ORIGINAL ARTICLE

Divergent strategy for the synthesis of bottlebrush polymers via postpolymerization modification of macromonomer

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Abstract

A simple and divergent synthetic strategy of bottlebrush polymers (BBPs) is presented, consisting of postpolymerization modification of a macromonomer and grafting-through polymerization. Beginning with a single macromonomer, its direct modification could build a library of macromonomers with an identical chain length, thus guaranteeing the precision in the synthesis of BBPs. In this study, a newly designed norbornenyl-terminated poly(methyl acrylate) (NB-PMA) is proposed as a chemically robust template. Ti-mediated transesterification of NB-PMA successfully produces structurally diverse polyacrylates while maintaining the terminal norbornenyl group intact. All macromonomers obtained from transesterification possess a good grafting-through ring-opening metathesis polymerization reactivity, furnishing homo, random, and block BBPs in a controllable manner. Moreover, atomic force microscopy analysis supports the controlled side-chain length distribution in the resulting BBPs.

KEYWORDS

bottlebrush polymers, grafting-through polymerization, postpolymerization modifications, ring-opening metathesis polymerization

1 | INTRODUCTION

Bottlebrush polymers (BBPs) are grafted or branched polymers with polymeric side chains attached to a linear polymeric backbone.[1] The highly compact and confined three-dimensional structures of these polymers have expanded the field of macromolecules; the synthesis and applications of these polymers are of great interest.[2] Based on the recent significant advances in techniques for the synthesis of polymers, such as living polymerizations, BBPs with high complexity and precision can be synthesized.[3]

BBPs are generally prepared via three strategies; (1) grafting-onto: the attachment of polymer side chains onto a polymer backbone, (2) grafting-from: the growth of side chains from a polymer backbone, and (3) grafting-through: the polymerization of macromonomers. Among

them, the grafting-though method using Ru-mediated ring-opening metathesis polymerizations (ROMP) of norbornene-bearing macromonomers has boosted the field of BBPs.[4] The high reactivity and excellent functional group tolerance of the third-generation Grubbs catalyst (G3) allow a high degree of macromonomer polymerization and precise control of the backbone length with narrow dispersity.[4c,d,5]

Post-polymerization modification (PPM), viz. the alteration or functionalization after polymerization, enables us to build libraries of polymers with identical topologies and sizes, and investigate the structure–property relationship with high precision.[6] Furthermore, the divergent approach allows a group of functional polymers with minimum synthetic operation. This working principle is useful in the synthesis BBPs. However, the

PPM strategy has only been applied in a few cases for the attachment of small functional molecules.[7] We envision that the PPM of parent macromonomers and subsequent ROMPs will formulate a facile synthesis of BBPs with structural diversities and precision. To verify our working hypothesis, herein we designed and synthesized an ω-norbornenyl poly(methyl acrylate) (NB-PMA) template and investigated its modification. Previously, several acrylate-based macromonomers were synthesized for BBP synthesis, where they generally adopted a parallel approach.[4c,d] Following recent successes in highly efficient transesterifications of poly(methyl acrylate)s (PMAs),[8] we elucidated the robust NB-PMA structure and transesterification conditions, producing a library of polyacrylate macromonomers having the identical chain length. Subsequent ROMP furnished a series of homo, block, and random BBPs in excellent synthetic efficiency. The details of our development are presented herein.

