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Narrow Polydispersity Block Copolymers by Free-Radical Polymerization in the Presence of Macromonomers

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In this paper we provide details of a new method of producing narrow polydispersity homopolymers and high-purity block copolymers by free-radical polymerization of monomers in the presence of macromonomers.

The traditional methods of producing block polymers, whether by living polymerization or by the linking of end-functional polymers, suffer many disadvantages. The living polymerization method, if by ionic, coordination, or group-transfer mechanisms, has limitations both for economic reasons (due to the stringent requirements on reaction conditions and monomer purity) and because of the limited range of monomers that are compatible with this technique.[1] The end-linking method suffers from problems associated with producing pure end-functional polymers and difficulties associated with conducting reactions between polymers.

These problems have brought about a marked growth in interest in methods for controlling polymer architecture by free-radical polymerization. Thus, various forms of living radical polymerization (also known as quasi- or pseudo-living radical polymerization) have been reported.[2–4] These methods rely on the use of a stable radical (T$^\bullet$) to reversibly terminate polymer chains by radical–radical combination (Scheme 1). One recent example of this methodology is alkoxyamine-initiated polymerization (in this case T$^\bullet$ is a nitroxide). This process has been used to synthesize end-functional and narrow polydispersity homopolymers[5–8] [including poly(methyl methacrylate)[5] and polystyrene[6,7]] and various block copolymers.[5,9] Living radical polymerizations involving tertiary radical propagating species (*e.g.*, those based on methacrylate ester monomers) are complicated by a side reaction that limits conversion and block purity. Disproportionation of the propagating species with T$^\bullet$ produces a macromonomer and the hydride of the stable radical TH (see Scheme 1).[9,10] The species TH may then terminate further chains by hydrogen atom transfer. A further disadvantage which limits the commercial application of the methodology is the requirement for an equimolar amount of the (often expensive) reagent (T$^\bullet$) or its precursor.

The present macromonomer method for producing block copolymers is based on the use of macromonomers of the general structure **1** which function as chain-transfer agents by an addition–fragmentation mechanism (Scheme 2). The method can provide high conversions and narrow polydispersities (see below). The macromonomers (**1**) are readily available by a variety of methods, for example, through radical polymerization in the presence of various addition–fragmentation chain-transfer agents[11–16] or catalytic chain-transfer agents.[15,17–19]

Various macromonomers (**1**, X = H, CH_3, CO_2R; Y, Z = Ph, CN, CO_2R) have seen utility both as precursors of graft copolymers[11,17,20–23] and as addition–fragmentation chain-transfer agents to control molecular weight.[11,20] Although the potential of these macromonomers (**1**) in forming block copolymers was recognized in an earlier work,[11] the conditions necessary for producing high-purity blocks were not established and the possibility of making narrow polydispersity polymers was not explored. The chemistry observed in polymerizations with these reagents (**1**) is determined both by the macromonomer structure and by the reaction conditions. In this paper we show that with appropriate control of these parameters, conditions can be found such that in free-radical polymerizations the only significant reaction is insertion of monomer units between the terminal $CH_2{=}C(Z){-}CH_2{-}$ unit and the $-[C(X)(Y){-}CH_2]_n$ segment of **1** (the A block) so as to form an AB block copolymer. The process is demonstrated for macromonomers based on methacrylic monomers (**1**, X = CH_3; Y, Z = CO_2R).

The proposed mechanism for block formation is outlined in Scheme 3 for production of poly(butyl methacrylate-*block*-phenyl methacrylate) from a phenyl methacrylate macromonomer. The reaction involves a butyl methacrylate propagating species (**2**) reacting with the phenyl methacrylate macromonomer (**3**) to form an adduct (**4**). This adduct (**4**) partitions between reverting to starting materials (**2 and 3**) or producing the new phenyl methacrylate propagating species (**5**) and butyl methacrylate macromonomer (**6**). Reaction of the new propagating species (**5**) with butyl methacrylate monomer produces the block copolymer propagating species (**7**). Further reaction of this species with a macromonomer (this may be **3**, **6**, or **8**) produces a block copolymer (**8**). Since the double bond is preserved in the process, the block copolymer (**8**) is itself a macromonomer and can undergo further reaction. This does not lead to byproduct formation, only to extension of the B block. In this sense the polymerization in the presence of macromonomers can be considered to be living and polymerization can be continued to give a B block of the desired length. It also offers scope for the introduction of an additional monomer (a C block or another A block) so as to form triblock or segmented copolymers.

