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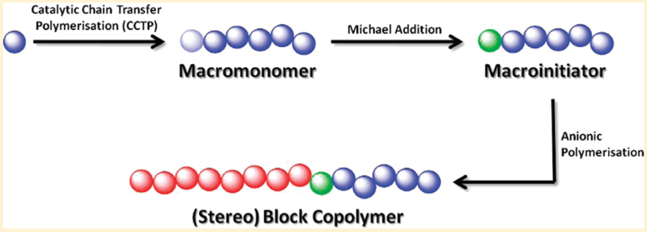
Methacrylic Stereoblock Copolymers via the Combination of Catalytic Chain Transfer and Anionic Polymerization

Gemma C. Sanders,[†,‡] Timo J. J. Sciarone,[†,‡] Hanneke M. L. Lambermont-Thijs,[†] Robbert Duchateau,[†] and Johan P. A. Heuts*[,†]

[†]Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
[‡]Dutch Polymer Institute (DPI), John F. Kennedylaan 2, 5612 AB Eindhoven, The Netherlands

S *Supporting Information*

ABSTRACT: A novel synthetic pathway toward stereoblock copolymers by combining catalytic chain transfer polymerization with anionic polymerization is described. Catalytic chain transfer polymerization (CCTP) has been used to synthesize vinyl-terminated polymers, which, after the Michael addition of α-lithioisopropyl isobutyrate, were used as macroinitiators for the anionic polymerization of methacrylate-type monomers. The resultant polymer consists of a predominantly atactic block (originating from the free radical polymerization) and a more isotactoid or syndiotactoid block (originating from the anionic polymerization).



INTRODUCTION

Block copolymers have sparked the interest of academic and industrial chemists alike for many decades because they provide a facile and versatile route to combining the properties of two or more homopolymers while obtaining a controlled architecture.[1−6] They have been synthesized via sequentially fed living polymerization techniques such as anionic[7] or cationic[8] polymerization, atom transfer radical polymerization (ATRP),[9] reversible addition–fragmentation chain transfer (RAFT) polymerization,[10] nitroxide-mediated radical polymerization (NMRP),[11] and more recently using sequentially fed coordinative chain-transfer olefin polymerization[12−14] and the so-called Dow shuttling chemistry.[15] The resultant polymers often show improved properties compared to blends of their homopolymer counterparts, contributing their greatest assets to the block copolymer. This opens the door to a broad range of applications areas, such as compatiblisers,[16−19] self-assembly,[20,21] drug delivery,[22,23] and surfactants,[24,25] which can benefit from the combined properties of the copolymer. Unfortunately, the use of a sole polymerization technique to synthesize the block copolymer frequently restricts the monomers that can be used and the properties that can be obtained. By combining one or more techniques, a vast array of block copolymers can be synthesized. Recently, living radical polymerization techniques (e.g., ATRP, RAFT, and NMRP) have been used in conjunction with catalytic olefin polymerization,[1] ring-opening polymerizations,[2] ring-opening metathesis polymerization,[3] and extensively with click chemistry.[6] Catalytic chain transfer polymerization (CCTP),[26−33] on the other hand, has rarely been used in combination with alternative polymerization mechanisms[2,24,34−37] and has never been combined with a non-radical technique.

Stereoblock copolymers of methacrylates were first synthesized by Doherty et al.[38] where blocks of syndiotactic and isotactic poly(methyl methacrylate) (pMMA) were made in the same polymer. This method, which involved the sequential anionic polymerization of diphenylmethyl methacrylate and trityl methacrylate followed by hydrolysis and methylation, is rather tedious. In 1994, a more direct route was developed involving the use of trialkylaluminum species to convert the selectivity of an isotactic pMMA macroinitiator toward syndiotacticity.[39] Group IV metallocenes have also been used in combination with boron or aluminum species to create stereoblock copolymers of methacrylates.[40] By exchanging a site-controlled polymerization with a chain-end controlled synthesis, the selectivity of the growing polymer chain could be effectively converted from being isotactic-rich to syndiotactic-rich pMMA. Group IV metallocene/Lewis acid hybrid catalysts have also been employed to synthesize isotactic–syndiotactic block copolymers via a diastereotopic ion-pairing polymerization method.[41] Although literature surrounding isotactic–syndiotactic pMMA block copolymers is prevalent, we are not aware of any information regarding stereoblock copolymers of pMMA in the literature, in which one block is atactic. Atactic–isotactic stereoblock copolymers of polyacrylamides, on the other hand, have been reported.[42−44] The first block, made via a conventional RAFT technique, is atactic, the selectivity of which switches to isotacticity upon addition of a Lewis acid. Carpentier and co-workers[45] reported, what they claimed to be, the first example of a block copolymer of polystyrene with syndiotactic and atactic blocks by combining Ziegler–Natta polymerization with ATRP.

The combination of CCTP with other polymerization mechanisms has, hitherto, been underexploited as a technique.

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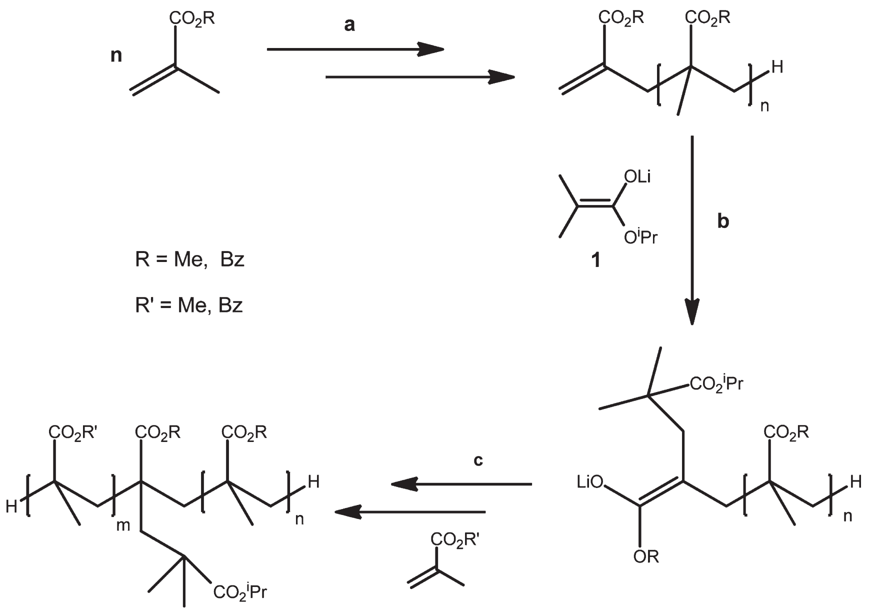
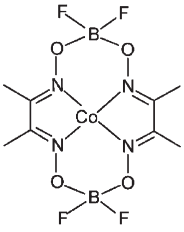
Scheme 1. Synthetic Approach to Block Copolymers: (a) Catalytic Chain Transfer Polymerization (CCTP); (b) Michael Addition of α-Lithioisopropyl Isobutyrate; (c) Anionic Polymerization



Herein, we demonstrate a novel route to synthesizing block copolymers via the combination of catalytic chain transfer polymerization and anionic polymerization, wherein the blocks have differing tacticities (Scheme 1). The inclusion of an anionically derived element allows the possibility of introducing "non-radical" properties to the block copolymer, such as tacticity and potentially crystallinity, via either side- or chain-end control producing iso- or syndiotactic polymers. This is impossible using CCTP alone. Block copolymers with differing tacticities are of interest in fields such as coatings and surface modifiers.[46] The atactic component can provide good miscibility with the substrate, while the isotactic or syndiotactic blocks tend to form crystalline domains capable of enhancing the scratch and chemical resistance of the coating, protecting the substrate.[47,48]

In CCTP, certain low-spin Co^{II} species such as bis[(difluoroboryl)dimethylglyoxymate]cobalt(II) (COBF) can be used in ppm quantities under free-radical conditions to catalyze the chain transfer to monomer reaction and thus efficiently control the molecular weight.[26−33] In addition, the polymers formed during CCTP contain a terminal double bond which gives rise to the name "macromonomers". CCTP is particularly efficient when methacrylate (as opposed to acrylate and styrenic) monomers are used; however, as with all free radical polymerization techniques, the resulting polymers are basically atactic. The polydispersity indices of polymers made via CCTP are consistent with that of chain transfer dominated polymerization reactions and are usually around 2. This can, however, be significantly reduced when CCTP is used in combination with ATRP[49] or RAFT.[50]



COBF

The anionic polymerization of methacrylates enables a degree of stereoregularity to be introduced, which is almost always impossible using radical methods.[51−54] The anionic polymerization of methacrylate monomers with lithium ester enolate-based initiators, such as α-lithioisopropyl isobutyrate (**1**, Scheme 1), proceeds via a Michael addition mechanism. Unfortunately, the use of this type of initiator means that the polymerization reactions are prone to two major problems.[55] First, lithium ester enolates, such as **1**, are known to have a tendency to cluster, resulting in inhomogeneous initiation and low initiator efficiency. In addition, due to the mechanism of this polymerization technique, a carbanion is formed, which can attack the ester carbonyl functionality in the methacrylate-based polymer, resulting in the formation of dead cyclic species. Luckily, there is extensive literature available with a huge selection of preventative methods for both aggregation and backbiting termination.[51,55] Care must be taken, however, as the choice of additives can greatly influence the tacticity of the growing polymer chain.