2 | EXPERIMENTAL SECTION

2.1 | General considerations

All transesterifications and ROMP were performed under a nitrogen atmosphere using a glove box and transferred to a heating bath with a designated temperature. Anhydrous reaction solvents were prepared by drying over a mixture of pre-activated alumina and 3 Å molecular sieves.[9] A preservative in commercial methyl acrylate was removed by basic alumina filtration before use. The G3 catalyst was prepared according to a procedure in the literature.[10] Other reagents from commercial sources (Aldrich, Tokyo Chemical Industries, Alfa Aesar, and Acros) were used without further purification. The ^{1}H-NMR spectra were recorded on a 400 MHz Bruker Avance III HD Fourier transform NMR spectrometer and referenced to the residual protonated solvent. GPC analyses with refractive index (RI) were used to determine the number average molecular weights (M_n), weight-average molecular weights (M_w), and polydispersities ($Đ$). The RIs were measured using an instrument composed of a Waters 1515 isocratic pump, a 2414 differential RI detector, and a column-heating unit with Shodex KF804, KF-803, and KF-802.5 columns in series. The columns were eluted with tetrahydrofuran (THF) (preservative-free HPLC grade, Daejung Chemical Company, Korea) at 40°C at 1.0 ml/min and were calibrated using 14 monodisperse polystyrene standards (purchased from Alfa Aesar). The morphology of the highly diluted bottlebrush polymers on the silicon substrate was investigated using the NX-10 atomic force microscope (Park Systems, Korea) in the non-contact mode. Dynamic light scattering (DLS) measurements were made at 25°C using a Malvern Zetasizer Pro DLS instrument. Samples were dissolved in THF at a concentration of 1 mg/ml. A fresh, clean, quartz cuvette was washed with compressed air to remove dust. The sample solution was passed through a 0.45 μm Teflon syringe filter prior to the measurements. Measurements were made in sets of three acquisitions and average hydrodynamic diameters were calculated using the DLS correlation function via a regularization fitting method.

2.2 | Synthesis of the NB-PMA template

An oven-dried 250 ml Schlenk flask was filled with methyl acrylate (50.8 ml, 0.560 mol) and degassed by three freeze/pump/thaw cycles. CuBr (0.536 g, 3.74 mmol) and N,N,N′, N″,N″-pentamethyldiethylenetriamine (780 μl, 3.74 mmol) were added to the flask in a glove box. The mixture was stirred for 5 min, and 2-bromo-1-((3aR,4R,7S,7aS)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindol-2(3H)-yl) propan-1-one (**NB-int**, 1.00 g, 3.74 mmol) was added. The polymerization started by placing the flask in a preset oil bath at 100°C for 40 min. The polymerization was quenched by soaking the flask in liquid nitrogen and exposing the reaction mixture to the air. The mixture was diluted with dichloromethane (DCM) and passed through a neutral alumina/silica column to remove the copper catalyst. The diluted mixture was concentrated via a rotary evaporator under reduced pressure. The product was purified by dialysis using regenerated Cellulose (MWCO 3500 Da) in acetone. The acetone was replaced three times at 4 h increments, and it was removed under reduced pressure; hexane was poured to precipitate the polymer. The resulting product was dried in vacuo at 70°C.

2.3 | Transesterification of NB-PMA

In a glove box, a flame-dried 20 ml vial with a Teflon-lined cap and a Teflon-coated stir bar was filled with NB-PMA (0.40 g, 4.6 mmol of methyl ester), 5 Å molecular sieves (1.5 g), anisole (4.9 ml), hexanol (4.9 ml), and Ti(Oi-Pr)$_4$ (0.23 ml). The vial was transferred to a preheated reaction block at 130°C. After 48 h, the transesterification was quenched by soaking the flask in liquid nitrogen, exposing the reaction mixture to the air, and adding 5 ml of acetone. After stirring for 10 min, the mixture was filtered through a pad of Celite 515, which was followed by washing with DCM. The diluted mixture was concentrated under reduced pressure. The product was purified by dialysis using regenerated Cellulose (MWCO 3500 Da) in acetone. The acetone was replaced three times at 4 h increments.

The polymer solution was passed through a neutral alumina column and polytetrafluoroethylene syringe filter (0.45 μm) to remove titanium impurities. The mixture was concentrated under reduced pressure and precipitated in methanol (Table 1, entry 1).

2.4 | Brush polymer synthesis: PNB-PMA$_{100}$

NB-PMA (18 mg, 4.5 μmol) was weighed into an oven-dried 1 ml V-shaped vial equipped with a Teflon-coated spin bar. In a glove box, THF (0.13 ml) was added and the vial was sealed. After stirring for dissolution, a solution of G3 in THF (0.025 ml, 0.045 μmol, 1.3 mg/ml) was injected using a micropipette. The reaction became viscous over 1 h and was quenched with one drop of ethyl vinyl ether. An aliquot was sampled for a conversion measurement via GPC. The reaction mixture was precipitated in methanol. The resulting product was dried in vacuo at 70°C (Table 2, entry 1).