It is important that chain transfer to macromonomer is the dominant mechanism for chain termination and initiation. In block copolymer synthesis, chains formed from initiator-derived radicals (*e.g.* **2**, R = initiator fragment; Scheme 3) can give (B block) homopolymer impurity. Chain termination by radical–radical reaction will give “dead polymer”. Thus, rates of initiation need to be minimized to an extent consistent with still obtaining an acceptable rate of polymerization. The lower the rate of initiation, the cleaner the block.

For macromonomers based on methacrylic monomers (**1**, X = CH_3; Y, Z = CO_2R), fragmentation of the adduct radical (*e.g.*, **4** in Scheme 3) always dominates over reaction with monomer.[11] Graft copolymerization does not occur. Because all chains continue to grow throughout the polymerization, polydispersities can be substantially less than those formed by conventional free-radical polymerization with termination by chain transfer. In theory[24] low conversion $\bar{M}_w/\bar{M}_n$ should be ~2.0 if termination is by conventional chain transfer.

The process is illustrated by two examples:

(a) Emulsion polymerization of butyl methacrylate in

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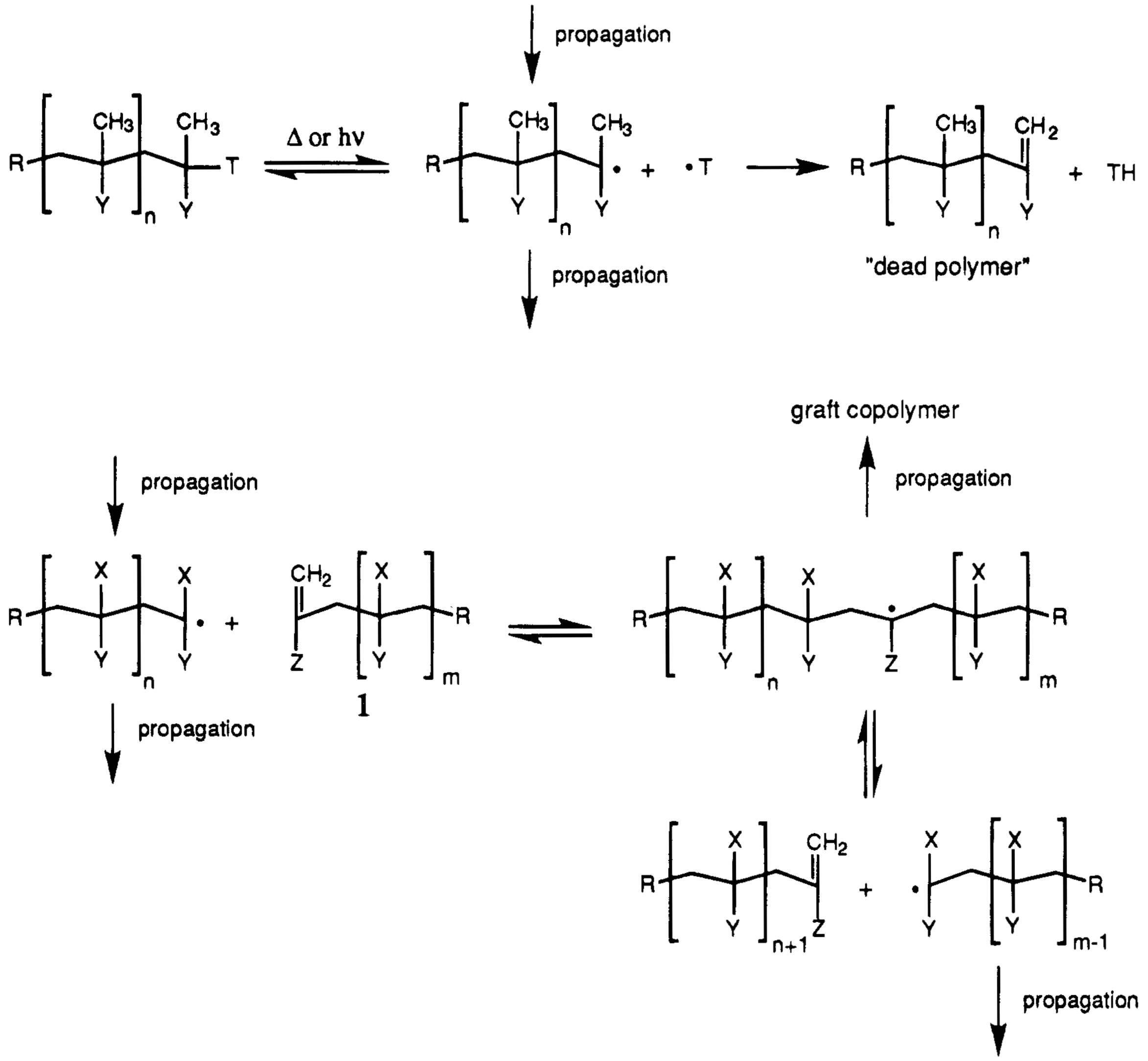
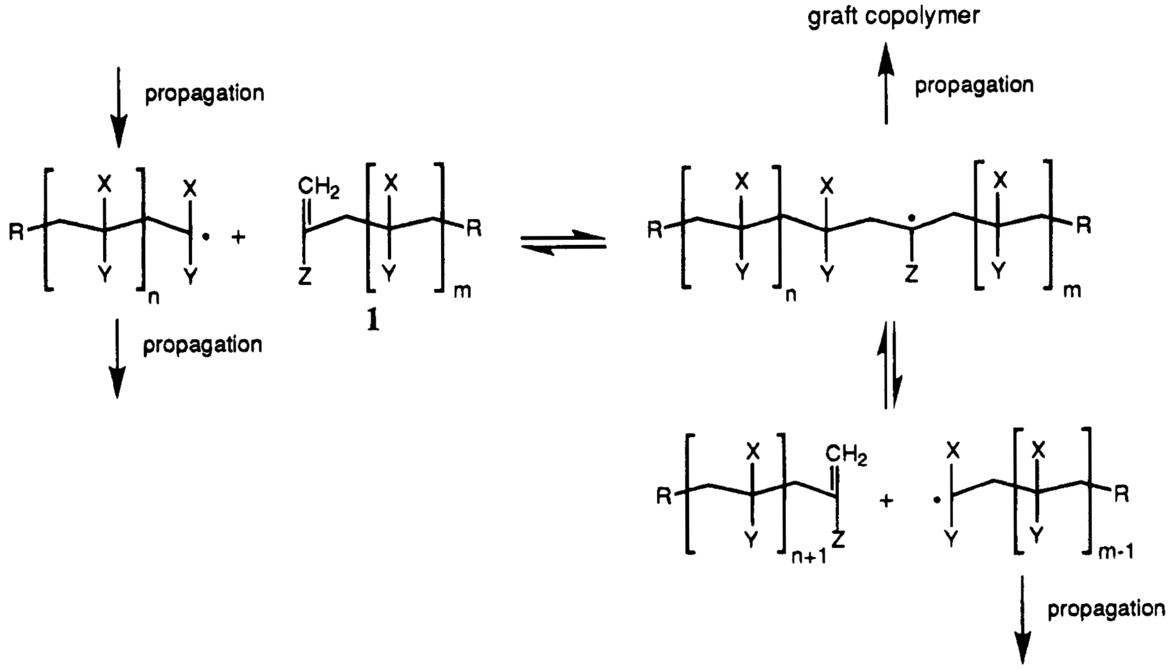
Scheme 1

