Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Polymer 46 (2005) 8469–8482
polymer
www.elsevier.com/locate/polymer

Design of novel poly(methyl vinyl ether) containing AB and ABC block copolymers by the dual initiator strategy

Katrien V. Bernaerts, Filip E. Du Prez*

Department of Organic Chemistry, Polymer Chemistry Research Group, Ghent University, Krijgslaan 281(S4-bis), 9000 Ghent, Belgium

Received 29 October 2004; accepted 5 January 2005
Available online 9 June 2005

Abstract

A new set of block copolymers containing poly(methyl vinyl ether) (PMVE) on one hand and poly(*tert*-butyl acrylate), poly(acrylic acid), poly(methyl acrylate) or polystyrene on the other hand, have been prepared by the use of a novel dual initiator 2-bromo-(3,3-diethoxy-propyl)-2-methylpropanoate. The dual initiator has been applied in a sequential process to prepare well-defined block copolymers of poly(methyl vinyl ether) (PMVE) and hydrolizable poly(*tert*-butyl acrylate) (PtBA), poly(methyl acrylate) (PMA) or polystyrene (PS) by living cationic polymerization and atom transfer radical polymerization (ATRP), respectively. In a first step, the Br and acetal end groups of the dual initiator have been used to generate well-defined homopolymers by ATRP (resulting in polymers with remaining acetal function) and living cationic polymerization (PMVE with pendant Br end group), respectively. In a second step, those acetal functionalized polymers and PMVE-Br homopolymers have been used as macroinitiators for the preparation of PMVE-containing block copolymers. After hydrolysis of the tert-butyl groups in the PMVE-*b*-ptBA block copolymer, PMVE-*b*-poly(acrylic acid) (PMVE-*b*-PAA) is obtained. Chain extension of the AB diblock copolymers by ATRP gives rise to ABC triblock copolymers. The polymers have been characterized by MALDI-TOF, GPC and ^{1}H NMR.

Keywords: Poly(methyl vinyl ether); Dual initiator; Block copolymer

1. Introduction

The combination of different ‘living’ polymerization techniques to produce block copolymers represents a significant challenge due to the synthetic limitations of the various techniques. Traditional techniques for the preparation of block copolymers are linked up with some disadvantages: (a) chain coupling is limited to the coupling of oligomers [1]; (b) sequential monomer addition is limited to one polymerization mechanism and is restricted by relative monomer reactivities [2]; (c) mechanism transformation includes the preparation of a prepolymer with a functional group that can initiate a monomer with a different mechanism [3]. The disadvantage of this technique is the need for intermediate protection and transformation steps.

As mentioned in our previous article [4], the use of a dual initiator shows many advantages compared to classical methods for block copolymerization. A dual initiator contains two different initiation functions and each functionality is selective for a different polymerization mechanism. This approach provides the opportunity to combine very different types of monomers into one macromolecule. Several articles reported the use of a dual initiator for the combination of for instance ATRP-stable free radical polymerization (SFRP) [5,6], ring opening polymerization (ROP)-ATRP [4,7–9] and SFRP-ROP [10–12].

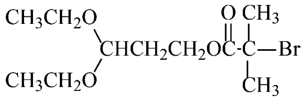
This report focuses on the synthesis and use of a new type of dual initiator (2-bromo-(3,3-diethoxy-propyl)-2-methylpropanoate in Scheme 1) for the preparation of well-defined block copolymers by the combination of two ‘living’ polymerization mechanisms: living cationic polymerization of methyl vinyl ether (MVE) [13–18] and living/controlled radical polymerization (ATRP) [19–22].

In general, the design of PMVE-containing block copolymers allows for the creation of interesting polymer architectures. First, the combination of the thermo-responsive

---

* Corresponding author. Tel.: +32 9 264 49 72; fax: +32 9 264 45 03.
E-mail address: filip.duprez@ugent.be (F.E. Du Prez).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.01.103



Scheme 1. Dual initiator 2-bromo-(3,3-diethoxy-propyl)-2-methylpropanoate.

PMVE with poly(acrylic acid) (PAA) provides multi-responsive (pH and temperature sensitive) block copolymers. Polymer structures that can be triggered by several stimuli are recently subject of extensive studies because of their potential application in drug delivery systems, in separation systems, etc. [23]. Most of the studies about pH/temperature sensitive multicomponent materials have been focused on block, graft and random copolymers or hydrogels with P(M)AA as a pH sensitive component and poly(*N*-isopropylacrylamide) or *N*-substituted poly(acrylamides) as a temperature sensitive segment [24–28]. On the other hand, PMVE is another example of a thermo-responsive polymer that shows a lower critical solution temperature (LCST) behavior in water around body temperature [29]. Secondly, the combination of PMVE with polystyrene (PS) has been investigated for many decades as one of the well-known examples of miscible polymer blends [30,31]. Although not part of this study, the corresponding PMVE-*b*-PS copolymer structures could be used to check for the influence of the polymer architecture on the miscibility behavior of PMVE and PS. PMVE-*b*-PS has been synthesized earlier by Sawamoto et al. via sequential monomer addition [32] and chain coupling techniques [33].

The first step in the preparation of block copolymers based on the dual initiator strategy, is the synthesis of well-defined homopolymers, which can be applied as a macroinitiator in the next step. The living cationic homopolymerization of MVE is performed with the acetal end group of the dual initiator as initiating site, based on the procedure described previously [13–18]. Because of the incorporation of the dual initiator, the resulting PMVE still contains an activated bromide function (PMVE-Br). Also, the ATRP homopolymerization of *tert*-butyl acrylate with the CuBr/PMDETA catalyst system from the bromoisobutyrate group of the dual initiator, results in ptBA with a remaining acetal function (ptBA-acetal), originating from the dual initiator. The second step in the preparation of block copolymers from the dual initiator, is the use of those well-defined PMVE-Br and ptBA-acetal homopolymers as macroinitiators for, respectively, ATRP of several monomers and cationic polymerization of MVE. Finally, the synthesis of ABC block copolymers via chain extension of the AB block copolymers will be described.

To the best of our knowledge, the synthesis of many of the block copolymers in this paper is described for the first time. The versatility of the dual initiator strategy will be clearly demonstrated.

2. Experimental part

2.1. Materials

tBA (Fluka, 98+%) was purified by vacuum distillation (60 °C/60 mmHg). The inhibitor in styrene (Acros, 99%) was removed by passing the monomer over basic aluminium oxide. MA (Acros, 99%) (79–81 °C) and MMA (Avocado, 99%) (100 °C) were distilled prior to use.

CuBr (Aldrich, 98%) and CuCl (Aldrich, 99+%) were purified by stirring with acetic acid, followed by washing with, respectively, methanol and ethanol, and finally by drying under vacuum at 70 °C. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, Acros, 99+%) was distilled (85–86 °C/12 mmHg). Toluene (Fisher Chemicals, HPLC) and diethyl ether (Pancreac, 99.7%) were distilled over sodium prior to use. ZnI_2 (Aldrich, 99.99+%) was dried under vacuum for 24 h before use. MVE (kindly donated by BASF, Ludwigshafen) was passed through a CaH_2 trap for drying purposes. Triethylamine (Et_3N, Riedel-de Haën, pure) was distilled over CaH_2 while methanol (MeOH, Acros, HPLC) was distilled over CaO before use. Dichloromethane (Fisher Chemicals, HPLC) was extracted three times with pure sulfuric acid, and washed three times with a concentrated solution of sodium hydroxide (10% w/v). Then, it was washed several times with distilled water until the pH was neutral. The purified dichloromethane was dried for several hours on magnesium sulfate, filtered off, and then refluxed for 2 h over calcium hydride. Dichloromethane was distilled, stored over calcium hydride and refluxed over calcium hydride prior to use. 2-Bromoisobutyryl bromide (Aldrich, 98%) was distilled before use (53 °C/18 mmHg). Tris(2-(dimethylamino)ethyl)amine (Me_6-TREN) was prepared from tris(2-aminoethyl)amine (98%, Aldrich), as described earlier [34]. 3,3-Diethoxy-1-propanol (Aldrich, 98%), 4-dimethyl-aminopyridine (Acros, 99%), trimethylsilyl iodide (TMSI, Aldrich, 97%) and trifluoroacetic acid (TFA) (Acros, 99%) were used as received.