2.5 | Diblock brush copolymer synthesis: PNB-PHA$_{50}$-g-PNB-PMA$_{50}$

NB-PHA (18 mg, 4.5 μmol) was weighed into an oven-dried 1 ml V-shaped vial equipped with a Teflon-coated spin bar. NB-PMA (18 mg, 4.5 μmol) was weighed into another oven-dried 1 ml V-shaped vial equipped with a Teflon-coated spin bar. In a glove box, THF (0.10 ml and 0.15 ml) was added into the vials containing NB-PHA and NB-PMA, respectively. After the macromonomers were completely dissolved, a solution of G3 in THF (0.050 ml, 0.090 μmol, 1.3 mg/ml) was injected via a micropipette to the NB-PHA vial. The reaction became viscous over 1 h, and an aliquot was sampled for a conversion measurement via GPC. A solution of the second macromonomer, NB-PMA, in THF was injected into the reaction using a micropipette. After 1 h, the reaction was quenched with one drop of ethyl vinyl ether. An aliquot was sampled for a conversion measurement via GPC. The reaction mixture was precipitated in methanol. The resulting product was dried in vacuo at 70°C (Table 3, entry 1).

3 | RESULTS AND DISCUSSION

3.1 | Robust macromonomer development

Recently, several synthetic systems for post-polymerization modification of PMA were developed.[8] However, the relatively high reaction temperatures and the use of strong bases or acids inevitably require a chemically robust parent macromonomer. We thus designed NB-PMA which exhibits good modification efficiency and structural robustness during Ti-mediated transesterification (Scheme 1).[11] NB-PMA was synthesized by atom transfer radical polymerization (ATRP) beginning with a norbornene-amide initiator (NB-int).[12] The resulting NB-PMA was turned into the corresponding bottlebrush polymer, poly(NB-PMA) with 99% conversion via grafting-through ROMP by G3 (1 mol%) and exhibited a steady molecular weight growth as the ratio of macromonomer to G3 was increased (Table S1 and Figure S1), which confirmed the quality as a macromonomer. The transesterification of NB-PMA with Ti(Oi-Pr)$_4$ and benzyl alcohol produced norbornenyl-terminated poly(benzyl acrylate) (NB-PBzA) quantitatively. The excellent ROMP efficiency (95%) of the resulting NB-PBzA proved the high fidelity of norbornenyl group during PPM.

3.2 | Macromonomer library synthesis

Ti-mediated transesterifications of robust NB-PMA were conducted with assorted alcohols (Table 1). Representative primary alcohols of n-hexyl, benzyl, 4,4,5,5,5-pentafluoropentyl, and cyclohexylmethyl groups converted NB-PMA quantitatively to norbornenyl-terminated poly(hexyl acrylate) (NB-PHA) (entry 1), poly(benzyl acrylate) (NB-PBzA) (entry 2), poly(pentafluoropentyl acrylate) (NB-PPFA) (entry 3), and poly(cyclohexylmethyl acrylate) (NB-PCyMA) (entry 4), respectively. Secondary alcohols also exhibited excellent replacement efficiencies of over 95%. Isopropyl and cyclohexyl alcohols afforded ω-NB-poly(isopropyl acrylate) (NB-PiPA) (entry 5) and ω-NB-poly(cyclohexyl acrylate) (entry 6), respectively. However, the tertiary alcohol such as 2,5-dimethyl-2-hexanol replaced only 14% of the methyl ester, probably owing to steric interference (entry 7). Thus, one parent macromonomer, NB-PMA, was readily expanded to six macromonomers with topological uniformity.

