially enhance the "key-and-lock" structure in P(MMA/BA), still remains a challenge.

The past decade witnessed the rapid development of diverse control strategies to form precisely sequence-controlled copolymers (including periodic and alternating).[30−32] The synthesis of alternating copolymers can employ very large differences in the polarity of comonomers,[33,34] complexation of one comonomer with Lewis acid,[35] steric hindrance via bulky pendant groups in a more reactive comonomer,[36] or cleavable cyclo-spacer in divinyl monomers.[37] The specific properties brought by regulated alternating sequential arrangements enabled promising applications such as electrolyte,[38] thermal response,[39] and water-repellent coating.[40] Furthermore, postpolymerization modification (PPM), which can either incorporate or alter the functionalities of presynthesized (co)polymers, provides great opportunities for the preparation of copolymers that are difficult to synthesize directly.[41−43] Therefore, despite the fact that direct copolymerization of MMA and BA with an alternating structure [P(MMA-*alt*-BA)] by ATRP is not possible, it can be achieved through copolymerization of another methacrylate carrying a bulky pendant group and BA with subsequent PPM. Herein, we present the first synthesis of an alternating P(MMA/BA) copolymer by ATRP. Inspired by a previous work,[44] 2-ethylfenchyl methacrylate (EFMA) was used in a copolymerization with BA. The steric hindrance of the bulky 2-ethylfenchyl group significantly diminished the homopolymerization of EFMA (only 4% conversion in 24 h).[44] Meanwhile, due to the lower reactivity ratios of acrylates compared with methacrylates during copolymerizations, homopolymerization of BA was also hampered in the presence of EFMA.[45] This selection of comonomers resulted in the EFMA/BA copolymer with a very high content of alternating sequences [P(EFMA-*alt*-BA)]. The subsequent PPM strategies, including hydrolysis of the 2-ethylfenchyl group and methylation, provided the alternating MMA/BA copolymer.

The assignment of all NMR signals in the EFMA monomer was accomplished, for the first time, by two-dimensional nuclear magnetic resonance spectroscopy (2D NMR; additional experimental data are in the Supporting Information; Figures S1−S5 and Table S1). Copolymerization of EFMA and BA with an equimolar initial feed ratio was carried out under activators regenerated by electron transfer (ARGET) ATRP with tin(II) 2-ethylhexanoate [Sn(Oct)$_2$] as the reducing agent (Figure 1a).[46,47] A kinetic study by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) indicated that comonomers steadily copolymerized at the same rate up to 12 h (Figure 1b). At 49 h, conversion of EFMA (55%) was slightly higher than that of BA (52%), but still close to the NMR integration accuracy (±2%). Based on the similar comonomer conversions, the cumulative and instantaneous incorporation of EFMA into the copolymer versus normalized chain length indicated the formation of a copolymer with essentially equimolar composition (Figure 1c). The cumulative PEFMA content ranged from the lowest value of 50.1 to the highest value of 51.8 mol %, with a final value of 51.7 mol %, while the calculated instantaneous composition varied along the chain length from the lowest value of 50.1 to the highest value of 52.5 mol %, with a final value of 51.0 mol %. This also reflects the accuracy of the determination of the instantaneous composition. The nearly "horizontal" instantaneous PEFMA compositional plots are in great contrast to those of the spontaneous gradient,[45] reverse gradient,[23,48] or the forced gradient copolymers,[49] which all underwent continuous compositional variations along the conversion of chain length. However, the kinetics could not differentiate between the alternating and statistical copolymer structure. Therefore, a detailed investigation into the resulting copolymer architecture