2.2. Synthesis of dual initiator 2-bromo-(3,3-diethoxy-propyl)-2-methylpropanoate (BrDEP)

To a dichloromethane solution (300 ml) of 3,3-diethoxy-1-propanol (10 ml, 63.5 mmol), 4-dimethyl-aminopyridine (0.0388 g, 0.32 mmol) and Et_3N (11 ml, 79.4 mmol), 2-bromoisobutyryl bromide (8.24 ml, 66.7 mmol) was added dropwise at 0 °C. The solution was stirred at that temperature for 15 min and was subsequently allowed to warm up to room temperature. It was then stirred for four more hours. The organic layer was successively washed with acidic (HCl) ice water, three times with saturated aqueous sodium hydrogen carbonate, twice with brine and finally with water. After being dried with $MgSO_4$, the organic phase was evaporated under reduced pressure. The crude product was purified by column chromatography (cyclohexane/ethylacetate 18/2) yielding 13.2 g (70%) of dual initiator as a light yellow liquid.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.20 (t, 6H, ($CH_3CH_2O)_2CH$–), 1.93 (s, 6H, –$C(CH_3)_2$), 3.51 and 3.66 (m, 4H, $CH(OCH_2CH_3)_2$), 4.66 (t, 1H, –CH–), 2.00 (q, 2H, –$CHCH_2$–), 4.27 (t, 2H, –CH_2O–).

APT NMR ($CDCl_3$, 125 MHz) δ (ppm): 15.2 (2C, ($CH_3CH_2O)_2CH$–), 62.4 (2C, $CH(OCH_2CH_3)_2$), 99.9 (1C, –CH–), 32.7 (1C, –$CHCH_2$–), 61.6 (1C, –CH_2O–), 171.4 (1C, –C(O)O–), 55.7 (1C, –$C(CH_3)_2$), 30.6 (2C, –$C(CH_3)_2$). TLC (cyclohexane/ethylacetate: 18/2): ratio to front (R_f) = 0.3. IR (KBr pellets, neat) ν (cm^{-1}): 2976 (m), 2931, 2899 (m), 1737 (vs) and 1110 (ester), 1464 (m), 1389 (m) and 1372, 1166 (s) and 1060 (s) (acetal ether), 1279 (s). GC-MS (*m/z*): 251/253 (M^+-OCH_2CH_3); 149/151; 121/123; 103; 85; 75; 57; 47. Anal. Calcd for $C_{11}H_{21}BrO_4$: C (44.46%) H (7.12%) Br (26.89%) O (21.53%). Found: C (44.71%) H (7.24%) Br (27.50%) O (21.11%).

2.3. ATRP of tert-butyl acrylate (tBA) with the dual initiator

A representative experiment (theoretical degree of polymerization of 25) is as follows: tBA (10 ml, 68.89 mmol), acetone (3.34 ml, 25 vol%) and PMDETA (575 µl, 2.76 mmol) were added into a dried two-neck flask and degassed by three freeze-thaw cycles. CuBr (395.3 mg, 2.76 mmol) was added under nitrogen and the reaction mixture was stirred until it turned homogeneously green. After the addition of the dual initiator (662 µl, 2.76 mmol), the flask was placed in an oil bath at 40 °C under reflux. The samples used for determining polymerization conversion and molecular weight were withdrawn from the polymerization system at definite time intervals and measured by ^{1}H NMR and GPC. Polymerization was stopped by cooling the flask in liquid nitrogen after a certain reaction time. Afterwards, the mixture was dissolved in acetone and was subsequently passed through a neutral aluminium oxide column for catalyst removal. After several precipitations of the resulting polymer in 1/1 v/v MeOH/water mixture, the white polymer was collected and dried by azeotropic distillation with toluene under reduced pressure at 40 °C (yield = 56%).

For the polymerization with $[M]_0/[I]_0 = 150$, the same procedure was followed, but at a higher temperature (70 °C) and with less acetone (15 vs 25 vol%).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.13 (s, 6H, –$C(CH_3)_2$), 1.20 (t, 6H, CH_3CH_2–), 1.3–2 (broad, 11H, CH_2 and $C(CH_3)_3$ protons of ptBA), 2.25 (s, 1H, CH protons of ptBA), 3.55 and 3.66 (4H, CH_3CH_2–), 4.11 (m, 3H, –$CH_2OC{=}O$– and R_2CHBr), 4.60 (t, 1H, –$CH(OCH_2CH_3)_2$).

IR (KBr pellets, CH_2Cl_2) ν (cm^{-1}): 3054–2934 (s), 1725 (s) (C=O, ester), 1445 (m), 1422 (m), 1393 and 1368 (asymmetric doublet for tBu), 1265 (w), 1151 and 1054 (s) (ν_{as} C–O–C).

2.4. Polymerization of MVE from the dual initiator by a semi-continuous reaction system

A typical polymerization procedure for $[M]_0:[I]_0 = 35$ was as follows: 1.653 ml (6.89 mmol) of BrDEP and 1.176 ml (8.26 mmol) of TMSI were added to 150 ml of dry toluene under nitrogen atmosphere at −40 °C. After 10 min, an initial amount of MVE (0.9 g, 0.016 mol) was added. The polymerization was started by the addition of ZnI_2 (219.8 mg, 0.69 mmol, dissolved in 4 ml of ether). At the same time, the addition of gaseous MVE was continued at a 50 g/h feed rate until the desired ratio of $[M]_0:[I]_0$ was reached (total 15 g, 0.258 mol). After 2 h, the reaction was terminated by the addition of methanol (1.395 ml, 34.44 mmol) and triethylamine (6.893 ml, 68.87 mmol).

The polymer solution was washed three times with 10% aqueous $Na_2S_2O_3$, then three times with deionized water, and dried over $MgSO_4$. The solution was filtered and the solvent was evaporated. The resulting yellow viscous liquid was dried under vacuum (yield: 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.18 (t, 3H, –OCH_2CH_3), 1.40–1.90 (2H, CH_2 protons of PMVE), 1.93 (s, 6H, –$C(CH_3)_2$–), 3.25–3.60 (broad, 4H, CH and CH_3 protons of PMVE), 4.30 (m, 2H, –OCH_2–), 4.55 (m, 1H, –$CH(OCH_2CH_3)_2$).

IR (KBr pellets, CH_2Cl_2) ν (cm^{-1}): 2983–2825 (m), 1732 (w) (C=O, ester from initiator), 1423 (m), 1382 (m), 1265 (m), 1187 and 1108 (s) (ν_{as} C–O–C).

2.5. Preparation of ptBA-b-PMVE by cationic polymerization of MVE with ptBA-acetal macroinitiator

The procedure is similar to that for the MVE homopolymerization. 0.5739 g (0.29 mmol) of ptBA-acetal, dried azeotropically with toluene under reduced pressure, and 49 µl (0.34 mmol, for experiment 1 in Table 1) or 61 µl (0.43 mmol, for experiment 2 in Table 1) of TMSI were added to 25 ml of dry toluene under nitrogen atmosphere at −40 °C. After 10 min, an initial amount of MVE (0.2 g, 2.69 mmol) was added. The polymerization was started by the addition of ZnI_2 (9.2 mg, 0.029 mmol, dissolved in 1 ml of ether). At the same time, the addition of gaseous MVE was continued at a 50 g/h feed rate until the desired ratio of $[M]_0/[I]_0$ was reached (total 2.5 g, 43.04 mmol). After some hours, the reaction was terminated by methanol (58 µl, 1.43 mmol) and triethylamine (287 µl, 2.87 mmol). The purification procedure is identical to that of PMVE-Br homopolymers.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm): 1.13 (s, 6H, –$C(CH_3)_2$–), 1.17 (t, 3H, CH_3CH_2O–), 1.30–1.90 (broad, 13H, CH_2 protons of PMVE and $CH_2/C(CH_3)_3$ protons of ptBA), 2.22 (s, 1H, CH protons of ptBA), 3.25–3.60 (broad, 4H, CH and CH_3 protons of PMVE), 4.13 (m, 3H, $CH_2OC{=}O$– and R_2CHBr), 4.54 (t, 1H, –$CH(OCH_3)_2$).