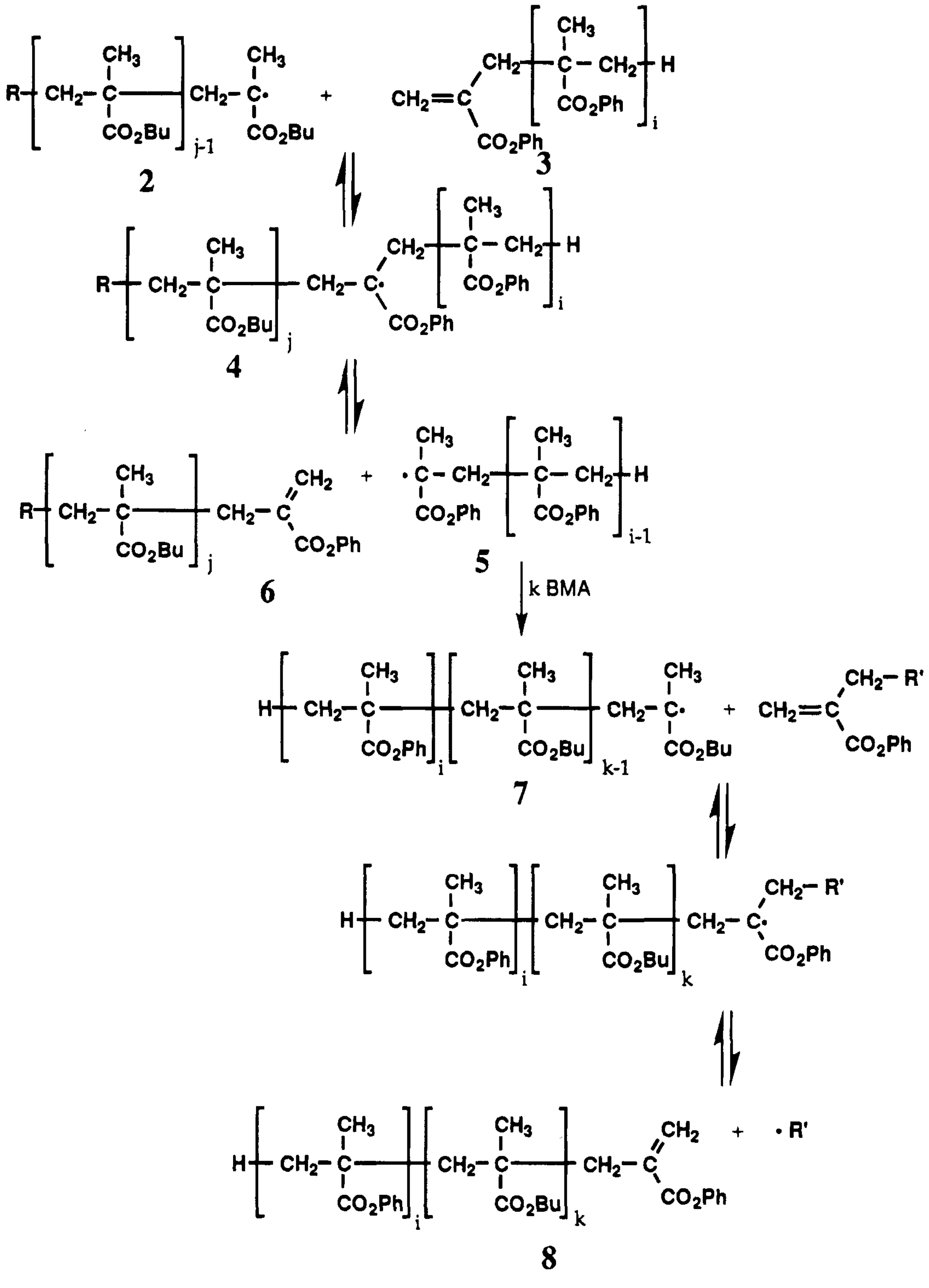


Scheme 2



the presence of methyl methacrylate macromonomer to form narrow polydispersity poly(butyl methacrylate-*block*-methyl methacrylate) (see Table 1 and Figures 1 and 2).

Scheme 3



(b) Emulsion polymerization of butyl methacrylate in the presence of phenyl methacrylate macromonomer, $\bar{M}_n$ 1100, to form ultimately poly(butyl methacrylate-*block*-phenyl methacrylate), $\bar{M}_n$ 14 500 (see Figure 3).

Additional examples are shown in Table 2. It is noteworthy that the process is compatible with the use of unprotected acid monomers (*e.g.*, methacrylic acid). The method thus offers advantages over block syntheses by ionic, coordination, or group-transfer mechanisms.