In this present study we investigate the use of CCTP-derived macromonomers, modified with **1**, as macroinitiators for the anionic polymerization of methacrylic monomers. By combining these two different polymerization mechanisms, stereoblock copolymers comprising of an atactic block and a syndio/isotactic block were synthesized. The versatility of this reaction toward macromonomers based on alternative methacrylic monomers and different chain lengths was also investigated.

■ EXPERIMENTAL SECTION

General Considerations. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in oven-dried Schlenk-type glassware on a dual manifold Schlenk line, a vacuum line (typically 1−100 mbar), or in a nitrogen-filled glovebox (typically <1.0 ppm of oxygen and moisture).

Materials. Methyl methacrylate (MMA, 99%) and benzyl methacrylate (BzMA, 96%) were purchased from Aldrich and passed over a column of activated basic alumina to remove the inhibitor. For anionic

Table 1. Properties of the Synthesised pBzMA and pMMA

			SEC[c]		^1H NMR[d]
	2 (ppm)[a]	x[b]	M_n/g mol^{-1}	PDI	M_n/g mol^{-1}
pBzMA$_2$	392				352
pBzMA$_6$	94	0.88	1150	1.6	1050
pBzMA$_{76}$	5.5	0.78	13500	2.2	14000
pMMA$_2$	191				200
pMMA$_{15}$	4.3	0.68	1700	1.6	1500
pMMA$_{40}$	3.3	0.40	3800	1.8	4000
pMMA$_{120}$	2.1	0.84	13000	2.6	12000

[a] The amount of **2** is defined as moles of **2** per 10^6 moles of monomer. [b] Monomer conversions determined gravimetrically. [c] Values reported against polystyrene standards. [d] Calculated based on the ratio of vinylic protons (5.4 and 6.2 ppm) to ester protons (BzMA: 5.0 ppm; MMA: 3.6 ppm).

polymerizations, MMA and BzMA were purified further by being dried over CaH_2 and distilled, followed by titration against neat trioctylaluminum and a second distillation. Triisobutylaluminum (TIBA) was purchased from Aldrich and used as received. Lithium chloride (98%) was purchased from Aldrich and dried in a vacuum oven at 100 °C overnight before introduction to the glovebox. Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol. The bis(methanol) complex of COBF, COBF·(MeOH)$_2$ (**2**), was prepared as described previously.[56,57] The chain transfer activity of the complex was determined in methyl methacrylate (MMA) bulk polymerization at 60 °C and found to be equal to 30 × 10^3. For all experiments, a single batch of catalyst was used. Toluene and tetrahydrofuran (THF) were purchased from Biosolve and used as received for the CCTP polymerizations. For use in the macroinitiation experiments, the solvents were dried over molecular sieves prior to use. α-Lithioisopropyl isobutyrate, **1**, and MeAl(BHT)$_2$ (**3**, BHT = 2,6-(t-Bu)$_2$-4-Me-C_6H_2O) were synthesized according to literature methods.[58,59]

Synthesis of Macromonomers via CCTP. Complex **2** (see Table 1) and AIBN (42 mg, 0.25 mmol) were placed in a flask equipped with a stirrer bar and underwent three vacuum−argon cycles. BzMA or MMA (50 mL) and toluene (50 mL) were deoxygenated and added using a syringe. The mixture was heated to 60 °C and allowed to react for 16 h, after which it was quenched by cooling in ice and addition of hydroquinone. For macromonomers with an M_n < 2000 g/mol, the residual monomer and solvent were removed via vacuum evaporation immediately after stopping the reaction. The resulting product was redissolved in THF, passed over a column of basic alumina, and dried at 80 °C in a vacuum oven for at least 48 h to remove all traces of solvent and water. For macromonomers with an M_n > 8000 g/mol, the product was further diluted with toluene, precipitated in a large excess of pentane, and then dried in a vacuum oven at 80 °C for at least 48 h to remove all traces of solvent and water.

Synthesis of pMMA$_2$. A 250 mL round-bottom flask was charged with AIBN (213 mg, 1.3 mmol) and **2** (100 mg, 0.26 mmol) inside a glovebox. The flask was closed with a rubber septum and removed from the glovebox. MMA (100 mL, 936 mmol) was injected via the septum, and the mixture was stirred at 80 °C for 6 h under a nitrogen atmosphere. The oligomerization was quenched by addition of hydroquinone and cooling in ice. Residual monomer was removed under reduced pressure at room temperature. The residual yellow oil was vacuum distilled (325 mTorr, 38 °C) to afford the pure dimer in 42% yield. ^1H NMR (400 MHz, chloroform-d_1, 298 K): δ 6.12 (s, 1H, $=CH_2$), 5.43 (s, 1H, $=CH_2$), 3.64 (s, 3H, OMe), 3.55 (s, 3H, OMe), 2.52 (s, 2H, CH_2), 1.07 (s, 6H, Me_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, chloroform-d_1, 298 K): δ 177.3 ($C=O_{ester}$), 176.8 ($C=O_{acryl}$), 137.3 ($C=CH_2$), 127.8 ($=CH_2$), 51.8 (OMe), 51.6 (OMe), 42.8 (CMe_2), 41.0 (CH_2), 24.8 (CMe_2) ppm.

Synthesis of pBzMA$_2$. A 250 mL round-bottom flask was charged with AIBN (100 mg, 0.61 mmol) and **2** (50 mg, 0.126 μmol) inside a glovebox. The flask was closed with a rubber septum and removed from the glovebox. BzMA (50 mL) was injected via the septum, and the mixture was stirred at 60 °C for 16 h under a nitrogen atmosphere. The oligomerization was quenched by addition of hydroquinone and cooling in ice. Residual monomer was removed under reduced pressure at elevated temperatures. The residual yellow oil was vacuum distilled using a Kugelrohr setup (10^{-3} mTorr, 200 °C) to afford the pure dimer in 60% yield. ^1H NMR (400 MHz, chloroform-d_1, 298 K): δ 7.38 (m, 10H, Ph), 6.29 (s, 1H, $=CH_2$), 5.53 (s, 1H, $=CH_2$), 5.20 (s, 3H, OCH_2), 5.10 (s, 3H, OCH_2), 2.74 (s, 2H, CH_2), 1.25 (s, 6H, Me_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, chloroform-d_1, 298 K): δ 176.7 ($C=O_{ester}$), 167.2 ($C=O_{acryl}$), 137.2 ($C=CH_2$), 136.0 ($=CH_2$), 28.5 ($C_{aromatic}$), 66.5 (OCH_2), 43.0 (CH_2), 40.9 (CMe_2), 24.9 (CMe_2) ppm.

Synthesis of Model "Macro"initiator. Compound **1** (10 mg, 72 μmol) was dissolved in 0.4 mL of C_6D_6 and the purity checked via ^1H NMR. pMMA$_2$ (14 mg, 72 μmol) was added and allowed to stir for 1 h. ^1H NMR was used to determine that all of the starting enolate **1** was consumed. The reaction mixture was then quenched with 10% HCl solution, and the product again was analyzed using ^1H NMR. ^1H NMR (400 MHz, THF-d_8/toluene-d_8, 298 K): δ 4.89 (septet, 1H, OCH(Me)$_2$), 3.40 (s, 6H, OMe), 3.39 (s, 6H, OMe), 2.55 (m, 1H, CH), 1.99−2.10 (m, 2H, CH_2), 1.50−1.59 (m, 2H, CH_2), 1.06−1.12 (m, 18H, 3 × Me_2) ppm.

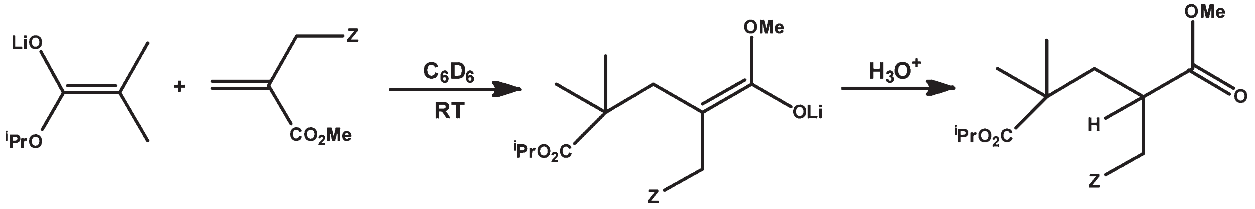
Anionic Polymerization from Model "Macro"initiator. Compound **1** (2.5 mg, 18 μmol) was dissolved in 0.5 mL of dry THF, pBzMA$_2$ (12.5 mg, 36 μmol) was then added, and the mixture allowed to stir for 15 min. MMA (90 mg, 900 μmol) was then added and stirred at 20 °C for 2 h. The reaction product was quenched with acidified ethanol and dried overnight in a vacuum oven. M_n = 31 000 g/mol, PDI = 1.7; conversion = 90%.