3.3 | "Grafting-through" brush copolymer synthesis

We applied the G3 catalyst to macromonomers obtained from Ti-mediated transesterification of NB-PMA (Table 2). The molecular weights of each macromonomer were deduced from the number average molecular weight (M_n) of NB-PMA measured via ^{1}H-NMR spectroscopy, assuming that the transesterification
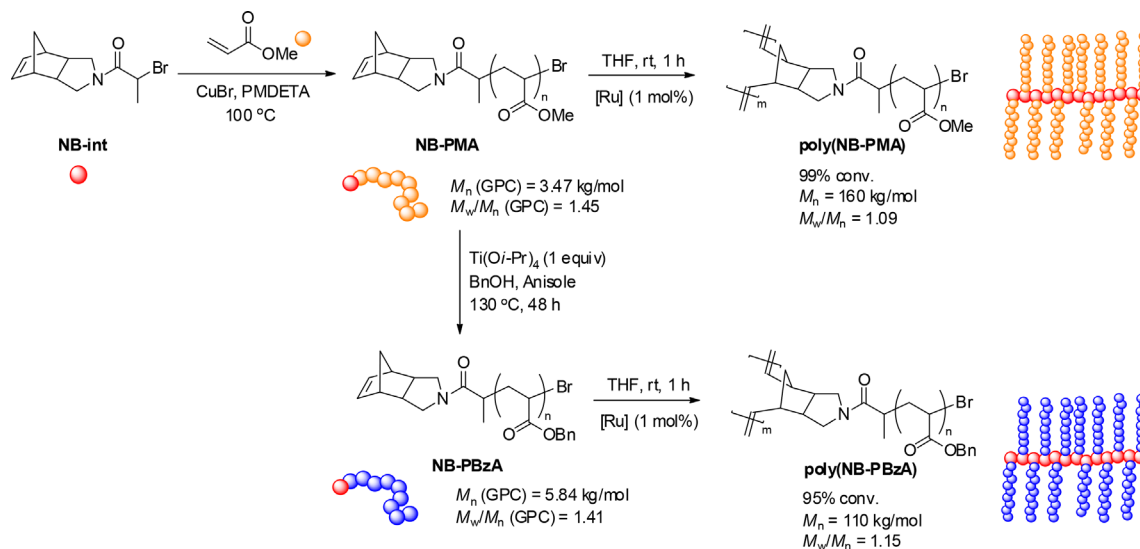
SCHEME 1 Poly(methyl acrylate) (PMA) macromonomer synthesis, postpolymerization modification, and grafting-through ring-opening metathesis polymerizations (ROMP) to bottlebrush polymers [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Macromonomer synthesis: Transesterification of NB-PMA
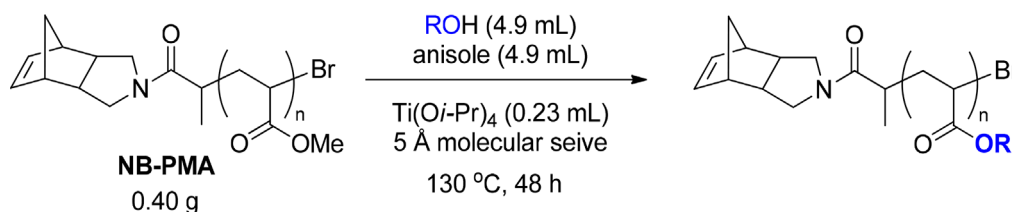
| Entry	ROH	Product	Conv (%)[a]	M_n (kg/mol)[b]	M_w (kg/mol)[b]	Đ	Yield (%)[c]
SM	—		—	3.95	5.32	1.35	
1	(hexanol) OH	NB-PHA	99	8.20	10.6	1.29	70
2	(benzyl) OH	NB-PBzA	99	6.82	9.39	1.38	70
3	C₂F₅ OH	NB-PPFA	99	10.5	13.1	1.25	58
4	(cyclohexylmethanol) OH	PNB-PCyMA	99	5.87	8.49	1.45	90
5	(isopropanol) OH	NB-PiPA	96	5.25	7.63	1.45	74
6	(cyclohexanol) OH	NB-PCyA	97	5.72	8.21	1.44	76
7	(tertiary alcohol) OH		14	4.31	5.67	1.31	87

Note: Reaction conditions: NB-PMA **1** 0.40 g (4.6 mmol based on M_n measured via ¹H-NMR spectroscopy), ROH (4.9 ml), anisole (4.9 ml), 5 Å molecular sieve (4.0 g), 130°C, 48 h.

Abbreviations: NB-PBzA, norbornenyl-terminated poly(benzyl acrylate); NB-PCyA, ω-NB-poly(cyclohexyl acrylate); NB-PHA, norbornenyl-terminated poly(hexyl acrylate); NB-PiPA, ω-NB-poly(isopropyl acrylate); NB-PMA, ω-norbornenyl poly(methyl acrylate); NB-PPFA, poly(pentafluoropentyl acrylate).

[a]Based on ¹H-NMR spectroscopy.
[b]Determined by GPC (RI) calibrated with polystyrene standards in THF at 40°C.
[c]Isolation yield.