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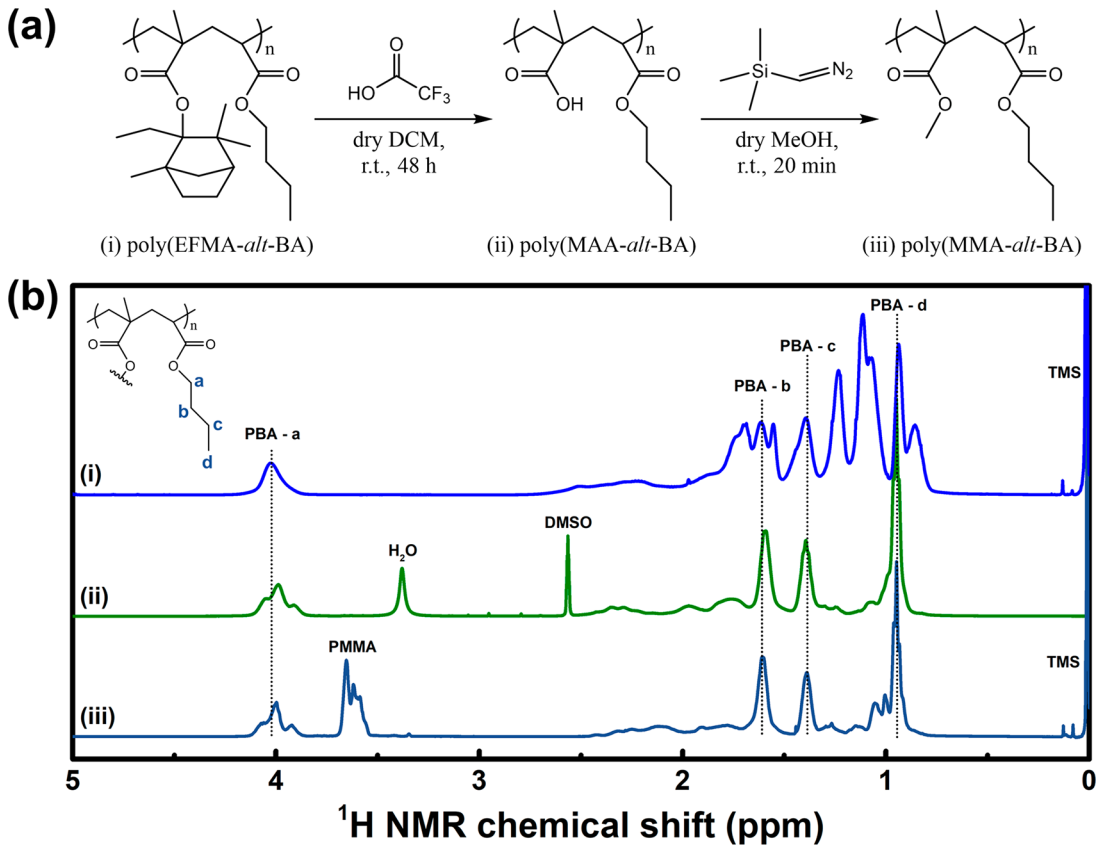

Figure 2. Postpolymerization modifications on alternating P(EFMA-*alt*-BA). (a) Synthetic route and (b) ^{1}H NMR spectroscopy of the alternating copolymers: (i) P(EFMA-*alt*-BA) dissolved in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS), (ii) P(MAA-*alt*-BA) in deuterated dimethyl sulfoxide (DMSO-d_6), and (iii) P(MMA-*alt*-BA) in $CDCl_3$ with TMS.

Table 1. P(MMA/BA) Copolymers by ATRP with Gradient, Statistical, and Alternating Copolymer Architectures for Structural Characterizations

entry[a]	conv.[b] (%)	*x*, PMMA[b] (mol %)	*x*, PBA (mol %)[b]	M_n[c]	M_w/M_n[c]	T_g[d] (°C)	T_g range[d] (°C)
GradMB	100	51.0	49.0	44000	1.31	12 ± 1	−16−34
StatMB	9	51.3	48.7	53000	1.13	13 ± 1	−15−22
AltMB	54	50.5	49.5	45400	1.27	10 ± 1	−14−16

[a]Reaction conditions are listed in the Supporting Information. [b]The comonomer conversions, overall PMMA and PBA fractions in the copolymers, were measured by ^{1}H NMR. [c]Apparent molecular weight (M_n) and polymer dispersity (M_w/M_n) were determined using THF GPC calibrated by PMMA standards. [d]The glass transition temperatures (and ranges) were determined by DSC.

was carried out after the PPM procedure and generation of P(MMA-*co*-BA) copolymer, because it has been investigated spectroscopically before with accurate assignments of various ^{13}C NMR signals.[50]