Reaction of 1 with 2 equiv of pMMA$_2$. Compound **1** (340 mg, 2.5 mmol) was suspended in toluene (20 mL), and then pMMA$_2$ (1.0 g, 5.0 mmol) was added dropwise. The clear solution was stirred at room temperature for 18 h. Toluene was evaporated under reduced pressure, and the residue was taken up in methanol (20 mL). All volatiles were evaporated under reduced pressure, and the resulting foam was taken up in Et_2O (50 mL). The organic layer was washed with hydrochloric acid (10%, 30 mL) and then separated, and the aqueous layer was extracted with Et_2O (30 mL). The combined organic fractions were dried over Na_2SO_4, and volatiles were removed under reduced pressure to give an oil. A small amount of the monoaddition product $Me_2C(CO_2Me)CH_2CH(CO_2Me)CH_2CMe_2CO_2iPr$ was removed of the oil by vacuum distillation (80 °C, 400 mTorr).

Typical Procedure for the Isotactic Anionic Polymerization of MMA. In a glovebox, **1** (14 mg, 100 μmol) and LiCl (4 mg, 100 μmol) were dissolved in 0.99 g of dry toluene. Outside the glovebox, 0.01 mL of THF was added. The vials were cooled to −78 °C. MMA (0.80 g, 8 mmol) was then added under an argon atmosphere, and the mixture was stirred for 30 min at −78 °C. The reaction was quenched with acidified ethanol and precipitated in pentane. The residual solvent was removed using a vacuum oven at 60 °C overnight. In some experiments, as indicated in text, LiCl was omitted and only toluene used as solvent.

Typical Procedure for the Isotactic Anionic Polymerization of MMA from a BzMA Macroinitiator. In a glovebox, **1** (14 mg, 100 μmol) and LiCl (4 mg, 100 μmol) were dissolved in 1 g of dry toluene. In a separate vial, the macromonomer (100 μmol) was dissolved in 0.99 g of dry toluene. After dissolution, the two crimp cap vials were removed from the glovebox. To the vial containing **1** and LiCl, 0.01 mL of THF was added. Both vials were cooled to the appropriate temperature. The two solutions where then combined under an argon atmosphere and allowed to mix for 5 min. Cold MMA (0.45 mL, 4.2 mmol)

Scheme 2. Reaction Scheme for the Synthesis of a Macroinitiator and Its Hydrolysis



was then added, and the mixture was stirred for 4 h at the desired temperature. The reaction was quenched with water. The residual solvent was removed using a vacuum oven at 60 °C overnight.

Typical Procedure for the Syndiotactic Anionic Polymerization of MMA from a BzMA Macroinitiator. Complex **3** (45 mg, 93.4 μmol) and macromonomer (47 μmol) were dissolved in toluene for 45 min. A solution of **1** (47 μmol) in toluene was added and allowed to stir for 60 min. MMA (0.22 g, 2.2 mmol) was added, and the reaction mixture was stirred for 1 h at room temperature. For longer macromonomers, the polymerization time was increased to 2 h and a solution of TIBA (typically 0.5 wt % of the macromonomer) was added to the macromonomer 2 h prior to the addition of **3** in order to remove any trace of water. Reaction mixtures were quenched with acidified ethanol, and the solvent was removed under vacuum. Polymers with an M_n > 8000 g/mol were precipitated twice from pentane.

Syndiotactic Anionic Polymerization of pBzMA. Complex **3** (12 mg, 24 μmol) and a solution of **1** in toluene (1.6 mg, 12 μmol) were dissolved in 1.5 g of toluene to cleanly generate an initiator/catalyst pair. BzMA (0.21 g, 1.2 mmol) was then added, and the mixture was stirred for 2 h at 20 °C. The reaction mixture was quenched with acidified ethanol and precipitated in pentane. 81% conversion; M_n = 15 200 g/mol, PDI = 1.5 (determined against PS standards in THF using SEC).

Syndiotactic Anionic Polymerization of pMMA. Complex **3** (12 mg, 24 μmol) and a solution of **1** in toluene (1.6 mg, 12 μmol) were dissolved in 1.5 g of toluene to cleanly generate an initiator/catalyst pair. MMA (0.12 g, 1.2 mmol) was then added, and the mixture was stirred for 2 h at 20 °C. The reaction mixture was quenched with acidified ethanol and precipitated in pentane. 98% conversion; M_n = 9900 g/mol, PDI = 1.4 (determined against PS standards in THF using SEC).

Measurements. Gel permeation chromatography was carried out using a Waters 2695 separations module, a Model 2487 UV detector (254 nm), and a Model 2414 differential refractive index detector (40 °C). Injection volume used was 50 μL. Tetrahydrofuran (Biosolve, stabilized with BHT) was the eluent, flow rate 1.0 mL/min. The column set used was a PLgel guard (5 μm particles) 50 × 7.5 mm precolumn, followed by two PLgel columns in series of 500 Å (5 μm particles) and 100 Å (5 μm particles), respectively. Calibration was performed using polystyrene standards (Polymer Laboratories, M_n = 370 up to M_n = 40 000 g/mol). Data acquisition and processing were performed using Waters Empower 2 software. ^{1}H NMR spectra were recorded on a Varian Mercury Vx (400 MHz) spectrometer at 400 MHz. Chloroform-d_1, THF-d_8, benzene-d_6, toluene-d_8, and tetramethylsilane were used as solvent and internal standard, respectively. MALDI-ToF-MS was carried out using a voyager DE-STR spectrometer from Applied Biosystems in reflector mode. *trans*-2-(3-(4-*tert*-Butylphenyl)-methyl-2-propenylidene)malononitrile doped with potassium trifluoroacetate was used as the matrix. It was deposited from THF solution onto a stainless steel sample substrate, and the solvent was allowed to evaporate. The polymer was then deposited as a dilute (~1 mg/mL) solution in THF. This resulted in each polymeric species being observed as its K^+ adduct with molecular mass M + 31. The spectrometer was calibrated using poly(ethylene oxide) standards for the lower mass range and polystyrene standards for the higher mass range. Gradient polymer elution chromatography (GPEC) was carried out using a Zorbax Eclipse XDB-C8 column, 4.6 × 150 mm, 5 μm on an Agilent 1100 series setup. Initially, the eluent was a 4:1 mix of methanol/THF for 2 min and then gradually changed to pure THF over 25 min. The flow rate was 1 mL/min. The temperature of the column was 50 °C. Detection was carried out using a Polymer Laboratories evaporative light scattering detector (ELSD). Differential scanning calorimetry (DSC) was performed on a TA Q100 DSC. Approximately 5 mg of dried polymer was weighed in aluminum hermetic pans. Temperature profiles from 0 to 200 °C with a heating and cooling rate of 1, 10, and 20 °C/min were applied. TA Universal Analysis software was used for data acquisition. Glass transition temperatures were determined from the second heating run.

RESULTS AND DISCUSSION

Model studies, based on dimers prepared by CCTP, were carried out to establish the reactivity of these species toward **1** as well as to probe their ability as initiators to polymerize methacrylic monomers anionically. Once established, macromonomers were used as macroinitiators. BzMA macromonomers were initially selected as the starting blocks for the block copolymer due to its UV activity; pBzMA is UV-active at 254 nm, whereas MMA shows no absorption at this wavelength, allowing the simple detection of pBzMA-containing (block) copolymers via SEC with UV detection.

Synthesis of Macromonomers. Poly(benzyl methacrylate) (pBzMA) and poly(methyl methacrylate) (pMMA) macromonomers were synthesized by CCTP in toluene at 60 °C using AIBN as the initiator. The final properties of these macromonomers are collected in Table 1. The macromonomers were analyzed using ^{1}H NMR to confirm that all had a terminal vinylic group. For the lower molecular weight macromonomers, this was also confirmed using MALDI-ToF-MS.

Synthesis of Macroinitiator (Model Studies). To investigate the conversion of the macromonomer into a macroinitiator, model studies were carried out. As a model for the macromonomer, an MMA dimer, pMMA$_2$, was synthesized using CCTP, followed by purification via vacuum distillation. Equimolar quantities of the stable enolate $Me_2C{=}C(O\mathit{i}Pr)OLi$ (**1**) and pMMA$_2$ were reacted in benzene-d_6 (Scheme 2).

The ^{1}H NMR spectrum of the initially formed product enolate features one broad signal for all methylene protons, while all other groups give their individual resonances with resolved coupling patterns. Hydrolysis using 10% aqueous HCl converts the spectrum into that of the product ester, displaying diastereotopic methylene protons as well as diastereotopic CMe_2 groups and a quintet at 2.55 ppm which corresponds to the newly formed proton adjacent to the ester functionality, confirming the formation of a "macro"-initiator (Figure S1, Supporting Information).