IR (KBr pellets, CH_2Cl_2) ν (cm^{-1}): 3055–2886 (m),

Table 1
Synthesis of homopolymers and diblock copolymers via the combination of cationic polymerization of MVE and ATRP of tBA, styrene or MA

Exp	Initiator	Monomer	$[M]_0/[I]_0$	Acetone (vol%)	T (°C)	Time (min)	Conversion (%)	$M_{n,th}$ [c]	$M_{n,NMR}$	$M_{n,GPC}$ [k]	M_w/M_n [k]	PMVE (mol%) [a]
ptBA-acetal (ptba15)	BrDEP	tBA	25	25	40	79	58 [a]	2200	2100 [d]	2000	1.12	0
PMVE-Br (pmve10)	BrDEP	MVE	37.5	–	−40	125	83 [b]	3300	2100 [e]	2900	1.14	100
1	ptBA-acetal	MVE	150	–	−40	180	36 [b]	5200	4700 [f]	6100	1.21	82
2	ptBA-acetal	MVE	150	–	−40	240	56 [b]	6900	5100 [f]	6100	1.10	83
3	PMVE-Br	tBA	10	50	50	10	28 [a]	2400	2400 [f]	3100	1.11	91
4	PMVE-Br	tBA	15	50	70	64	62 [a]	3300	3400 [f]	4700	1.06	73
5	PMVE-Br	tBA	150	33	70	180	27 [a]	7300	6800 [f]	7900	1.06	42
6	PMVE-Br	tBA	150	33	70	360	72 [a]	16,000	17,200 [f]	18,400	1.06	19
7 [i]	PMVE-Br	MA	150	–	40	190	20 [a]	4600	4700 [g]	5800	1.11	53
8 [j]	PMVE-Br	MA	150	–	40	60	77 [a]	15,050	14,700 [g]	21,600	1.05	14
9	PMVE-Br	Styrene	150	–	100	4.5	4 [a]	2700	2700 [h]	4700	1.12	74
10	PMVE-Br	Styrene	150	–	100	15	10 [a]	3750	4750 [h]	6300	1.09	38
11	PMVE-Br	Styrene	150	–	100	27.5	26 [a]	6200	6500 [h]	8400	1.07	27
12	PMVE-Br	Styrene	150	–	100	75	53 [a]	10,500	10,100 [h]	14,200	1.08	16

[a] Determined by ^{1}H NMR data.

[b] Determined gravimetrically.

[c] $M_{n,th}=([M]_0/[I]_0)\times M_{monomer}\times\%$ conversion $+M_{initiator}$ where $[M]_0$ and $[I]_0$ are the initial concentrations of the monomer and initiator, respectively; $M_{monomer}$ and $M_{initiator}$ are the molecular weights of the monomer and initiator.

[d] $M_{n,NMR}=(6I_{1.30-2}(\text{ptBA})/11I_{1.13}(\text{end group}))\times M_{tBA}+M_{BrDEP}$ where I is the integral value (subscript is ppm value) and M stands for the molar mass.

[e] $M_{n,NMR}=(2I_{3.25-3.60}(\text{PMVE})/4I_{4.29}(\text{end group}))\times M_{MVE}+M_{BrDEP}$.

[f] $M_{n,NMR}=(9I_{1.30-1.90}(\text{ptBA})/11I_{1.13-1.17}(\text{end groups}))\times M_{tBA}+M_{n,NMR}(\text{PMVE-Br})$ where $M_{n,NMR}$(PMVE-Br) is the molecular weight of the initial macroinitiator.

[g] $M_{n,NMR}=(2I_{2.30}(\text{PMA})/1I_{4.13}(\text{end group}))\times M_{MA}+M_{n,NMR}(\text{PMVE-Br})$.

[h] $M_{n,NMR}=(6I_{6-7.5}(\text{PS})/5I_{0.9}(\text{end group}))\times M_{styrene}+M_{n,NMR}(\text{PMVE-Br})$.

[i] [MA]:[PMVE-Br]:[Me_6TREN]:[CuBr] = 150:1:0.15:0.15 in bulk.

[j] [MA]:[PMVE-Br]:[Me_6TREN]:[CuBr]:[$CuBr_2$] = 150:1:0.5:0.5:0.1 in 20 vol% toluene.

[k] GPC with $CHCl_3$ as an eluent and calibrated with PS standards.

1725 (s) (C=O, ester), 1478 (w), 1448 (w), 1393 and 1368 (asymmetric doublet for tBu), 1266 and 1152 (s) (ν_{as} C–O–C).

2.6. Preparation of PMVE-b-ptBA by ATRP of tBA with PMVE-Br macroinitiator

In a typical procedure, PMVE-Br macroinitiator, tBA, PMDETA (molar ratio tBA:PMVE-Br:PMDETA = 150:1:1 or 10:1:1) and acetone as a solvent (50 vol% for $[M]_0:[I]_0=10$ and 33 vol% for $[M]_0:[I]_0=150$) were weighed into a flame-dried round-bottom flask equipped with a stirring bar. After deoxygenation with three freeze-thaw cycles, CuBr (molar ratio PMDETA:CuBr = 1:1) was added under nitrogen. When the mixture turned completely homogeneous and green, the mixture was heated under reflux to 50 °C ($[M]_0:[I]_0=10$) or 70 °C ($[M]_0:[I]_0=150$) and stirred for a given polymerization time. After polymerization, the reaction mixture was cooled with liquid nitrogen, diluted with acetone and filtered through a column of neutral aluminium oxide. The resulting polymer was precipitated in 1/1 v/v MeOH/water mixture for $[M]_0:[I]_0=150$ yielding a white powder. Residual monomer and solvent were evaporated at 40 °C under vacuum (15 mbar) for $[M]_0:[I]_0=10$ and 15, resulting in a yellow, viscous liquid. ^{1}H NMR and IR data are identical to those for ptBA-*b*-PMVE.

2.7. Preparation of PMVE-b-PS by ATRP of styrene with PMVE-Br macroinitiator

PMVE-Br macroinitiator, styrene and PMDETA were added into a round flask (molar ratio styrene:PMVE-Br:PMDETA = 150:1:1). The mixture was degassed with three freeze-thaw cycles and CuBr (molar ratio PMDETA: CuBr = 1:1) was added under nitrogen stream. The flask was then sealed and immersed in an oil bath at 100 °C for a certain time. The polymerization was stopped by cooling with liquid nitrogen and exposing the reaction mixture to air. After polymerization, the catalyst was removed by an adsorption filtration through a neutral alumina column, the resulting polymer was precipitated from THF into MeOH and the white powder (yellow viscous liquid at very low PS-content) was dried under vacuum.

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.91 (m, 6H, $-C(CH_3)_2-$), 1.14 (t, 3H, CH_3CH_2O-), 1.25–2.25 (broad, 5H, CH_2 protons of PMVE and CH_2/CH protons of PS), 3.25–3.60 (broad, 4H, CH and CH_3 protons of PMVE), 4.33–4.65 (d, 2H, $-CH(OCH_3)_2$ and $-CH(Ph)Br$), 6.24–7.24 (broad, 5H, phenyl protons of PS).

IR (KBr pellets, CH_2Cl_2) ν (cm^{-1}): 3082, 3060 and 3026 (m), 2925 and 2821 (s), 1946, 1875 and 1807 (w) (overtones aromatic groups), 1727 (w) (C=O, ester from initiator), 1601 (m), 1583 (w), 1493 and 1454 (s) (ν C–C aromatic), 1379 (s), 1265 and 1187 (s) (ν_{as} C–O–C).

2.8. Preparation of PMVE-b-PMA by ATRP of MA with PMVE-Br macroinitiator

The desired amounts of MA (1.5 ml, 16.7 mmol), PMVE-Br macroinitiator (0.2221 g, 0.111 mmol), Me_6TREN (0.0128 g, 0.056 mmol) and 20 vol% toluene were introduced to a flask equipped with a magnetic stirring bar. The flask was degassed three times by freeze/pump/thaw cycles and CuBr (0.008 g, 0.056 mmol) and $CuBr_2$ (0.0025 g, 20 mol% relative to CuBr) were added under nitrogen atmosphere. The reaction was performed in an oil bath thermostated at 40 °C and stopped after a certain reaction time by cooling the flask in liquid nitrogen. The polymer was dissolved in THF and then filtered through a column of alumina to remove the copper catalyst. It was precipitated into cold methanol and then the colorless polymer was dried under vacuum.

^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.07–1.21 (m, 9H, $–C(CH_3)_2–$ and $CH_3CH_2O–$), 1.34–2.02 (broad, 4H, CH_2 protons of PMVE and CH_2 protons of PMA), 1.30 (s, 1H, CH protons of PMA), 3.25–3.60 (broad, 4H, CH and CH_3 protons of PMVE), 3.65 (s, 3H, OCH_3 protons of PMA), 4.12 (t, 2H, $CH_2OC{=}O–$), 4.23 (t, 1H, R_2CHBr), 4.54 (t, 1H, $–CH(OCH_3)_2$).

IR (KBr pellets, CH_2Cl_2) ν (cm^{-1}): 2983–2837 (s), 1738 (vs) (C=O, ester of PMA), 1440 (s), 1380 (m), 1336 (m), 1260–1165 (s) (ν C–O), 1113 and 1082 (m) (ν_{as} C–O–C).