A typical experiment was conducted as follows. A methyl methacrylate macromonomer latex $\bar{M}_n$ 2300, $\bar{M}_w/\bar{M}_n$ 1.6; 30 g, 28% solids; prepared with 0.3% sodium dodecyl sulfate surfactant) was heated to 80 °C in a multineck flask under nitrogen. Potassium persulfate solution (0.4 wt % in water, 19 mL/h) and butyl methacrylate (10 g/h) were added by syringe pumps. Samples were taken for GPC and NMR analysis at intervals specified in Table 1. After the monomer addition was complete, the reaction was heated at 85 °C for 90 min. The conversion of monomer to polymer in each stage of the polymerization was quantitative within experimental error. The results of this experiment are summarized in Table 1 and Figures 1 and 2.

Various criteria have been applied to assess the success of the block copolymerizations.

Table 1. Variation in Molecular Weight and Polydispersity with Monomer Addition for Poly(butyl methacrylate-*block*-methyl methacrylate) Synthesis[a]

BMA (g)	BMA (mol equiv)[b]	time (min)	$\bar{M}_w/\bar{M}_n{}^c$	$\bar{M}_n{}^{c,d}$	$\bar{M}_n$(calc)[e]
0	0	0	1.5	2 300[f]	2 300
25.7	49	154	1.2	8 200	9 300
33.6	64	202	1.2	10 200	11 400
50.3	96	302	1.2	14 600	15 900
59.8	114	359	1.2	17 600	18 500
67.1	128	403	1.2	19 600	20 500
88.2	168	529	1.4	24 300	26 200

[a] Initial amount of methyl methacrylate macromonomer ($\bar{M}_n$ 2300), 8.5 g. Details of the experimental procedure are given in the text. [b] Moles of BMA/moles of macromonomer (rounded to the nearest integer). [c] Average of two determinations. [d] GPC molecular weight obtained as polystyrene equivalents and corrected using universal calibration assuming Mark–Houwink constants for the block are the same as those for the BMA homopolymer.[26] [e] Calculated $\bar{M}_n$ = ([BMA]/[macromonomer] × 142) + macromonomer $\bar{M}_n$. [f] GPC molecular weight obtained as polystyrene equivalents and corrected using universal calibration.

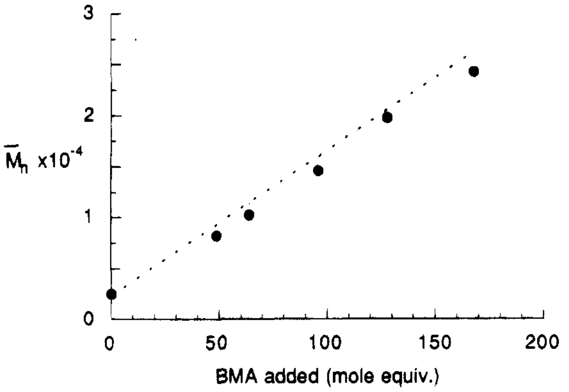


Figure 1. Variation in molecular weight with monomer addition for poly(butyl methacrylate-*block*-methyl methacrylate) synthesis. Data are for the example given in the text and reported in Table 1. Calculated molecular weights (- - -). The initial macromonomer (8.5 g) had $\bar{M}_n$ = 2300.

(a) Control experiments showed that polymer formed in the absence of the macromonomer is of substantially higher molecular weight. This provides evidence that chain transfer is the dominant mechanism for chain termination. For example, poly(butyl methacrylate) homopolymer formed in the absence of macromonomer under similar conditions to the butyl methacrylate block copolymers shown in Tables 1 or 2 has $\bar{M}_n$ > 100 000.

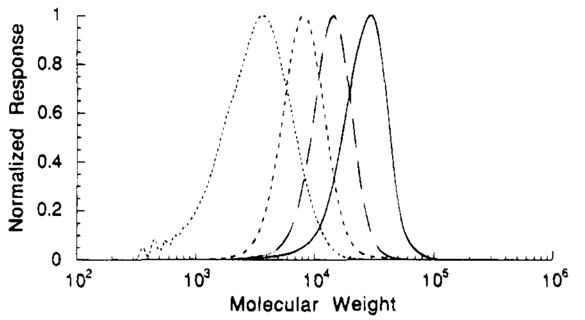


Figure 2. Molecular weight distributions for methyl methacrylate macromonomer (- - -) and for poly(butyl methacrylate-*block*-methyl methacrylate) synthesis after additions of 33.6 (– –), 59.8 (– •• –), and 88.2 g (—) of BMA. Data are for the example given in the text and reported in Table 1 and Figure 1.