In a separate experiment to confirm that the resulting coupling product of the methacrylic dimer with **1** is indeed capable of inducing initiation, the UV-active BzMA dimer, pBzMA$_2$, was reacted with lithium ester enolate, **1**, followed by the addition of MMA.

Polymerization ensued, and the resultant product was analyzed using SEC equipped with dual UV/DRI detectors. The molecular weight distribution (Figure 1) shows that a polymeric material has been synthesized with an M_n of 31 000 g/mol and that the UV and DRI signals overlay. Since pBzMA$_2$ is UV-active at 254 nm, whereas MMA is inactive, this result is indicative that pBzMA$_2$ has indeed acted as a macroinitiator and has been incorporated into the polymer.

The addition of 2 equiv of pMMA$_2$ to **1**, however, resulted in a backbitten species (**6**, Scheme 3). The presence of this species was confirmed via MALDI-ToF-MS (Figure S2, Supporting Information). Backbiting of **4** does not occur as this would result in the formation of an unstable 4-membered ring. The observed predominance of backbiting in this reaction, which is in fact a model reaction for propagation of pMMA$_2$, precludes the lithium enolate initiated anionic (homo) polymerization of CCT-derived macromonomers.

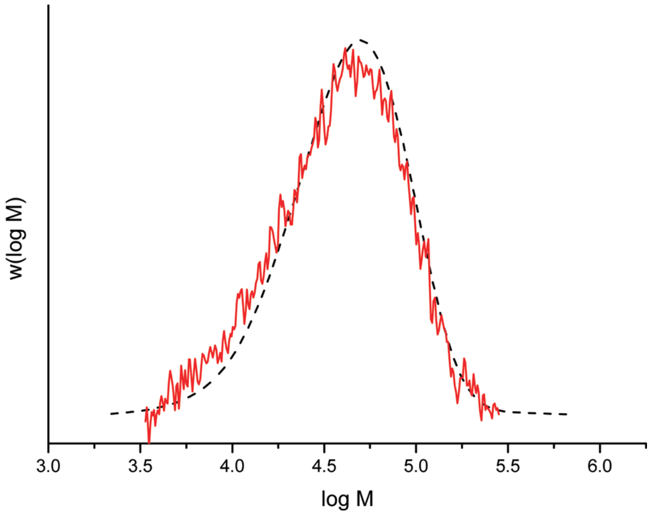


Figure 1. Molecular weight distribution (relative to PS, measured in THF) illustrating that pBzMA$_2$ is capable of initiating the anionic polymerization of MMA: (- - -) DRI signal, (—) UV signal. Experimental conditions: solvent = THF, temperature = 20 °C, reaction time = 2 h.

We can, nevertheless, conclude that (the models for) macromonomers can act as macroinitiators for the anionic polymerization of MMA, allowing this synthesis of block copolymers.

Block Copolymer Synthesis. *Atactic—Isotactic Block Copolymers.* One of the most common methods to synthesize isotactic pMMA from lithium ester enolates, such as **1**, is by carrying out the polymerization in toluene.[55] Under these conditions and at room temperature, isotactic pMMA with an [mm] = 74% can be synthesized.[60] However, as illustrated by the model reactions, the polymerization of MMA from a macroinitiator suffers significantly from backbiting reactions, more so than the simple polymerization of pMMA from **1**; in other words, the (macro)-initiator efficiency is lower than that of **1**. The addition of 1% THF and the lowering of the temperature to −78 °C assist in minimizing backbiting termination reactions,[55] although the addition of THF also affects the tacticity, decreasing the degree of isotacticity (Figure S3, Supporting Information). Further addition of THF (i.e., >1%) results in a significant loss in stereocontrol,[61] justifying the choice of a 99:1 ratio of toluene to THF as a suitable solvent mixture to perform the polymerizations.

The *in situ* formation of a macroinitiator was carried out by reaction of pBzMA$_6$ macromonomer and **1**, followed by the addition of MMA at a range of temperatures and in the absence and presence of LiCl (Table 2). Temperature choice is paramount in anionic polymerizations, especially when there is an

Scheme 3. Mechanistic Reaction Scheme of the Backbiting Reaction of Macroinitiators

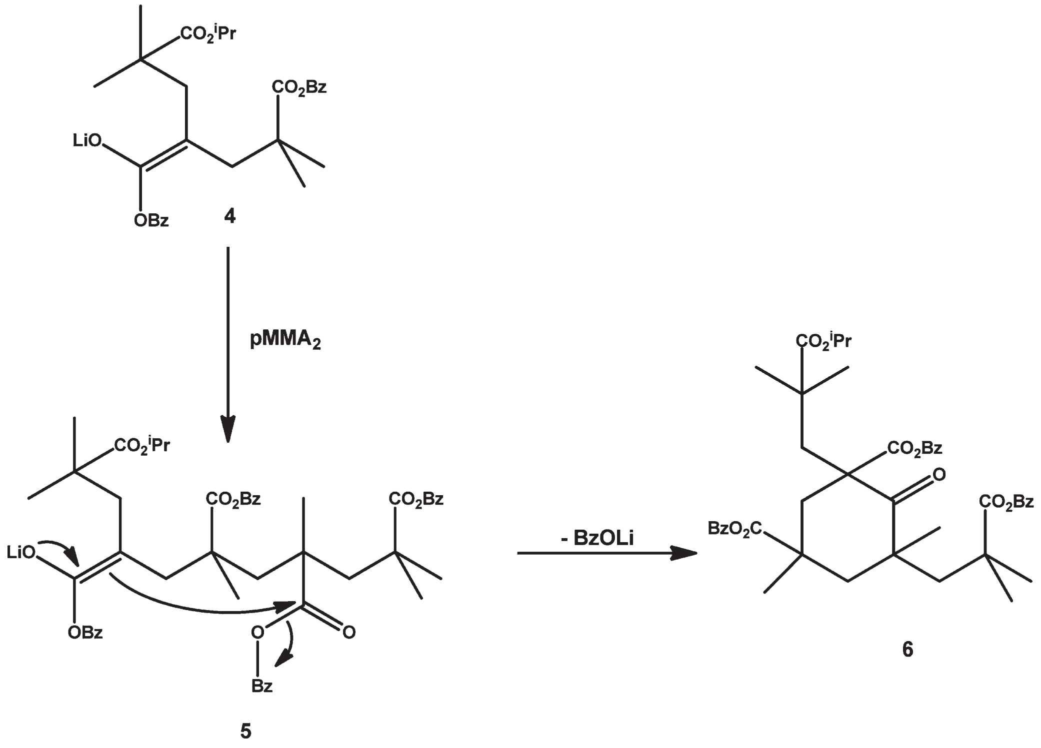


Table 2. Conditions and Results for the Anionic Polymerization of MMA Using pBzMA$_6$ as the Macroinitiator (pBzMA$_6$/1/MMA = 1:1:10)

	temp/°C	equiv of LiCl[a]	M_n[b]/g mol^{-1}	PDI[b]	MMA conv[c]
1	20	0	2100	15[d]	0.94
2	0	0	2400	33[e]	1.00
3	−78	0	1920	1.9	0.26
4	20	1	2020	1.7	0.82
5	0	1	2500	1.9	1.00
6	−78	1	1800	1.6	0.50

[a] Molar equivelents of LiCl with respect to **1**. [b] Determined using SEC, measured against PS standards in THF using DRI detector. [c] Conversion of monomer determined gravimetrically after 4 h reaction time. [d] Bimodal M_p = 2600 and 83 900 g mol^{-1}. [e] Bimodal M_p = 2700 and 122 500 g mol^{-1}.

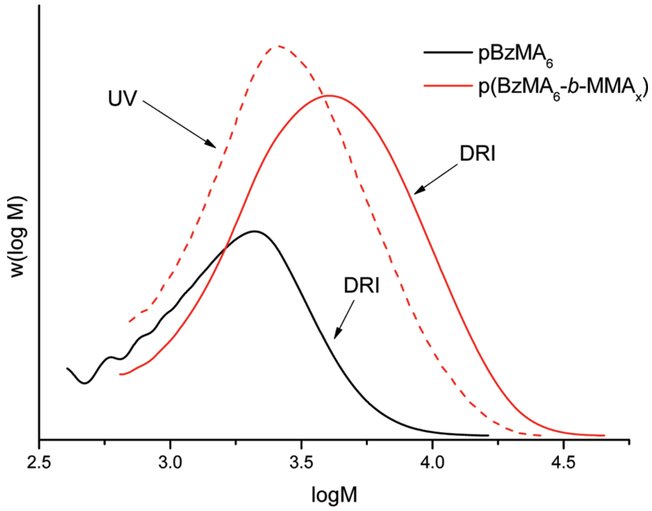


Figure 2. Molecular weight distribution (relative to PS, measured in THF) of pBzMA$_6$ and p(BzMA$_6$-*b*-MMA$_x$) (entry 5, Table 2) normalized to the amount of polymer.

opportunity for backbiting, as well as other side reactions, to occur. In general, anionic polymerizations of this type are carried out at −78 °C.[55] The reactions shown in Table 2 also show a strong dependence on temperature. As can be seen in entries 1−3 and 4−6, decreasing the temperature decreases the PDI of the resulting polymer. In comparing entries 1 and 3, this difference is most obvious as the molecular weight distribution of resultant polymer transforms from bimodal to monomodal. This suggests a significant reduction in the amount of side reactions that have occurred. The use of lower temperatures also suppresses the rate of polymerization, decreasing the degree of conversion obtainable after 4 h.