The synthesized P(EFMA-*alt*-BA) was purified by repetitive precipitation in methanol and dissolution in anhydrous dichloromethane (DCM). Postpolymerization modification of the copolymer was carried out with trifluoroacetic acid (TFA) to selectively hydrolyze the tertiary ester, without affecting the *n*-butyl pendant group of BA (Figure 2a). Via efficient hydrolysis, the PEFMA was converted into poly(methacrylic acid) (PMAA) forming MAA/BA copolymer with anticipated alternating structure [P(MAA-*alt*-BA)]. After methanol dialysis and drying, (trimethylsilyl)diazomethane (2.0 M solution in hexane) was added into the P(MAA-*alt*-BA) dissolved in methanol. With generated methyl groups, P(MAA-*alt*-BA) was transformed into P(MMA-*alt*-BA), to complete the PPM procedure.

The modification process was monitored by ^{1}H NMR (Figure 2b). For all copolymers during the PPM, the characteristic peaks (chemical shifts at around 4.0, 1.6, 1.4, and 0.9 ppm) of the *n*-butyl pendant in PBA remained. The TFA treatment did not impact PBA, yet it hydrolyzed all EFMA pendant groups that could be barely seen in P(MAA-*alt*-BA). Upon methylation, the broad characteristic peak of the pendant methyl group in PMMA (chemical shift at around 3.6 ppm) emerged, with no obvious change in other peak intensities. Integrations of PMMA and PBA peaks in P(MMA-*alt*-BA) indicated PMMA compositions at 51.4 mol % (Figure S6). This value corresponds to the final cumulative PEFMA compositions of 51.7 mol % in P(EFMA-*alt*-BA), confirming the high post-modification yield. Gel permeation chromatography (GPC) was used to analyze all three copolymers during the PPM (Figure S7). Due to different solubilities, three copolymers were analyzed by different GPC systems. Since the hydrodynamic volume of copolymers depends on their solubility in the GPC elution solvent as

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well as the calibration method, the apparent molecular weights were not accurate and could provide only a qualitative analysis. Nonetheless, the molecular weights with similar dispersities without any bimodality or shoulder peaks confirmed the high efficiency of the modifications without degradation of the polymer backbone.

Upon completion of PPM procedures, more detailed structural analyses were performed on the resynthesized alternating MMA/BA copolymers (AltMB) with 50.5 mol % PMMA composition, together with the spontaneous gradient (GradMB) and statistical (StatMB) analogues of similar compositions and molecular weights (Table 1). The GradMB was synthesized by reaching a full conversion in the miniemulsion ARGET ATRP, where termination by combination was largely inhibited due to the physical boundaries of miniemulsion droplets.[51,52] In addition, the StatMB was synthesized starting at a 30/70 MMA/BA molar ratio and stopping the reaction at <10% conversion to prevent comonomer feed drift, as discussed before.[29] All three copolymers had similar molecular weights and low dispersities (Figure S8) and similar PMMA and PBA compositional ratios, as determined by ^{1}H NMR.

First, carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was used to analyze the architecture and compare the three copolymers, also PBA and PMMA homopolymers. The signals of the carbonyl groups from MMA/BA copolymers spreading over 4 ppm in chemical shifts were analyzed (Figure 3).[50,53,54] The PBA homopolymer had peaks around 174.0 ppm representing repeating BA units (i.e., BBB triads), whereas the PMMA homopolymer showed signals around 177.5 ppm, corresponding to highly syndiotactic PMMA pentads (i.e., *rrrm* and *rrrr*, where *r* means *racemo* and *m* means *meso*) and around 176.5 ppm to heterotactic pentads (*rmrm*/*mmrm* and *rmrr*/*mmrr*), according to the literature.[55] Most of the heterotriads, including MMB, MBM, BMM, BBM, BMB, and MBB, have peaks in the central region from 177.0 to 174.3 ppm. The signal position and intensity of these heterotriads originate not only from different sequences, but also from the different stereochemical arrangements (i.e., tacticity).[53]

For the StatMB copolymer, the anticipated content of the MB/BM heterodyad should be 57.6%, with 21.2% for BB and MM homodyads.[29] This can be correlated with an anticipated content of MMM and BBB homotriads of 9% (eqs S1 and S2), as confirmed by weak signals at >177.1 and <174.3 ppm. For the GradMB system, the intensity of the signals attributed to the homopolymer regions for MMM and BBB sequences was higher due to MMM-rich sequences at the beginning and BBB-rich sequences at the end of every chain.