TABLE 2 ROMP of macromonomers obtained via transesterification of NB-PMA
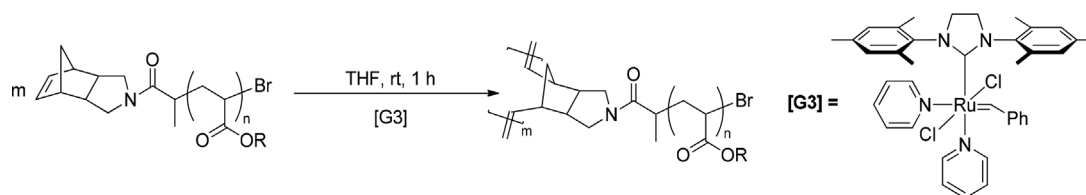
Entry	Macromonomer	[M]/[G3]	Conv (%)[a]	M_n (kg/mol)[b]	M_w (kg/mol)[b]	Đ	Yield (%)[c]
1	NB-PMA(3.9 k)	100	99	155	164	1.06	80
2		200	99	254	340	1.34	86
3	NB-PHA(6.9 k)	100	97	196	221	1.13	95
4		200	96	307	391	1.27	97
5	NB-PBzA(7.2 k)	100	95	141	164	1.16	93
6		200	94	158	212	1.34	94
7	NB-PPFA(10 k)	100	91	201	225	1.12	77
8		200	76	252	330	1.31	81
9	NB-PCyMA(7.1 k)	100	94	164	185	1.13	92
10		200	92	245	315	1.29	94
11	NB-PiPA(5.2 k)	100	96	186	215	1.16	81
12		200	95	250	336	1.34	83
13	NB-PCyA(6.8 k)	100	94	182	212	1.16	91
14		200	93	219	284	1.30	91

Note: ROMP conditions: THF, 1 h, rt.

Abbreviations: NB-PBzA, norbornenyl-terminated poly(benzyl acrylate); NB-PCyA, ω-NB-poly(cyclohexyl acrylate); NB-PHA, norbornenyl-terminated poly(hexyl acrylate); NB-PiPA, ω-NB-poly(isopropyl acrylate); NB-PMA, ω-norbornenyl poly(methyl acrylate); NB-PPFA, poly(pentafluoropentyl acrylate); ROMP, ring-opening metathesis polymerizations.
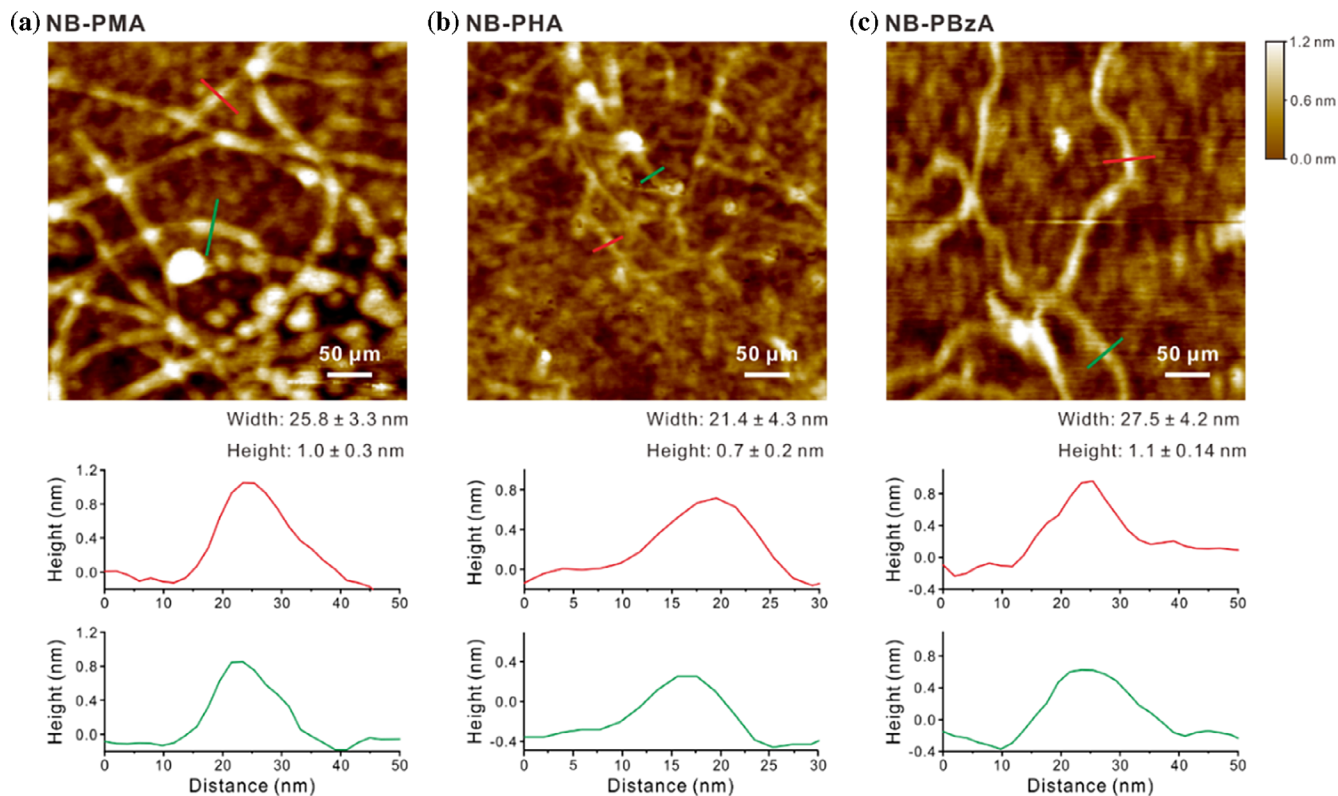
[a]Based on ^{1}H-NMR spectroscopy.
[b]Determined via GPC (RI) calibrated with polystyrene standards in THF at 40°C.
[c]Isolation yield.