The use of salts, such as lithium chloride, has been reported to assist in the deaggregation of lithium ester enolate clusters, allowing homogeneous initiation to occur.[62,63] From Table 2 it is evident that the presence of lithium chloride does have a profound effect on the polydispersity of the polymers synthesized. At all temperatures, a decrease in PDI is observed when the reaction is carried out in the presence of lithium chloride. The most noticeable being the decrease from a bimodal distribution with PDI of >15 to a monomodal distribution with PDI of <1.9 when the reaction is carried out in the presence of LiCl at 0 °C or even at room temperature. Although the PDI of the polymer decreases when the temperature is decreased from 0 °C to −78 °C when lithium chloride is used, the difference is not great. It should also be noted here that the observed PDIs are larger than one would normally expect from an anionic polymerization, but one must recall that the starting macroinitiator already has a PDI ≈ 1.6. In addition, the rate of reaction is compromised. Lithium chloride does not have a pronounced effect on the tacticity of the polymer formed (Figure S3, Supporting Information).

A more in-depth analysis was carried out on the polymer formed in entry 5 (Table 2). A UV detector was used in tandem with a DRI detector for SEC measurements. The DRI signal produced using SEC for the polymer made in entry 5 clearly shows a shift toward a higher molecular weight after the reaction has taken place. A shift in the UV signal is also observed, although the UV and DRI chromatograms of the block copolymer do not overlap perfectly. This illustrates that while the UV-active macromonomer does form part of the block copolymer, it may not have been distributed evenly, suggesting that some pMMA homopolymer has also been produced; pMMA can be formed as a result of initiation from unreacted **1**. The perfect overlap of DRI and UV signals observed in Figure 1 is not observed here in Figure 2 as a balance exists between the conversion of macromonomer (*n* > 1) to macroinitiator and backbiting, which does not exist for the dimers (*n* = 1), as detailed in Scheme 3.

Gradient polymer elution chromatography (GPEC) was carried out to further confirm the presence of a block copolymer (Figure 3). By using an analytical technique which separates based on chemical composition as opposed to hydrodynamic volume, it was possible to distinguish between the two homopolymers (pBzMA$_6$ and pMMA) and the block copolymer p(BzMA$_6$-*b*-MMA$_x$) (Figure 3). The observed oligomeric distribution of the macromonomer has been reported before in the literature.[64] It is obvious that the resultant product contains both unreacted pBzMA$_6$ macromonomer and pMMA homopolymer (13−28 and 37−38 min, respectively), but a broad third peak corresponding to a copolymer can also be seen, spanning between the two homopolymers. The broadness is as expected because the polymer consists of a variety of block sizes originating mainly from the macroinitiator pBzMA$_6$ and also somewhat from the second block.

The existence of a copolymer was further confirmed using MALDI-ToF-MS (Figure 4a) in which multiple distributions were observed. As depicted in the spectrum, a distribution with a repeat unit of 176 Da, corresponding to pBzMA homopolymer, is seen. The end group of this pBzMA has been identified as the result of backbiting (i.e., after reaction of the macromonomer with **1**, the chain end has bitten back onto itself to form a six-membered ring, as shown in Scheme 3, preventing the initiation of MMA polymerization from this polymer chain). Minimal unreacted macromonomer is observed in the spectrum, indicating that the first step of the reaction with the lithium enolate gives almost 100% conversion. A distribution with a repeat unit of 100 Da is also seen establishing the presence of pMMA, but the end group could not as yet be determined. Enolates are known to have limited thermal stability and thus decompose to a wide variety of species. It is assumed that one of these species is responsible for initiating the polymerization of MMA or that this decomposition reaction has occurred after completion of the reaction. Underlying these two distributions, which show a much

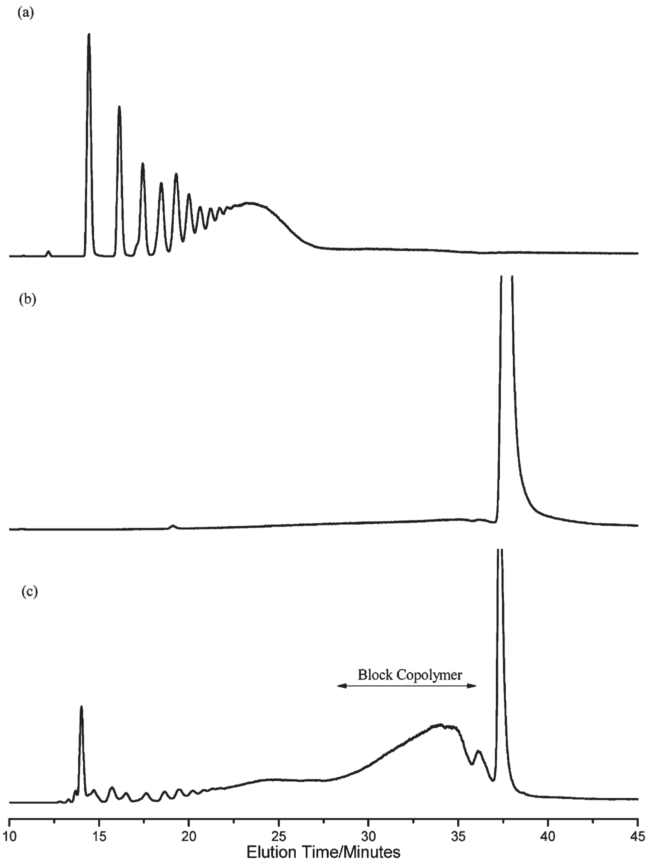


Figure 3. Gel permeation elution chromatogram showing (a) pBzMA$_6$, (b) pMMA, and (c) the presence of a p(BzMA$_6$-*b*-MMA$_x$) (entry 5, Table 2) as well as some residual macromonomer and pMMA.

higher intensity, is a third distribution with a difference of 24 Da between the peaks. This is consistent with the difference between two MMA units and one BzMA unit, verifying the presence of a copolymer of MMA and BzMA. Again, the end group could not be elucidated, but it appears to be different than the end group of pMMA.

To unequivocally prove the existence of the block copolymer, isolation of the copolymer was attempted using GPEC fractionation. Several fractions were taken between 25 and 35 min. This procedure was repeated 15 times in order to obtain sufficient material to acquire a MALDI-ToF-MS spectrum; the fractions were run a second time to check the purity. In each case, some residual homopolymer remained in the spectra. Fortunately, one fraction eliminated all traces of pBzMA giving a much clearer spectrum containing only pMMA and p(BzMA$_6$-*b*-MMA$_x$) (Figure 5). The MALDI-ToF-MS spectrum of the fractionated species shows two distributions (Figure 4b). One corresponds to pMMA and the other to p(BzMA-*b*-MMA), the end groups of which are consistent with those in the unfractionated spectrum (Figure 4a). Note that the intensities observed in MALDI-ToF-MS are not representive of the actual amounts of polymer present as the measurement is not quantitative.

Free-radical polymerizations are generally highly random and as such produce atactic chains. However, from literature[60] and model studies we know that **1** is capable of producing isotactic pMMA, characterized by a high degree of [mm] triads. Under the conditions used here, pMMA with an isotactoidal tendency is formed, although the degree of [mm] triads is lower than if only toluene is used as the solvent (Figure S3, Supporting Information). ^{1}H NMR was used to determine the extent of the tacticity of p(BzMA$_6$-*b*-MMA$_x$) (entry 5, Table 2) as shown in Figure 6. The CH$_3$ protons of the pMMA, between 0.6 and 1.2 ppm, can be used to indicate the tacticity of the pMMA component of the polymer. At 1.2 ppm a quintessential [mm]

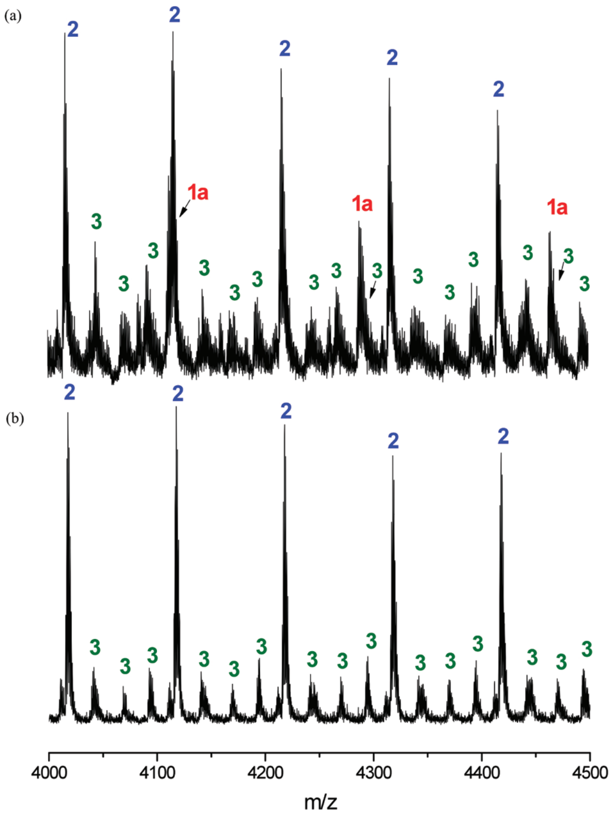


Figure 4. MALDI-ToF-MS spectrum of p(BzMA$_6$-*b*-MMA$_x$) (entry 5, Table 2): (a) unfractionated and (b) fractionated, showing multiple distributions, where **1a** = pBzMA, **2** = pMMA, and **3** = p(BzMA$_6$-*b*-MMA$_x$).