2.9. Chain extension experiments

2.9.1. Synthesis of PMVE-b-ptBA-b-PS by ATRP of styrene from PMVE-b-ptBA-Br

ATRP of styrene from PMVE-*b*-ptBA-Br was performed at 100 °C in a similar way as for the preparation of PMVE-*b*-PS diblock copolymers. Molar ratio of styrene:PMVE-Br:PMDETA:CuBr equals to 500:1:1:1. The obtained triblock copolymer (white powder) was purified similarly to PMVE-*b*-PS.

^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.15 (s, 6H, $–C(CH_3)_2–$), 1.20 (t, 3H, $CH_3CH_2O–$), 1.23–2.13 (broad, 16H, CH_2 protons of PMVE, $CH_2/C(CH_3)_3$ protons of ptBA and CH_2/CH protons of PS), 2.22 (s, 1H, CH protons of ptBA), 3.25–3.60 (broad, 4H, CH and CH_3 protons of PMVE), 4.16 (t, 2H, $–CH_2OC{=}O–$), 4.50 (d, 1H, R_2CHBr), 6.24–7.24 (broad, 5H, phenyl protons of PS).

IR (KBr pellets, CH_2Cl_2) ν (cm^{-1}): 3060–3820 (s) (ν C–H), 1947, 1880 and 1803 (w) (overtones aromatic groups), 1732 (s) (C=O ester of ptBA), 1602 (m), 1494 and 1454 (s) (ν C–C aromatic), 1393 and 1367 (s) (asymmetric doublet for tBu), 1257 and 1150 (s) (ν C–O), 1106, 1030.

2.9.2. Synthesis of PMVE-b-ptBA-b-PMMA by ATRP of MMA from PMVE-b-ptBA-Br

Toluene (50 vol%), MMA (0.5 ml, 4.3 mmol) and PMDETA (3 μl, 0.0145 mmol) were added into a flask containing the PMVE-*b*-ptBA-Br macroinitiator (0.1188 g, 0.0145 mmol). After the macroinitiator was completely dissolved, CuCl (1.4 mg, 0.0145 mmol) was added. The mixture was degassed by freeze-pump-thaw for three times and then placed in an oil bath with a preset temperature of 90 °C. After polymerization, the mixture was opened to air and cooled in liquid nitrogen. The catalyst was removed by passing the polymer solution (after dilution with THF) through a short aluminium oxide column. The crude polymer was purified by precipitation in pentane and the white powder was dried under vacuum.

^1H NMR ($CDCl_3$, 300 MHz) δ (ppm): 0.63–1.32 (3 broad singlets, 3H, CH_3 protons of PMMA), 1.30–2.12 (broad, 15H, CH_2 protons of PMVE, $CH_2/C(CH_3)_3$ protons of ptBA and CH_2 protons of PMMA), 2.22 (s, 1H, CH protons of ptBA), 3.25–3.50 (broad, 4H, CH and CH_3 protons of PMVE), 3.60 (s, 3H, OCH_3 protons of PMMA), 4.14 (m, 2H, $–CH_2OC{=}O–$).

IR (KBr pellets, CH_2Cl_2) ν (cm^{-1}): 2990–2846 (m), 1731 (vs) (C=O, ester), 1485 (m), 1450 (m), 1390 and 1367 (w) (asymmetric doublet for tBu), 1272 (m), 1242 (m), 1192 and 1149 (s) (ν C–O), 1063 (w), 988 and 962 (w).

2.9.3. Synthesis of PMVE-b-PS-b-ptBA by ATRP of tBA from PMVE-b-PS-Br

A procedure was followed as for PMVE-*b*-ptBA. The reaction was performed with molar ratios tBA:PMVE-*b*-PS-Br:PMDETA:CuBr = 200:1:1:1 in 20 vol% acetone at 70 °C. ^1H NMR and IR data are identical to those for PMVE-*b*-ptBA-*b*-PS.

2.10. Hydrolysis of ptBA blocks in PMVE-b-ptBA

The PMVE-*b*-ptBA block copolymer (for example PMVE-*b*-ptBA 6) (5 g, 35.26 mmol ester) was dissolved in dichloromethane (50 ml) and a five-fold molar excess of trifluoroacetic acid (13.10 ml, 0.176 mol) with respect to the tBA ester groups was added. The mixture was stirred at room temperature for 24 h. During the hydrolysis, the resulting PMVE-*b*-PAA block copolymer precipitated in CH_2Cl_2 gradually if the PMVE content was not too high. In the next step, solvent and TFA were removed by rotary evaporation with a membrane pump. The polymer was dissolved in THF and precipitated in cold pentane twice. The final polymer was dried under vacuum. The hydrolysis of the block copolymers was confirmed by NMR and FT-IR analysis. ^1H NMR (DMSO-d_6, 500 MHz) δ (ppm): 1.09 (9H, $CH_3CH_2O–$ and $C(CH_3)_3–$), 1.25–2 (broad, 4H, CH_2 of PAA and CH_2 of PMVE), 2.21 (s, 1H, CH of PAA), 3.20–3.60 (broad, 4H, CH and CH_3 protons of PMVE), 4.03 (m, 3H, $–CH_2OC{=}O–$ and R_2CHBr), 12.25 (s, 1H, $COOH$ of PAA).

IR (KBr pellets, THF) ν (cm^{-1}): 3700–2300 (broad, carboxylic acid), 1719 (s), 1450, 1244–1176 (ν_{as} C–O–C), 1054.

3. Characterization

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM500 or Bruker Avance 300 spectrometer, and were measured in $CDCl_3$ or DMSO-d_6 at room temperature. Gel permeation chromatography (GPC) was performed on a Waters instrument, using a refractive index detector (2410 Waters), equipped with 10^3–10^4–10^5 Å serial columns. PS standards were used for calibration with $CHCl_3$ as eluent at a flow rate of 1.5 ml/min. MALDI-TOF spectra were recorded with a PerSeptive Biosystems Voyager-DE STR MALDI-TOF spectrometer equipped with 2 m linear and 3 m reflector flight tubes and a 337 nm nitrogen laser (3 ns pulse). All mass spectra were obtained with an accelerating potential of 20 kV in positive ion and linear or reflectron mode. The data were processed with the Polymerix software. Dithranol (20 mg/ml THF) was used as a matrix, sodium trifluoroacetate (NaTFA) (5 mg/ml THF) as cationating agent. Polymer samples were dissolved in THF (1 mg/ml THF).

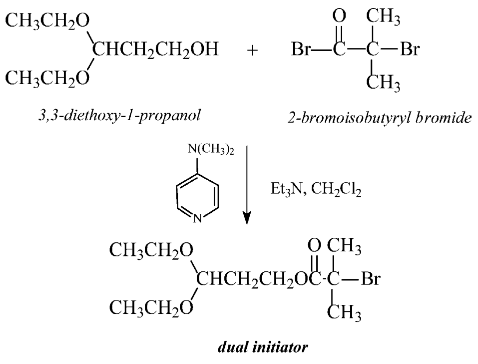
For Karl Fisher titrations, a Mitsubishi CA-06 moisture meter was used. IR spectra were recorded on a Perkin–Elmer 1600 series FTIR apparatus.

4. Results and discussion

4.1. Synthesis of the dual initiator

A novel dual initiator 2-bromo-(3,3-diethoxy-propyl)-2-methylpropanoate (BrDEP) was prepared by a 4-dimethylaminopyridine (DMAP) catalyzed acylation reaction between 3,3-diethoxy-1-propanol and 2-bromoisobutyryl bromide (70% yield) (Scheme 2).

Our approach to prepare PMVE-*b*-ptBA and PMVE-*b*-PAA block copolymers (Scheme 3) is based on a two-step sequence consisting of (1) the synthesis of well-defined macroinitiators ptBA-acetal and PMVE-Br, which are used for (2) the initiation of cationic polymerization of MVE and ATRP of tBA, respectively. PMVE-*b*-PAA block copolymers are obtained after hydrolysis of the tBA groups in PMVE-*b*-ptBA.



Scheme 2. Reaction scheme for the synthesis of dual initiator 2-bromo-(3,3-diethoxy-propyl)-2-methylpropanoate.

4.2. Synthesis of ptBA-acetal by ATRP

Acetal-terminated ptBA macroinitiator was synthesized using dual initiator BrDEP and the CuBr/PMDETA (1/1 molar ratio) catalytic system (Scheme 3(b)). Some characteristics of the acetal functionalized ptBA are collected in Table 1 (experiment ptBA-acetal).