step did not alter the chain length. The parental NB-PMA exhibited excellent conversions at both 100 and 200 of monomer-to-G3 catalyst ratios (entries 1 and 2). NB-PHA prepared from NB-PMA and *n*-hexanol maintained high ROMP efficiencies of 97 and 96% at 100 and 200 equivalent-loading to G3, respectively (entries 3 and 4). Another macromonomer, NB-PzBA, derived from primary benzyl alcohol, exhibited similar conversions and backbone length distributions (entries 5 and 6). Although the GPC result of the product of 1 mol% G3-loading showed excellent control on the molecular weight distribution (Đ = 1.06–1.16), a slight broadening in dispersity (Đ = 1.27–1.34) was found after a lower catalyst-loading (0.05 mol%). The relative molecular weight measurements using an RI detector showed much lower values than expected, which again provides a strong evidence for the formation of highly confined BBPs with relatively small hydrodynamic volumes.

In addition, we performed atomic force microscopy (AFM) of selected BBPs to directly visualize the structural uniformity (Figure 1). Each BBPs exhibited worm-like morphologies similar to those of typical BBPs with an average width corresponding to 25.8 ± 3.3, 21.4 ± 4.3, and 27.5 ± 4.2 μm for poly(NB-PMA) (Table 1, entry 1), poly(NB-PHA) (Table 1, entry 3), and poly(NB-PBzA) (Table 1, entry 5), respectively (averaged over 20 samples for each). DLS measurements were carried out to evaluate the size in solution. Hydrodynamic diameter (D_h) of poly(NB-PMA) (Table 1, entry 1) and poly(NB-PHA) (Table 1, entry 3) in THF were 25.5 ± 1.3 and 29.2 ± 0.3 nm, respectively. These studies demonstrate that our PPM strategy leads to highly controlled BBP structures.

The macromonomer NB-PPFA with high fluorine content was further investigated. At (monomer)/(G3) = 100, ROMP afforded the corresponding graft polymer with good efficiency (91%) and low dispersity