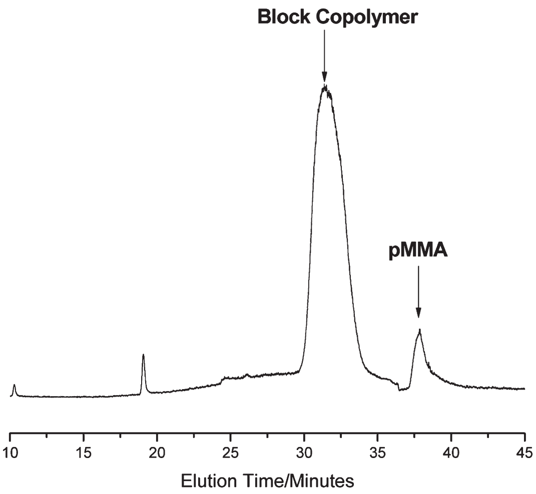


Figure 5. GPEC chromatogram showing the results of fractionation of p(BzMA$_6$-*b*-MMA$_x$) (entry 5, Table 2).

triad can be seen; however, both [mr] and [rr] triads, at 1.0 and 0.8 ppm, respectively, are also present. This suggests that the polymer is partially isotactic in nature, although there is an element of atacticity derived from the macromonomer (acting either as the first block or as unreacted material). It was also difficult to determine the exact degree of isotacticity due to the underlying atacticity of the macromonomer.

It is clear from the evidence presented above that block copolymers of atactic benzyl methacrylate and isotactic-rich methyl methacrylate can be made via the combination of CCTP and anionic polymerization. However, this route proved to be rather inefficient due to backbiting termination of the macroinitiator as well as the formation of pMMA from unreacted **1**.

Atactic–Syndiotactic Block Copolymers. Aluminum compounds have been used previously to control the tacticity of methacrylic monomers during anionic polymerizations.[60,65] Rodriguez-Delgado et al.[60] reported the use of MeAl(BHT)$_2$ (**3**) in combination with **1** as an effective route to preventing both clustering of lithium ester enolates and backbiting termination. Furthermore, the polymerization of MMA under these conditions can be carried out in toluene at room temperature to produce syndiotactic pMMA (71.3% [rr], 24.7% [mr], 4.0% [mm]). Further reduction in the temperature to 0 and −40 °C increases the stereoselectivity toward higher syndiotacticity, but only by around 8%.

To first determine whether this route is feasible, a short BzMA-based macromonomer (pBzMA$_6$) was used as a macroinitiator. After mixing with 2 equiv of **3**, 1 equiv of **1** was added to form a macroinitiator *in situ*, followed by 47 or 100 equiv of MMA (entries 1 and 2 in Table 3, respectively). Figure 7 shows the molecular weight distributions of the starting macromonomer and the final polymer synthesized in entry 2 (Table 3). A clear increase in the molecular weight from the macromonomer to the block copolymer can be observed from 1150 to 24 000 g/mol. In addition, the signals recorded from the UV and DRI detectors of the SEC instrument correlate well with each other, indicating the inclusion of the pBzMA$_6$ macromonomer in the final polymer. A small amount of unreacted macromonomer remains, which is more obvious in the UV trace of the product mixture.

The molecular weight of the block copolymer obtained in entry 2 is too high for analysis via MALDI-ToF-MS; however, the block copolymer made in entry 1 (Table 3) has a molecular weight that can be easily analyzed using this technique (Figure 8). Three distinct distributions can be seen. Distribution 3 indicates that a copolymer has been synthesized; the difference

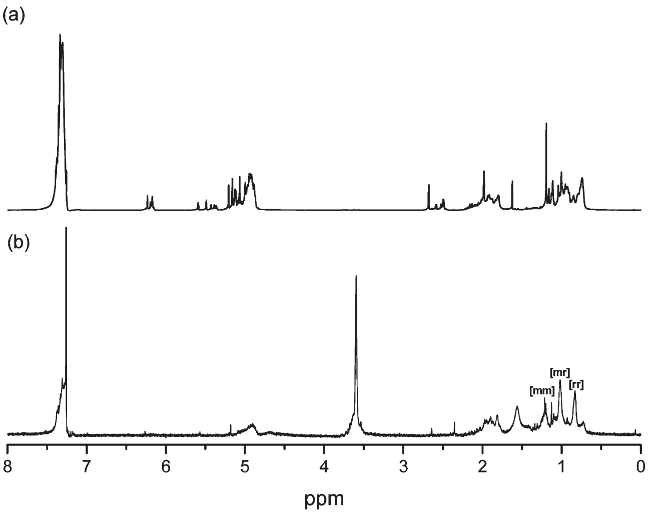


Figure 6. ^{1}H NMR (400 MHz, CDCl$_3$) of (a) pBzMA$_6$ and (b) block copolymer p(BzMA$_6$-*b*-MMA$_x$) (entry 5, Table 2).

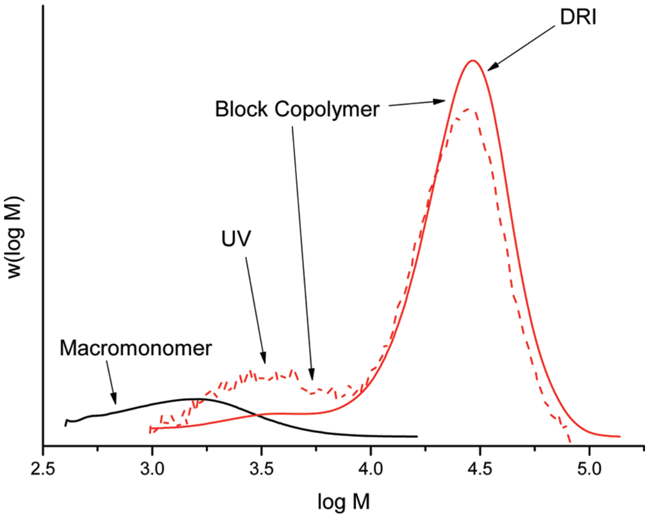


Figure 7. Molecular weight distribution of p(BzMA$_6$-*b*-MMA$_{95}$) normalized based on amount of polymer.

Table 3. Conditions and Results for the Anionic Polymerization of MMA or BzMA Using a Methacrylic Macromonomer as the Macroinitiator in the Presence of 3

	block copolymer[a]	theor final M_n[b]/g mol^{-1}	M_n[c]/g mol^{-1}	PDI[c]	block 1:block 2[d]	monomer conv[e]
1	p(BzMA$_6$-*b*-MMA$_{47}$)	4500	5300	2.6	6:30	0.75
2	p(BzMA$_6$-*b*-MMA$_{95}$)	10600	17400	1.6	6:142	0.94
3	p(BzMA$_{76}$-*b*-MMA$_{77}$)	22000	19500	1.9	76:114	0.73
4	p(BzMA$_{76}$-*b*-BzMA$_{18}$)	18000	16200	2.2		0.24[f]
5	p(MMA$_{15}$-*b*-BzMA$_{43}$)	9500	6000	2.2	15:29	0.97
6	p(MMA$_{40}$-*b*-BzMA$_{29}$)	9900	10100	1.7	40:12	0.57
7	p(MMA$_{40}$-*b*-MMA$_{50}$)	8800	8000	1.7		1.00
8	p(MMA$_{120}$-*b*-BzMA$_{26}$)	22000	17600	1.7	120:31	0.50
9	p(MMA$_{120}$-*b*-MMA$_{110}$)	21300	24000	1.5		0.83

[a] Ratio of monomers determined via SEC. [b] Corrected for conversion. [c] Determined using SEC, measured against PS standards in THF. [d] Determined using ^{1}H NMR based on $CO_2\underline{CH_2}Ph$ (BzMA, 4.8 ppm) and $CO_2\underline{CH_3}$ (MMA, 3.6 ppm) integrals. [e] Determined gravimetrically after 2 h reaction time. [f] 4.5 h reaction time.