The presence of the initiating moiety and the bromine end group were verified by ^1H NMR and MALDI-TOF. The 6/4 molar ratio in NMR for $–C(CH_3)_2Br$ at 1.13 ppm and for $(CH_3CH_2O)_2–$ at 3.55–3.66 ppm, provides proof of the preservation of the acetal end group. Moreover, no aldehyde peaks due to degradation of the acetal with liberation of ethanol could be observed.

The main series of peaks in the MALDI-TOF spectrum (Fig. 1(a) and(b)) is separated by 128 Da (tBA monomer unit) and can be attributed to the desired Br and acetal functionalized ptBA macroinitiator. The minor series with monoisotopic peak at 1650.01 Da in Fig. 1(b) is assigned to ptBA ($n=11$) with a hydrogen end group instead of a Br end group. Bednarek et al. described earlier that this side series is attributed to proton abstraction by exchange of a hydrogen from PMDETA with the Br end group from the polymer [35]. The preservation of the acetal end group during ATRP is crucial as it will be applied for MVE initiation in the next step. M_n calculated by MALDI in linear mode (2000 Da) is in good agreement with M_n calculated by NMR (Table 1). The monomodal and narrow GPC trace of the macroinitiator is shown in Fig. 2(a).

Fig. 3(a) shows the kinetic plots of the ATRP of tBA with

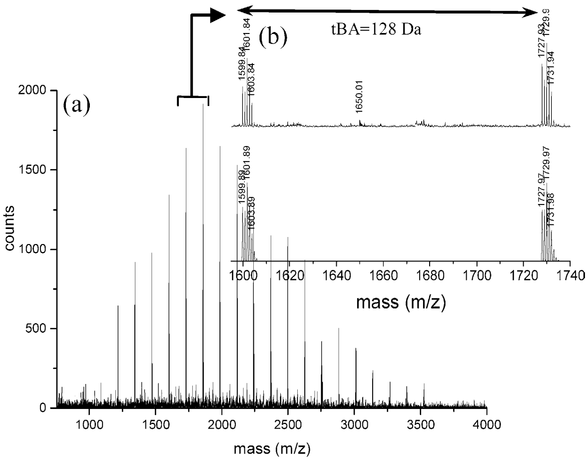
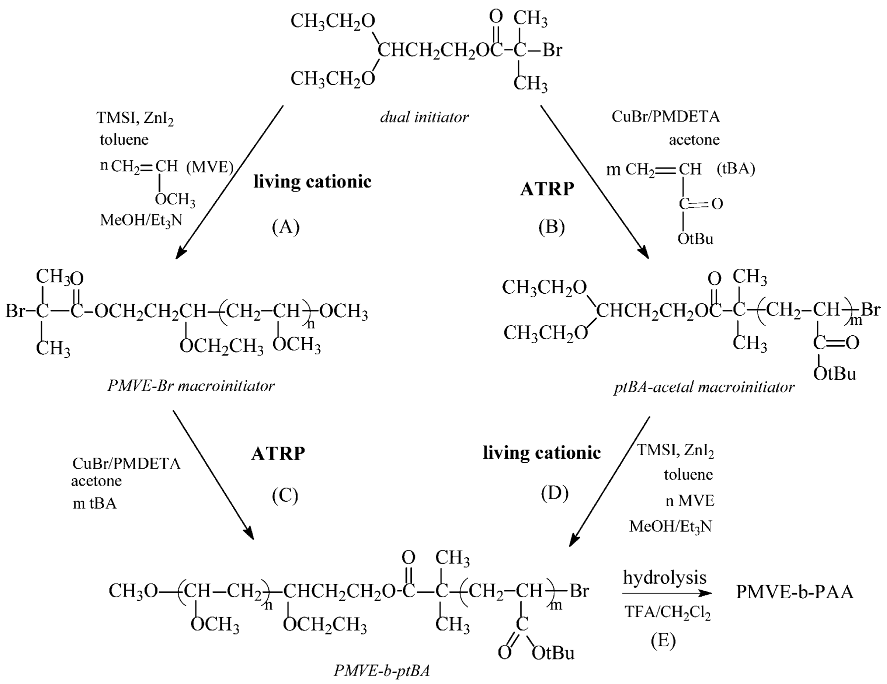


Fig. 1. Reflectron mode MALDI-TOF of ptBA-acetal macroinitiator (ptBA13) with dithranol/NaTFA (a) complete spectrum and (b) determination of the chain-end structures, with experimental (top) and simulated (bottom) isotope distributions.



Scheme 3. Reaction scheme for the synthesis of PMVE-*b*-ptBA and PMVE-*b*-PAA block copolymers with dual initiator BrDEP.

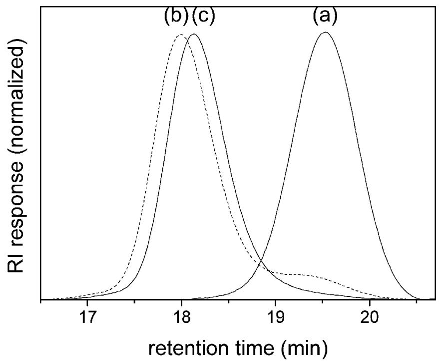


Fig. 2. GPC traces (RI detection) of (a) ptBA-acetal macroinitiator and ptBA-*b*-PMVE block copolymers (b) entry 1 in Table 1 (- - -) and (c) entry 2 in Table 1 (—).

dual initiator BrDEP for different targeted degrees of polymerization. In all cases, $\ln([M]_0/[M])$ increases linearly with increasing reaction time t, demonstrating that the radical concentration remains constant during the reaction. Fig. 3(b) shows the evolution of molecular weights and molecular weight distributions. In general, the polydispersities are below 1.1. M_n increases linearly with increasing monomer conversion and $M_{n,NMR}$ corresponds to the theoretical values. These results demonstrate that the homopolymerization of tBA with dual initiator BrDEP proceeds in a controlled manner with a high initiation efficiency.

4.3. Homopolymerization of MVE by living cationic polymerization with dual initiator

Br terminated poly(methyl vinyl ether) was prepared by carrying out the polymerization in toluene with BrDEP/trimethyl silyl iodide (TMSI) as initiating system and ZnI_2 as activator at −40 °C, which is known to produce living vinyl ether polymerizations [13–18] (Scheme 3(a)). The

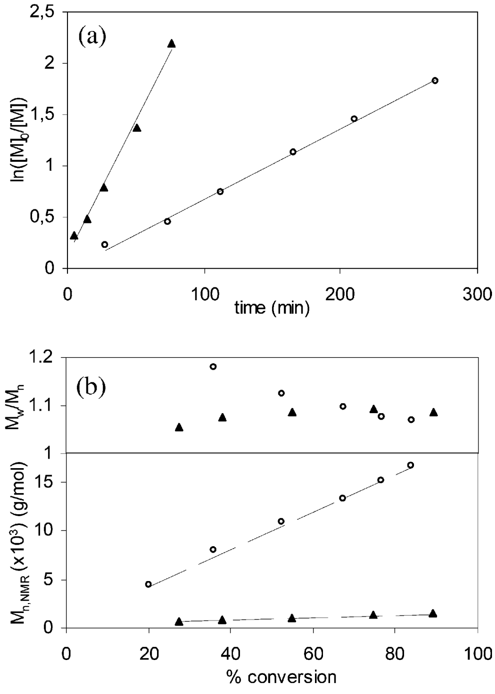


Fig. 3. (a) Kinetic plot of $\ln([M]_0/[M])$ vs reaction time and (b) molecular weights and molecular weight distributions vs monomer conversion for the ATRP of tBA with $[tBA]_0/[CuBr]_0/[PMDETA]_0/[BrDEP]_0 = 10/1/1/1$ in 25 vol% acetone at 40 °C (▲) and $[tBA]_0/[CuBr]_0/[PMDETA]_0/[BrDEP]_0 = 150/1/1/1$ in 15 vol% acetone at 70 °C (○). The theoretical molecular weights are represented with a dotted line.