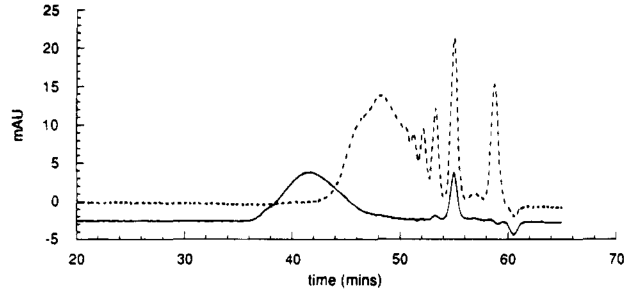


Figure 3. GPC traces for phenyl methacrylate macromonomer $\bar{M}_n$ 1100 (- - -) and poly(butyl methacrylate-*block*-phenyl methacrylate) $\bar{M}_n$ 14 500 (—). Detector wavelength 240 nm.

(b) GPC analyses performed on the block copolymers demonstrated that the original macromonomer had substantially reacted and that the polydispersities are lower than the original macromonomer (see Table 2). For the example shown in Figures 1 and 2, determinations of the molecular weight at intermediate stages of the polymerization showed that the molecular weight of the block increases continuously with monomer addition and in the way expected of a living polymerization process.

(c) Where the monomers in the A block (macromonomer) and B blocks have different chromophores, GPC analysis with diode-array UV detection demonstrated the compositional homogeneity of the block copolymer and allowed residual macromonomer to be detected in high molecular weight blocks. For the example shown in Figure 3, this analysis shows that the phenyl methacrylate macromonomer is distributed evenly throughout the block copolymer. The trace also shows that a significant amount of unreacted "dimeric" macromonomer remains—this is attributed to the relatively lower transfer constant of the dimer.[25] The presence of dimer and trimer in the macromonomer also accounts for a broader than usual polydispersity for this block copolymer.

(d) Quantitative end-group analysis by ^{1}H NMR was carried out for certain samples $\bar{M}_n \leq 5000$ to show that the double bond content remains constant on a molar basis during the polymerization. Graft copolymerization (see Scheme 2) would lead to the double bonds being irreversibly consumed.

In conclusion, free-radical polymerization in the presence of macromonomers offers a route to narrow poly-

Table 2. Methacrylic Block Copolymers Prepared from Macromonomers

macromer	$\bar{M}_n{}^b$	$\bar{M}_w/\bar{M}_n$	monomer	final block composition[a]	$\bar{M}_n{}^b$	$\bar{M}_w/\bar{M}_n$
MAA	950[c]		MMA	$(\mathrm{MAA})_{11}{}^c//(\mathrm{MMA})_{14}$	3 010	1.4
MMA	2 300	1.5	*n*-BMA	$(\mathrm{MMA})_{23}//(n\text{-BMA})_{168}$	24 300[d]	1.4[e]
MMA	3 500	1.6	*n*-BMA	$(\mathrm{MMA})_{35}//(n\text{-BMA})_{178}$	28 100[d]	1.4
t-BMA	2 400	2.1	*n*-BMA	$(t\text{-BMA})_{17}//(n\text{-BMA})_{24}$	5 780	1.3
PhMA[f]	1 100	2.2	*n*-BMA	$(\mathrm{PhMA})_7//(n\text{-BMA})_{94}$	14 500	2.3

[a] Estimated from GPC data. [b] GPC (polystyrene equivalents). [c] MAA block length estimated from ^{1}H NMR data. [d] GPC molecular weights obtained with polystyrene standards and corrected using universal calibration assuming Mark–Houwink constants for the block are the same as those for the BMA homopolymer.[26] [e] Intermediate molecular weights and polydispersities shown in Table 1. [f] Example shown in Figure 3.

dispersity block copolymers. The process has been demonstrated for methacrylic monomers and macromonomers. Further details of the scope and application of this novel process will be published in the near future.

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