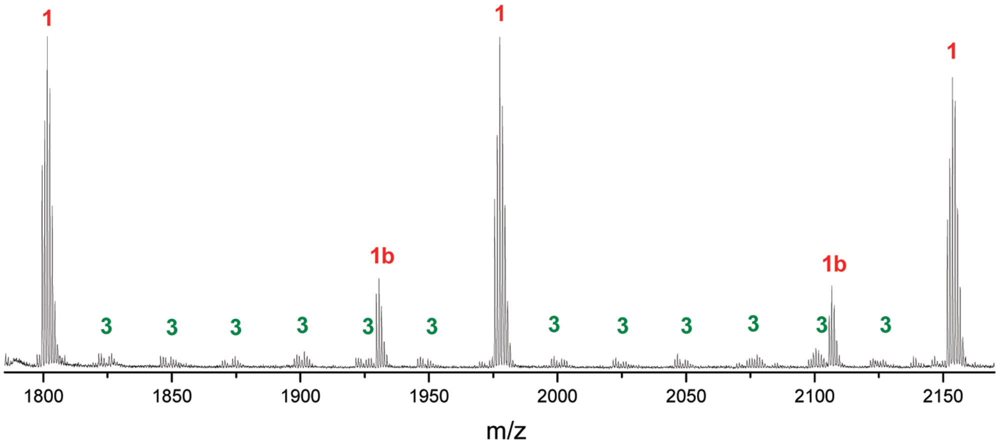


Figure 8. MALDI-ToF-MS of p(BzMA$_6$-*b*-MMA$_{47}$), where **1** = unreacted pBzMA$_6$, **1b** = hydrolyzed pBzMA macroinitiator, and **3** = p(BzMA-*b*-MMA).

between the peaks is 24 Da (consistent with the difference between two MMA units and one BzMA unit) and an end group corresponding to two protons and a connecting group originating from the lithium ester enolate (see overall scheme, Scheme 1). The most intense distribution (1) corresponds to unreacted macromonomer, but quantitative conclusions are difficult to draw from the intensity of the peaks due to the intrinsic nature of the MALDI-ToF-MS technique and the fact that at lower masses the block copolymer is less prevalent. In addition, a third distribution is seen (1b), which corresponds to the hydrolyzed macroinitiator. This suggests that **3** is highly efficient at preventing backbiting as the backbitten product is not observed in this spectra (contrary to the case where 1% THF in toluene is used to prevent backbiting, *vide supra*). The most important result, however, is that no pMMA is observed, which considering the high propensity and ease of pMMA to "fly" in MALDI-ToF-MS strongly suggests that reaction of **1** with the macromonomer is more efficient in the presence of **3**.

On the basis of the SEC and MALDI-ToF-MS data presented above, it can be concluded that the use of **3** in the polymerization of MMA from a pBzMA macromonomer is a successful route to synthesizing (stereo) block copolymers.

The limits of the polymerization technique have also been investigated by using longer macromonomers as macroinitiators. In entries 3 and 4 (Table 3), a benzyl methacrylate macromonomer with an M_n = 13 500 g/mol was used to prepare the macroinitiator for the polymerization of both MMA and BzMA. Note that here the use of a 1:1:2 molar ratio of macromonomer/**1**/**3** (as per entries 1, 2, and 5, Table 3) resulted in the incomplete conversion of the macromonomer into the macroinitiator (as evidenced by the residual vinylic protons attributed to the macromonomer seen by ^{1}H NMR). It was thought that this may arise from residual water trapped within the macromonomer due to the increased viscosity of higher molecular weight macromonomers. Indeed, the addition of a small amount of TIBA (typically 0.5 wt % compared to the macromonomer) to the macromonomer solution prior to the reactions alleviated this issue to a certain extent as TIBA acts as a scavenger for water. Although **3** can also act as a scavenger, the reactivity is much lower than that of TIBA. Further, TIBA is known to give no adverse effect in terms of the polymerization mechanism or tacticity.[60] In both cases, where MMA and BzMA were used as monomers for the second block, an increase in molecular weight is observed, accompanied by a slight decrease in polydispersity index.

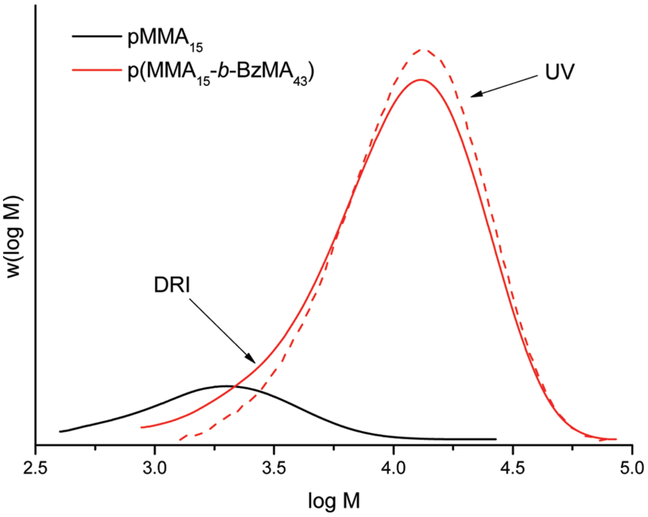


Figure 9. Molecular weight distribution of pMMA$_{15}$ and p(MMA$_{15}$-*b*-BzMA$_{43}$), normalized based on amount of polymer.

To investigate the versatility of this reaction toward macromonomers based on different methacrylic monomers, a short MMA-based macromonomer (pMMA$_{15}$), which has a similar molecular weight to pBzMA$_6$ of around 1000 g/mol, was used as the macroinitiator. A second block of BzMA was polymerized anionically from pMMA$_{15}$ as shown in entry 5 (Table 3). Again, an increase in molecular weight was seen (from 1700 to 6000 g/mol, Figure 9), and the DRI and UV detector signals of the block copolymer overlap well. MALDI-ToF-MS (Figure S4, Supporting Information) also confirms the presence of a block copolymer. Longer pMMA macromonomers (pMMA$_{40}$ and pMMA$_{120}$) can also be used to produce macroinitiators for both MMA and BzMA polymerization (entries 6−9, Table 3).

The use of **3** in the anionic polymerization of methacrylates using CCTP-derived macromonomers as macroinitiators proves to be a highly effective route to synthesizing block copolymers and has proven its versatility toward different methacrylic monomers as well as varying chain lengths.

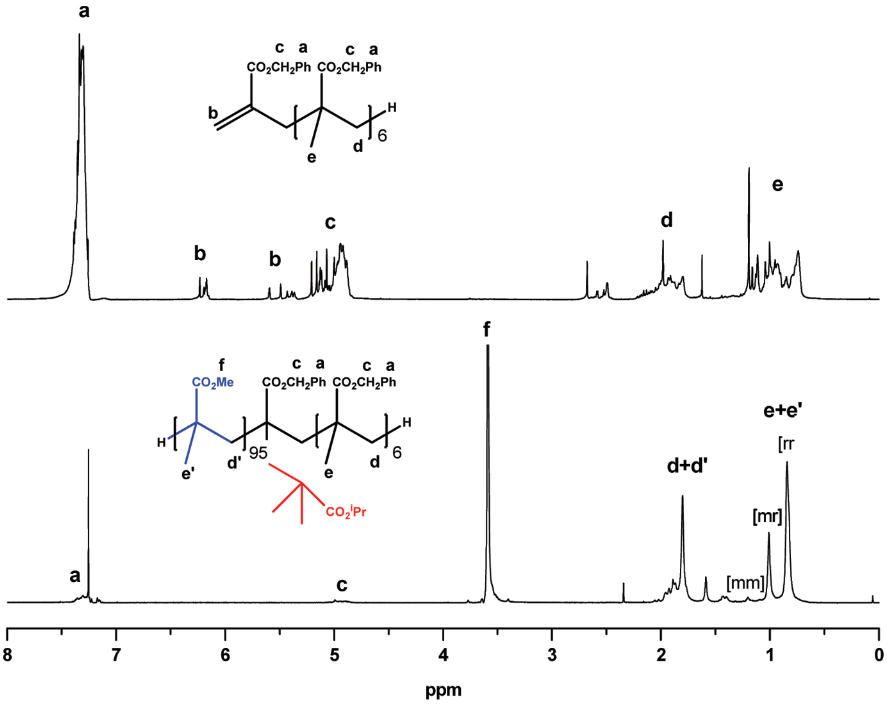


Figure 10. ^{1}H NMR (400 MHz, chloroform-d_6) of (a) p(BzMA)$_6$ macromonomer and (b) p(*a*BzMA)$_6$-*b*-(*s*MMA)$_{95}$.

As reported by Rodriguez-Delgado et al.,[60] the use of **3** in toluene for the polymerization of methacrylic monomers results in syndiotactic polymers. The tacticity of syndiotactic methacrylic polymers is characterized by an [rr] triad, which can be observed easily in ^{1}H NMR. At room temperature, pMMA with a tacticity of 71.3% [rr], 24.7% [mr], and 4.0% [mm] was obtained.[60] The polymerization of BzMA under these same conditions has not been investigated in the aforementioned article. However for completeness, pBzMA has been synthesized under the same conditions for the purposes of this article and using ^{1}H NMR the tacticity determined to be 77.5% [rr], 20.9% [mr], and 1.6% [mm]. Compared to the tacticity of pBzMA made via CCTP (60.6% [rr], 34.5% [mr], and 4.8% [mm], Figure S5), it is clear that a more syndiotactic pBzMA can be made under the anionic polymerization conditions described by Rodriguez-Delgado et al.