(a) NB-PMA

(b) NB-PHA

(c) NB-PBzA

Width: 25.8 ± 3.3 nm

Height: 1.0 ± 0.3 nm

Width: 21.4 ± 4.3 nm

Height: 0.7 ± 0.2 nm

Width: 27.5 ± 4.2 nm

Height: 1.1 ± 0.14 nm

FIGURE 1 Representative height-mode AFM images of the prepared bottlebrush polymers. (a) poly(NB-PMA) (Table 2, entry 1), (b) poly(NB-PHA) (Table 2, entry 3) and (c) poly(NB-PBzA) (Table 2, entry 5) with corresponding line scan profiles. Concentrations of polymers are in the range of 0.04–0.05 mg/ml. AFM, atomic force microscopy; NB-PBzA, norbornenyl-terminated poly(benzyl acrylate); NB-PHA, norbornenyl-terminated poly(hexyl acrylate); NB-PMA, ω-norbornenyl poly(methyl acrylate) [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Bottlebrush copolymer synthesis: random and block copolymers
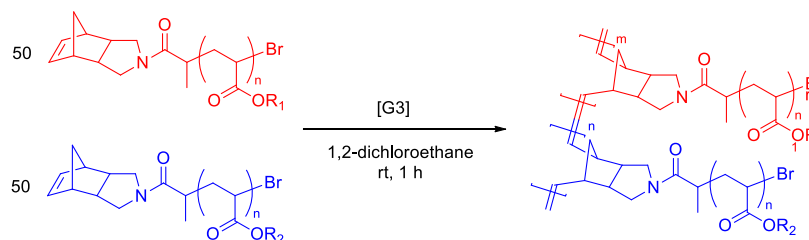
Entry	Product	Conv (%)[a]	M_n (kg/mol)[b]	M_w (kg/mol)[b]	M_w/M_n	Yield (%)[c]
1[d]	Poly(NB-PHA)-*block*-poly(NB-PMA)	96	131	145	1.11	80
2[e]	Poly(NB-PMA)-*block*-poly(NB-P*i*PA)	99	132	155	1.17	83
3[f]	Poly(NB-PHA)-*ran*-poly(NB-PMA)	98	131	148	1.13	84
4[g]	Poly(NB-PMA)-*ran*-poly(NB-P*i*PA)	95	123	136	1.11	84

Abbreviations: NB-PHA, norbornenyl-terminated poly(hexyl acrylate); NB-P*i*PA, ω-NB-poly(isopropyl acrylate); NB-PMA, ω-norbornenyl poly(methyl acrylate).

[a]Based on ^{1}H-NMR spectroscopy.

[b]Determined via GPC (RI) calibrated with polystyrene standards in THF at 40°C.

[c]Isolation yield.

[d]NB-PHA(4.0 k) and NB-PMA(2.4 k) were used.

[e]NB-PMA(2.4 k) and NB-P*i*PA(3.0 k) were used.

[f]NB-PHA(6.1 k) and NB-PMA(3.9 k) were used.

[g]NB-P*i*PA(5.2 k) and NB-PMA(3.9 k) were used.

($Đ$ = 1.12) (entry 7). However, NB-PPFA was converted by only 76% for (monomer)/(G3) = 200 (entry 8). The phase separation of fluorinated brush polymers at a low degree of polymerization might inhibit the chain propagation further, as similarly observed in the low efficiency of grafting-through strategy for highly polar macromonomers.[13] Macromonomers with more sterically demanding side groups were tested (entries 9–14). It was found that the size of the ester substituents did not considerably affect the efficiency of the ROMP.

The synthesis of BBPs with increased complexity was successful as well. Representative combinations of NB-PMA/NB-PHA and NB-PMA/NB-P*i*PA were subjected to either random polymer or block copolymer syntheses (Table 3). The sequential addition of two distinctive macromonomers successfully gave the desired bottlebrush block copolymers (entries 1 and 2). The second monomer was added after the first monomer was consumed by over 95%. The polymerization of mixtures of macromonomers proceeded smoothly as well, resulting in brush copolymers in a random distribution (entries 3 and 4).

4 | CONCLUSION

The divergent synthesis of polyacrylate-based BBPS was realized through PPM of a macromonomer and subsequent grafting-through ROMP. A library of polyacrylate macromonomers was readily built from a single PMA template via Ti-mediated transesterification. This route allows us to access macromonomers with diverse chemical structures and topological uniformity. The grafting-through ROMP using the G3 catalyst proceeded smoothly and afforded bottlebrush polymers with homo, block, and random composition. In addition to the facile operation, the PPM strategy allowed the synthesis of structurally regulated bottlebrush polymers as confirmed via AFM and DLS. We anticipate that this study will provide a platform to access the diverse bottlebrush polymers with side-chain structural uniformity toward the systematic investigation of the effect of side chains on the properties of BBPS.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.