For the AltMB copolymer, there are essentially no signals of MMM sequences and only a small peak in the high-field region. Considering the nearly equimolar PMMA/PBA compositional ratio, since there were almost no MMM triad signals, the presence of small signals below 174.3 ppm, was assigned to the BMB configuration triad with specific tacticity (i.e., B-*m*-M-*m*-B and B-*r*-M-*m*-B) according to literature.[50] Tacticity may also play a key role in the interdigitated alternating MMA/BA pendants and could be estimated using a Bernoullian statistics simulation.[50] It is difficult to estimate the effect of the bulky 2-ethylfenchyl group on the tacticity of the initial EFMA/BA copolymer, which should be preserved during the PPM procedure. Tacticity control still remains a challenge in any radical polymerization.[26,56] Nevertheless, ^{13}C NMR analysis indicated the absence of the homopolymer

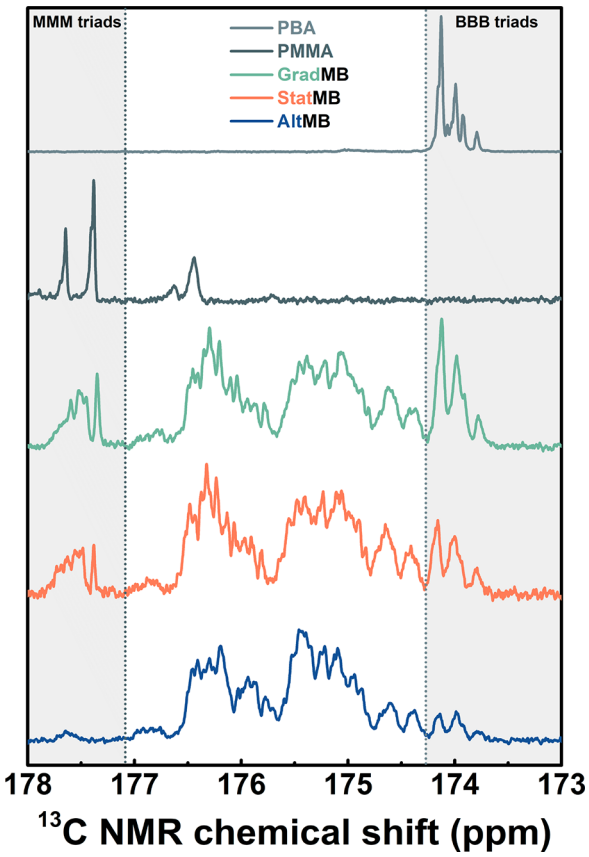

Figure 3. ^{13}C NMR of PBA homopolymer (light gray), PMMA homopolymer (dark gray), P(MMA-*grad*-BA) (GradMB, green), P(MMA-*stat*-BA) (StatMB, orange), and P(MMA-*alt*-BA) (AltMB, blue). All (co)polymers were dissolved in acetone-d_6. The shaded areas highlighted the characteristic peaks of MMM triads (left) and predominantly BBB triads (right).

MMM and BBB sequences that were abundant in both gradient and statistical copolymers and confirmed the successful synthesis of an alternating MMA/BA copolymer.

Then, differential scanning calorimetry (DSC) was utilized to elucidate the effect of the copolymer architecture on glass transitions (Figure 4a). For each copolymer, the glass transition temperature (T_g) was determined by the peak position of the differential heat flow derivative (DDSC). The breadth of the entire glass transition (termed as T_g range) was evaluated using the peak onset and offset in the DDSC curve (Figure 4b). The T_gs of GradMB, StatMB, and AltMB were 12, 13, and 10 °C, respectively, which were close to the predicted T_g by the empirical Flory−Fox equation (eq S3) with a PMMA/PBA molar ratio around 51/49 in the copolymer (Table S2). Despite the similar T_gs, the narrowest glass transitions (30 °C range) were observed for AltMB. This value can be compared with the gradient (50 °C range) and statistical copolymer analogues (37 °C range). Since the broadest transition in GradMB was associated with continuous compositional change, that is, inhomogeneity in the copolymer chain,[48] the narrowest transition in AltMB suggested the most homogeneous copolymer structure. We interpret the increase in breadth of the glass transition as a consequence of a more inhomogeneous microstructure in case of statistical and gradient copolymers due to the less regular chain architecture. A more thorough analysis of the effect of copolymer chain