Figure 10 shows both the ^{1}H NMR spectra of p(*a*BzMA)$_6$ (a) and p(*a*-BzMA)$_6$-*b*-(*s*-MMA)$_{95}$ (b). The block copolymer made in entry 2 (Table 3) was chosen due to its high degree of polymerization of MMA compared to BzMA. In this way, the tacticity of the pMMA block made via anionic polymerization can be probed more accurately, with minimal interference of the atactic pBzMA macromonomer. As anticipated, pBzMA$_6$ is clearly atactic demonstrated by the methyl protons around 1 ppm (**e**) in Figure 10a. On the other hand, the methyl protons around 1 ppm of p(*a*-BzMA)$_6$-*b*-(*s*-MMA)$_{95}$ (Figure 10b) show a high concentration of racemic [rr] triads which is indicative of a highly syndiotactic material (71% [rr], 27% [mr], and 2% [mm]), which is comparable to the values obtained for the homopolymer of pMMA under these conditions.[60] The determination of the tacticity of the remaining polymers synthesized in Table 3 was investigated using ^{13}C NMR. This was necessary particularly for the BzMA−MMA copolymers, where the characteristic triads for pMMA and pBzMA were indistinguishable due to overlapping peaks. In fact, only the C═O region (175−179 ppm) in ^{13}C NMR allowed the adequate separation of the peaks and thus accurate determination of the tacticity of the copolymers. For the longer macroinitiators, the syndiotacticity calculated for the second block, regardless of the nature of the starting macromonomer or the monomer added for the second block, was 79−81% (Figure 11).[66] Although the starting macromonomers synthesized via CCTP (Table 1) generally have a slight tendency toward syndiotacticity ([rr] = 60−65%),[67] the second blocks show an increase in syndiotactoid character. The lower molecular weight macroinitiators show a slightly broader degree of syndiotacticity from [rr] = 74% to [rr] = 82% (Figure 12).[68] It is assumed that even higher syndiotacticities can be achieved when polymerizing at lower temperatures;[60] however, this is beyond the scope of the current paper.

Further examination of the tacticity of the two blocks was attempted using DSC. Unfortunately, only a marginal difference in T_g between the syndiotactic and atactic homopolymers was found, spanning the range in which an accurate T_g can be determined (Figure S6, Supporting Information). The relatively short chain lengths as well as the respective degrees of syndio- and atacticity are thought to play a role. Applying the Fox−Flory equation, a T_g of 103 and 117 °C for atactic and syndiotactic pMMA was found for the homopolymers made via CCTP and anionic polymerization, respectively (with similar molecular weights to that of the block copolymers). In addition, a T_m could not be identified even using a range of heating rates (1−20 °C/min), due to the difficulties in achieving thermal crystallization of syndiotactic pMMA.[69,70] Regardless, given that the homopolymers of pMMA and pBzMA made under these anionic conditions give rise to syndiotactic polymers and the NMR evidence presented in Figures 10−12, it is feasible to assume that the second blocks made via this route do indeed consist of methacrylic polymers with a syndiotactoid character.

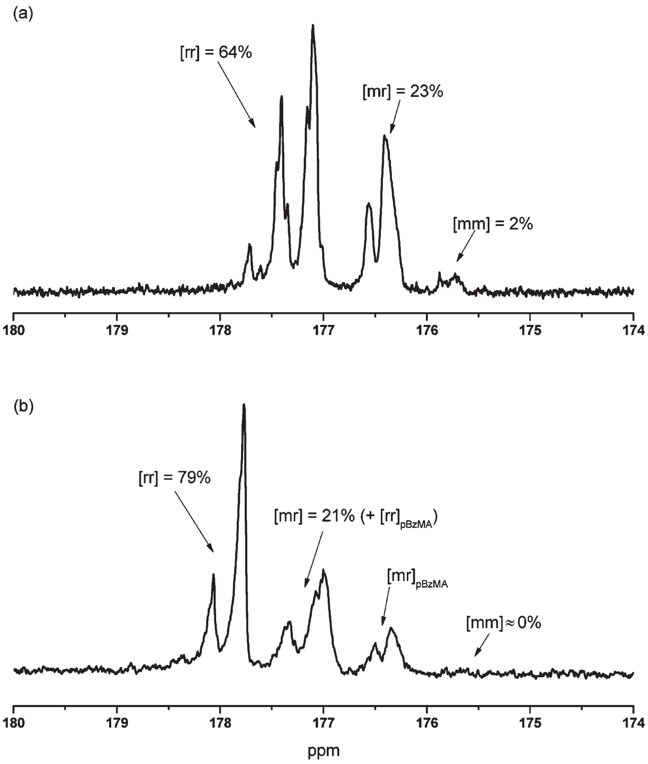


Figure 11. ^{13}C NMR (100 MHz, chloroform-d_6) showing the tacticity of (a) $pMMA_{15}$ and (b) p(MMA_{15}-*b*-$BzMA_{43}$).

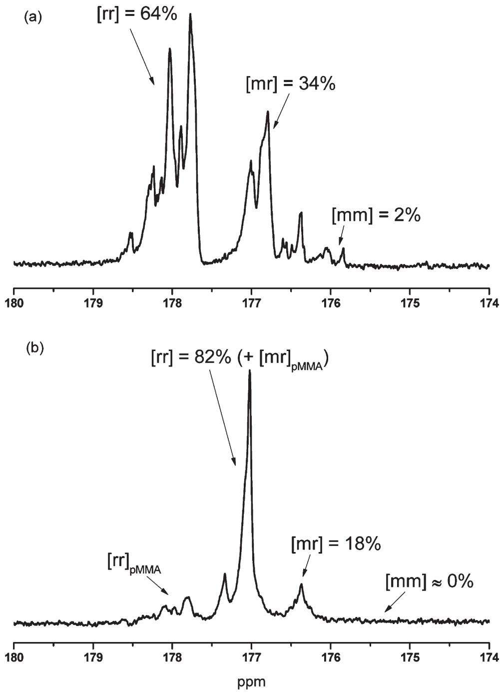


Figure 12. ^{13}C NMR (100 MHz, chloroform-d_6) showing the tacticity of (a) $pBzMA_{76}$ and (b) p($BzMA_{76}$-*b*-MMA_{77}).

■ CONCLUSION

The results of this work show a proof of principle that (stereo) block copolymers can be synthesized via a combination of catalytic chain transfer polymerization (CCTP) and anionic polymerization techniques. This provides a novel route to synthesizing block copolymers containing blocks of different tacticities. CCTP has been used to synthesize an atactic block; the second block was then made via anionic polymerization. The anionic polymerization was carried out either in the presence of lithium chloride and a toluene/THF solvent mixture to give an isotactoid block or in the presence of $MeAl(BHT)_2$ (**3**) to give rise to a second block syndiotactoid in nature. Although block copolymers could be made using both methods, the use of $MeAl(BHT)_2$ was much more efficient, particularly with respect to the conversion of the macromonomer into a macroinitiator as no evidence of homopolymerization of the second monomer was observed. The method also proved to be versatile toward macromonomers of different methacrylates and chain lengths. Although the synthetic procedures described in this paper require further optimization and/or purification steps (depending on the monomers and method used), we believe this to be the first example of atactic–syndiotactic and atactic–isotactic methacrylic block copolymers.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** ^{1}H NMR spectrum of the "macro"initiator derived from $pMMA_2$ and **1**, MALDI-ToF-MS of cyclic backbitten product of the macroinitiator, ^{1}H NMR of pMMA made anionically from **1** under a range of conditions, MALDI-ToF-MS spectrum of p(MMA_{15}-*b*-$BzMA_{43}$), and ^{1}H NMR of pBzMA made via CCTP and anionic polymerization and DSC of pMMA. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: j.p.a.heuts@tue.nl.

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(66) Second block tacticities, for example, p(MMA_{120}-*b*-$BzMA_{26}$) = 81:19:0; p(MMA_{120}-*b*-MMA_{110}) = 80:19:1; p($BzMA_{76}$-*b*-MMA_{77}) = 79:21:0; p($BzMA_{76}$-*b*-$BzMA_{18}$) = 81:19:0 ([rr]:[mr]:[mm]).

(67) Macromonomer tacticities, for example, $pMMA_{15}$ = 64:34:2; $pMMA_{120}$ = 60:39:1; $pBzMA_{6}$ = 25:40:34; $pBzMA_{76}$ = 65:33:2 ([rr]:[mr]:[mm]).

(68) Second block tacticities, for example p($BzMA_{6}$-*b*-MMA_{95}) = 74:21:1; p(MMA_{15}-*b*-$BzMA_{43}$) = 82:18:0 ([rr]:[mr]:[mm]).

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