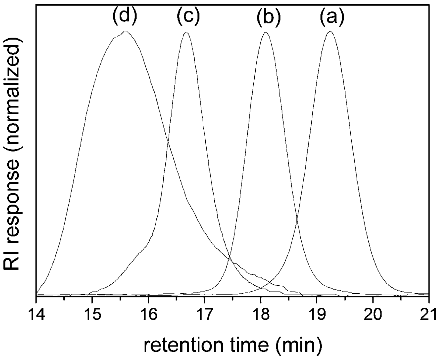


Fig. 4. GPC traces (RI detection) of (a) PMVE-Br macroinitiator, (b) PMVE-*b*-ptBA-Br (entry 5 in Table 1), (c) PMVE-*b*-ptbA-*b*-PS (entry 13 in Table 2) and (d) PMVE-*b*-ptBA-*b*-PMMA (entry 15 in Table 2).

polymerization was finally deactivated by adding a mixture of methanol and triethylamine in order to convert the α-iodo ether ends into acetal termini.

The results for the synthesis of the PMVE macroinitiator are shown in Table 1 (entry PMVE-Br). Fig. 4(a) depicts a symmetrical and narrow GPC trace for PMVE, indicating a controlled reaction.

The presence of end groups was verified by ^{1}H NMR and MALDI-TOF. NMR analysis shows that Br end functionality was maintained during vinyl ether polymerization (ratio $-\mathrm{C}(\mathrm{C}H_3)_2\mathrm{Br}$ at 1.93 ppm to $-\mathrm{C}H_2\mathrm{OC{=}O}-$ at 4.30 ppm equals to 6/2). As the PMVE will be used as a macroinitiator for ATRP, the preservation of the Br functionality during living cationic polymerization is necessary.

Considering the MALDI-TOF mass spectrum (Fig. 5(a)), the molecular weight difference between two consecutive peaks is 58 Da, which corresponds to the mass of one MVE monomer unit. The inset of Fig. 5(a) shows an enlarged spectrum ($m/z = 1812$–1880 Da) of the same sample. The MALDI-TOF spectrum is used for determination of chain end structures, by comparison of experimental (top) and simulated (bottom) isotope distributions (Fig. 5(b)).

The main series (A) is attributed to the desired Br functionalized PMVE. Minor series due to aldehyde formation (B1), ethanol termination (B2) and proton initiation (C) are also observed. Aldehyde formation (B1) can be ascribed to aqueous work-up of the acetal terminated polymer or due to water (in the MeOH terminating agent) termination of the cationic growing PMVE chain [36,37]. In fact, the aldehyde end groups originate from the formation of an instable hemiacetal intermediate and the elimination of methanol (Scheme 4). Also in NMR, approximately 7% aldehyde formation with peaks for $\mathrm{HC({=}O)C}H_2-$ at $\delta = 2.63$ ppm and for $H\mathrm{C({=}O)}-$ at $\delta = 9.81$ ppm is observed.

Residual water in the reaction medium can result in some other side reactions [38]. It is well-known that unavoidable water traces are present in TMSI [39], while also the dual initiator contains 35 ppm water after the purification procedure, as determined with the Karl Fisher method.

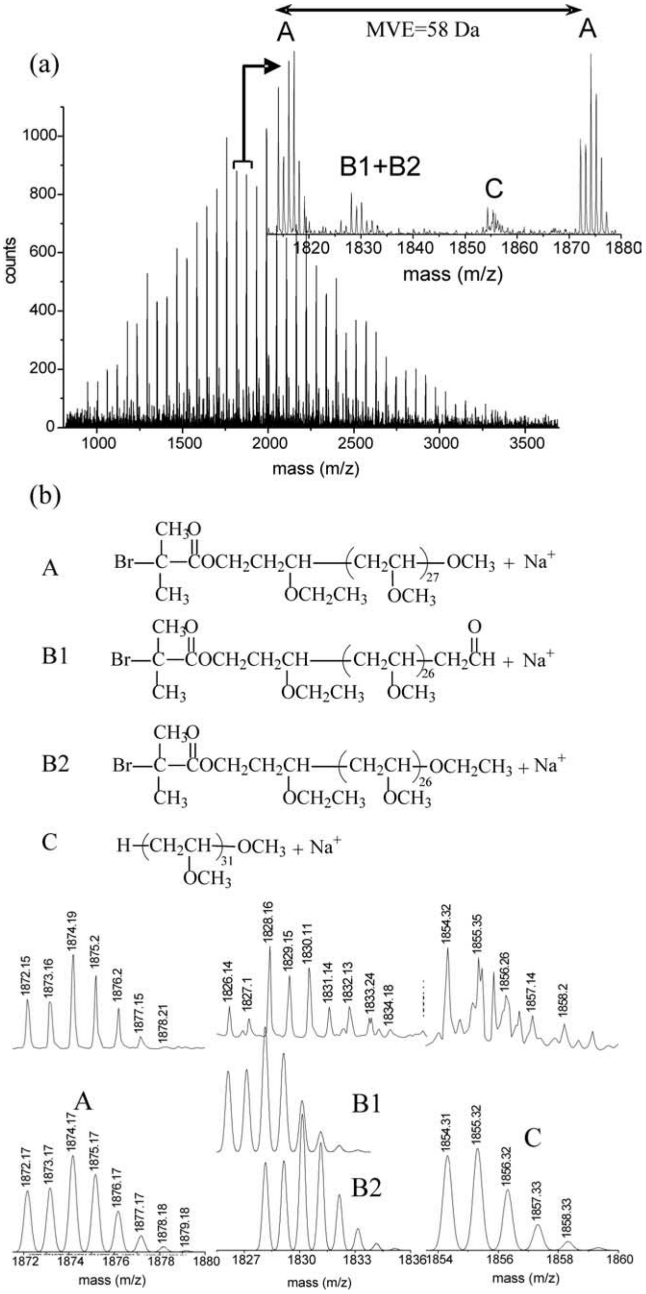
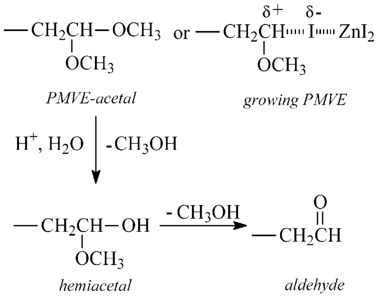
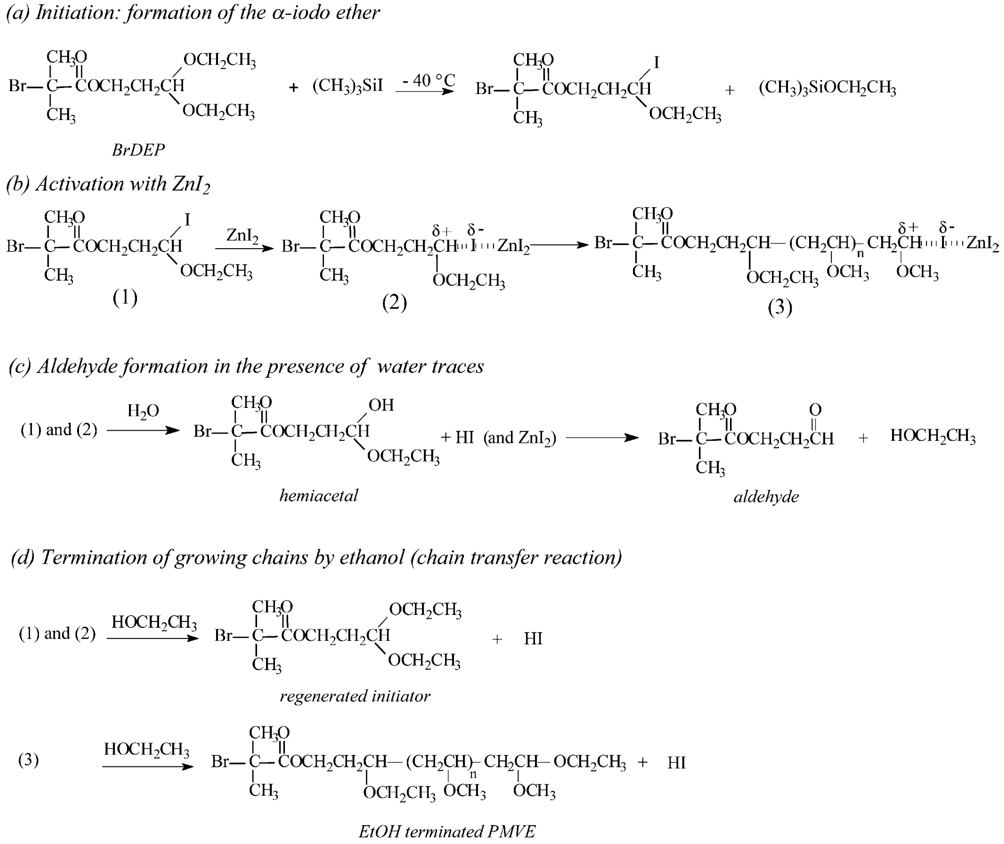


Fig. 5. Reflectron mode MALDI-TOF of PMVE-Br macroinitiator with dithranol/NaTFA (a) complete spectrum and the inset of $m/z = 1812$–1880 Da (b) determination of the chain-end structures, with experimental (top) and simulated (bottom) isotope distributions.