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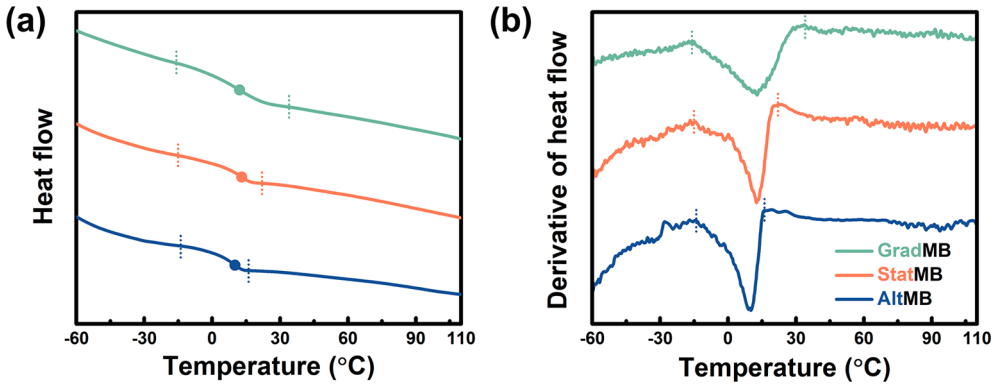

Figure 4. (a) Differential scanning calorimetry (DSC) and (b) derivative of heat flow given by DSC (DDSC) curves of different MMA/BA copolymers, including P(MMA-*grad*-BA) (GradMB, green), P(MMA-*stat*-BA) (StatMB, orange), and P(MMA-*alt*-BA) (AltMB, blue). The dash lines mark copolymer glass transition onsets and offsets. T_gs (and ranges) are summarized in Table 1.

architecture on the microstructure, properties, and ability to "self-heal" will be the subject of a forthcoming publication.

In summary, an MMA/BA copolymer with an alternating structure was synthesized via ARGET ATRP by copolymerization of equimolar amounts of EFMA and BA with subsequent postpolymerization modifications. The steric hindrance from an EFMA bulky pendant group, together with the low reactivity ratio of BA in the copolymerization with methacrylates, contributed to the suppressed homopolymerization of each comonomer. Therefore, the alternating EFMA/BA sequences were formed, as evidenced by essentially "horizontal" cumulative and instantaneous compositional kinetic plots. The cumulative PEFMA contents varied from the lowest value of 50.1 to the highest value 51.8 mol % along the chain length, while the calculated instantaneous composition varied along the chain length from the lowest value of 50.1 to the highest value of 52.5 mol %. The efficient transformation of P(EFMA-*alt*-BA) into P(MMA-*alt*-BA) was accomplished by postpolymerization modifications using the selective hydrolysis of a tertiary ester with trifluoroacetic acid and a subsequent methylation using (trimethylsilyl)diazomethane. The successful modifications were confirmed by ^{1}H NMR and shifted GPC eluograms without bimodal or shoulder peaks. A ^{13}C NMR study was performed to analyze copolymer architecture and compare the features of the alternating MMA/BA copolymer with gradient and statistical analogues of similar molecular weights and PMMA/PBA molar ratios. In the P(MMA-*alt*-BA) copolymer, the signals corresponding to MMM homotriads or BBB homotriads were essentially absent. Such signals were abundant in statistical and especially in the gradient copolymers. Values of T_g for three copolymers were similar according to DSC, but DDSC curves showed the narrowest glass transition in P(MMA-*alt*-BA) among three MMA/BA copolymers. Such copolymers could potentially show excellent self-healing properties, which are now being evaluated.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00517.

Details of experimental procedures (EFMA monomer synthesis, 2D NMR, postpolymerization modifications); additional polymerization and characterization results (PDF)

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contributions of all authors. CRediT: **Khidong Kim** visualization (equal).

Notes

The authors declare no competing financial interest.

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