Scheme 4. Aldehyde formation for PMVE.

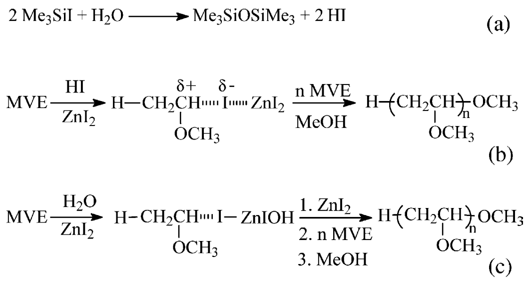


Scheme 5. Side reactions due to the presence of water traces during the initiation step of the MVE polymerization.

The presence of water traces in the reaction medium during the initiation step induces the termination of some chains with an aldehyde group (Scheme 5(a)–(c)). Simultaneously, ethanol is released, which can induce termination of active chains (series B2) (Scheme 5(d)). Finally, the generated HI can initiate the MVE polymerization as indicated in Scheme 6(b), with the formation of series C.

On the other hand, the formation of HI and thus series C can also originate from the hydrolysis of TMSI and subsequent proton initiation (Scheme 6(a)) [40]. A third possibility for the formation of series C, is that water initiates the polymerization of MVE directly [36,37] as shown in Scheme 6(c).

All series in the MALDI-TOF spectrum, except series C, still contain the desired Br end functionality and the polymer is thus applicable as a macroinitiator for ATRP of tBA. M_n obtained with MALDI in linear mode (2000 Da) is comparable with $M_{n,NMR}$, which is calculated from the integral values for PMVE and of the end group at $\delta = 4.29$ ppm. $M_{n,GPC}$ deviates from $M_{n,MALDI}$ and $M_{n,NMR}$ as GPC is calibrated with linear polystyrene standards.



Scheme 6. (a) Hydrolysis of TMSI, (b) HI initiation of MVE and (c) direct water initiation of MVE polymerization.

4.4. Block copolymerization with ptBA-acetal macroinitiator

The acetal terminated ptBA macroinitiators have been used to initiate living cationic polymerization of MVE to produce AB block copolymers (Scheme 3(d)). A similar procedure as for the MVE homopolymerization was applied to initiate the growth of the ptBA-acetal chain, i.e. 1.2 equiv. TMSI (with respect to acetal ends) was added to the α-acetal terminated ptBA to obtain the α-iodo ether function. Addition of MVE and ZnI_2 activator gives rise to block copolymerization (Table 1, entry 1). For this entry, block copolymerization was not quantitative, as demonstrated by the low molecular weight shoulder in GPC at the same retention time as the macroinitiator (Fig. 2(b)). Loss of the acetal initiation function from ptBA macroinitiator (with the formation of aldehyde) could not be detected by NMR nor MALDI. Even if the acetal end group should be partially transformed to an aldehyde, it should still initiate vinyl ether polymerization, as shown before by Haucourt et al. [13].

Another reason for the remaining macroinitiator could be incomplete functionalization of the acetal end group to α-iodo ether. In order to achieve quantitative conversion of the acetal groups of the ptBA macroinitiator, a larger excess of TMSI (1.5 equiv. instead of 1.2 equiv.) was used (Table 1 entry 2). From literature [41], it is known that an excess of TMSI does not disturb the polymerization, as TMSI is inert towards vinyl ethers in living polymerization conditions. The disappearance of the low molecular weight shoulder in the GPC trace for ptBA-*b*-PMVE 2 (Fig. 2(c)) and the decrease in polydispersity (1.21 vs 1.10) compared to ptBA-*b*-PMVE 1, demonstrate that this route results in an almost quantitative initiation. The small low molecular weight tailing is attributed to some unavoidable side reactions occurring during MVE polymerization, as described earlier (Scheme 6).

The composition of the block copolymers was calculated from the relative intensity of the ^{1}H NMR signals between 3.25 and 3.60 ppm for PMVE (C*H* and C*H*$_3$ protons) and the signal between 1.30 and 2 ppm (after substraction of 2H PMVE) for ptBA (C*H*$_2$ and C(C*H*$_3$)$_3$) (Fig. 6(a)). The molecular weight of the ptBA segments has been calculated from the integration of signals for ptBA at 1.30–1.90 and end group signals at 1.13–1.17 ppm.

4.5. Block copolymerization of PMVE-Br macroinitiator with tBA

In order to demonstrate the feasibility of the reverse reaction sequence, living PMVE chains with Br end groups have been prepared by cationic polymerization of MVE.

For this block copolymerization, similar conditions as those used for the ATRP homopolymerization of tBA were applied: the polymerization was performed with PMVE-Br macroinitiator in acetone as a solvent with the catalytic system CuBr/PMDETA (1/1) (Scheme 3(c)). By variation of the ratio [tBA]$_0$/[PMVE-Br]$_0$ and reaction time, block copolymers with many different compositions were prepared. The results are summarized in Table 1, entries 3–6.

The GPC trace shown in Fig. 4(b) reveals a shift in elution volume of the block copolymer to a higher molecular weight than the original PMVE-Br macroinitiator, without detectable amount of remaining PMVE. This result indicates that, although MALDI-TOF shows one minor series (C) without Br end group, the functionality of the Br end groups in PMVE is close to one, leading to high blocking efficiency.

The block copolymer formation has been confirmed by ^{1}H NMR (Fig. 6(a)) because the peak at 1.93 ppm for –C(C*H*$_3$)$_2$– in the PMVE-Br macroinitiator shifts to 1.13 ppm after the attachment of ptBA.

From Table 1, it can also be observed that the theoretical and experimental molecular weights are in good agreement and that block copolymers with low polydispersity were obtained. The discrepancy between the molecular weight determined by GPC and ^{1}H NMR can be attributed to GPC being calibrated with linear PS standards.

Compared to the ATRP-living cationic route, the living cationic-ATRP route is more efficient as it is an easier, less laborious and robuster way to prepare block copolymers, without remaining macroinitiator. The versatility of this approach will be demonstrated in a later section.

The kinetics of the polymerization and evolution of M_n and M_w/M_n with monomer conversion are presented in Fig. 7 for [tBA]$_0$/[PMVE-Br]$_0$ equal to 150. The semi-logarithmic kinetic plot shows a linear increase of ln([*M*]$_0$/[*M*]) vs time, indicating constant radical concentration during polymerization (Fig. 7(a)). The evolution of the number average molecular weight (M_n) and polydispersity (M_w/M_n) vs conversion is shown in Fig. 7(b). The molecular weight increases linearly with conversion with low polydispersities throughout the polymerization, characteristic for a controlled polymerization.

Moreover, ATRP chain extension experiments of PMVE-*b*-ptBA-Br with, respectively, styrene and methyl methacrylate (MMA) have been performed to confirm the controlled character of the block copolymerization. ATRP of styrene was done with the CuBr/PMDETA (1/1) catalytic system, while for MMA polymerization halogen exchange (CuCl/PMDETA 1/1) was applied in order to ensure

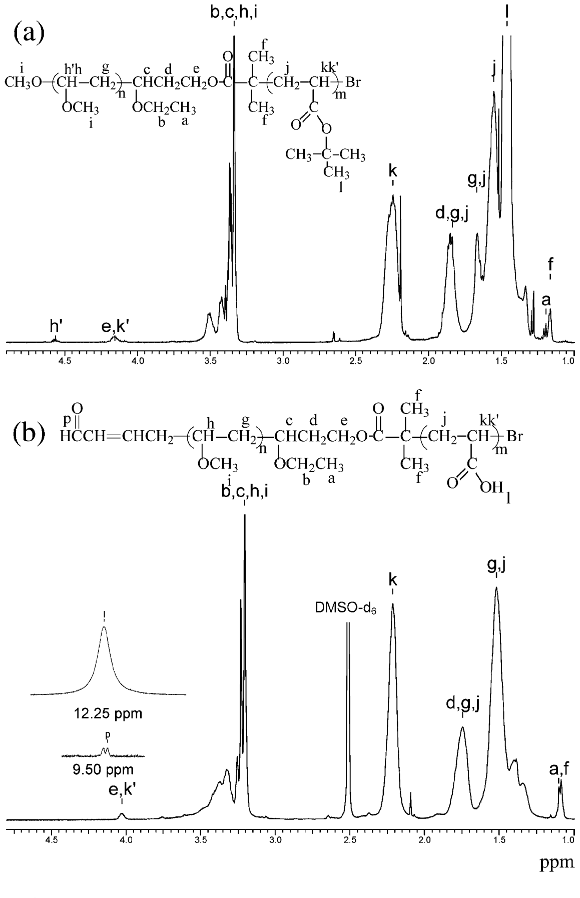


Fig. 6. ^{1}H NMR spectra of (a) PMVE-*b*-ptBA 6 (CDCl$_3$, 500 MHz) and (b) PMVE-*b*-PAA 6 (DMSO-*d*$_6$, 500 MHz).

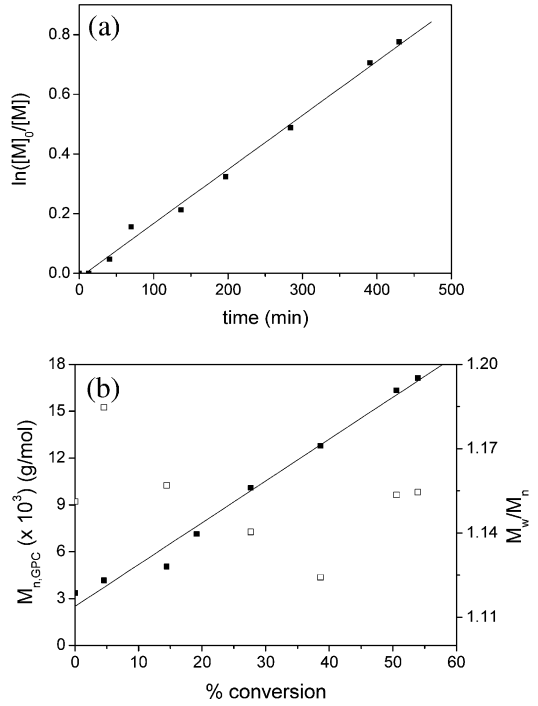


Fig. 7. (a) Kinetic plots of $\ln([M]_0/[M])$ vs reaction time and (b) molecular weights (filled symbols) and molecular weight distributions (open symbols) vs monomer conversion for the ATRP of tBA with $[tBA]_0/[CuBr]_0/[PMDETA]_0/[PMVE\text{-}Br]_0=150/1/1/1$ in 33 vol% acetone at 70 °C.

efficient cross propagation [42,43]. Clean shifts of the GPC traces to higher molecular weights are observed upon formation of ABC triblocks, implying that the Br functionalization of the AB diblock is high, and thus that the block copolymerization was controlled (Fig. 4(c) and (d)). The experimental conditions and characteristics of the ABC triblock copolymers are given in Table 2 (entries 13–15).

4.6. Hydrolysis of PMVE-b-ptBA block copolymers

ptBA block copolymers were selectively hydrolyzed in order to obtain PMVE-*b*-PAA block copolymers. For the hydrolysis of the *tert*-butyl ester groups, trifluoroacetic acid (CF_3COOH) in methylene chloride (CH_2Cl_2) has been used, following a well-established procedure [44–46] (Scheme 3(e)). Trifluoroacetic acid is considered to be a selective reagent for the hydrolysis of *tert*-butyl ester groups in the presence of other ester groups. Nevertheless, we verified if there was any cleavage at the junction between the PMVE block and the polyacrylate block during the hydrolysis of the ptBA to PAA. Therefore, the hydrolyzed block copolymer was soxhlet extracted with CH_2Cl_2, a selective solvent for PMVE and a non-solvent for PAA. The composition of PMVE-*b*-PAA, determined from ^{1}H NMR (Fig. 6(b)) by comparison of 4 H_{i+h} of PMVE ($\delta=3.20$–3.60 ppm) and 1 H_k of PAA ($\delta=2.21$ ppm), did not change within the experimental error margins before and after soxhlet extraction. This demonstrates the stability of the ester linkage between the two blocks and thus the absence of homopolymers. However, the acetal end group was transformed to an unsaturated aldehyde (doublet at $\delta=9.50$ ppm) during the hydrolysis. The successful hydrolysis could also be confirmed by FTIR-analysis.

From the IR spectra of PMVE-*b*-ptBA, we observe typical *tert*-butyl absorption peaks caused by the symmetric stretching vibration of $-C(CH_3)_3$ at 1368 and 1393 cm^{-1} (asymmetric doublet), the stretching vibration of ester carbonyls at 1725 cm^{-1}, and the stretching vibration of the PMVE and ptBA C–O–C at 1176–1245 cm^{-1}. After hydrolysis to PMVE-*b*-PAA, the asymmetric doublet of *tert*-butyl groups $-C(CH_3)_3$ at 1368 and 1393 cm^{-1} has disappeared and is replaced by carboxylic acids as

Table 2
Synthesis of ABC triblock copolymers by ATRP chain extension of Br terminated AB diblock copolymers (CuBr/PMDETA = 1/1)

Exp	Macroinitiator	Monomer	$[M]_0/[I]_0$	T (°C)	Time (min)	Conversion (%)[a]	$M_{n,GPC}$ [b]	M_w/M_n [b]	Composition (mol%)[c]
13	PMVE-*b*-ptBA 5	Styrene	500	100	153	23	20,800	1.19	11% PMVE, 23% ptBA, 66% PS
14	PMVE-*b*-ptBA 5	Styrene	500	100	90	12	11,000	1.17	22% PMVE, 36% ptBA, 42% PS
15[d]	PMVE-*b*-ptBA 5	MMA	300	90	90	63	36,200	1.37	5% PMVE,14% ptBA, 81% PMMA
16[e]	PMVE-*b*-PS 9	tBA	200	70	185	25	12,000	1.16	32% PMVE, 7% PS, 62% ptBA

[a] Determined by ^{1}H NMR data.

[b] GPC with $CHCl_3$ as an eluent and calibrated with PS standards.

[c] Determined by ^{1}H NMR from the ratio of integrated peak areas for PMVE ($\delta=3.25$–3.60 ppm), ptBA ($\delta=1.30$–1.90 ppm) and PS ($\delta=6$–7.5 ppm) or PMMA ($\delta=3.60$ ppm) respectively.

[d] In 50 vol% toluene.

[e] In 20 vol% acetone.

indicated by the broad, strong band in the 3700–2300 cm^{-1} region.

The pH and thermo-responsive solution properties of the novel block copolymers are currently under investigation.

4.7. Block copolymers of PMVE-Br macroinitiator with other monomers

It was shown earlier that the easiest way to incorporate PMVE in a block copolymer via the dual initiator strategy is the reaction sequence living cationic polymerization followed by ATRP. In this paragraph, the versatility of PMVE-Br as a macroinitiator for other monomer types will be discussed.

ATRP of methyl acrylate (MA) was performed with Me_6TREN as a ligand, as it has been shown earlier to be an effective ligand for polymerization of MA, even at low temperatures [47]. The amount of catalyst seems to be critical: with 0.15 equiv. Me_6TREN/Cu, the reaction stops at low conversion (entry 7 in Table 1), while with higher (0.5 equiv.) catalyst concentrations, conversions could be increased to about 80% (entry 8 in Table 1). This phenomenon was also observed by Matyjaszewski et al. for the polymerization of (meth)acrylamides with Me_6TREN and was explained by deactivation of the catalyst [48]. In order to avoid termination reactions at high catalyst concentrations, an initial amount of Cu(II) (20 mol% relative to Cu(I)) was added in combination with 20 vol% toluene as a solvent [49]. Well-defined block copolymers PMVE-*b*-PMA (Table 1) are obtained and unimodal, narrow GPC traces (Fig. 8(d)) are indicative for high initiation efficiency.

The synthesis of diblock copolymers consisting of PS and PMVE segments was performed by polymerizing styrene with CuBr/PMDETA, using PMVE-Br as a macroinitiator. The other conditions and results are given in Table 1 (entries 9–12). The GPC traces of macroinitiator PMVE-Br and PMVE-*b*-PS copolymers (entries 9 and 11 in Table 1) are shown in Fig. 8(b) and (c). The absence of the PMVE-Br macroinitiator peak on the GPC trace of the block copolymer indicates that the macroinitiator is fully converted and that PS is incorporated into the block copolymer, as was also the case with tBA and MA. As can be deduced from Table 1, there is a good agreement between $M_{n,th}$ and $M_{n,NMR}$, both for PMVE-*b*-PMA and PMVE-*b*-PS. Compositional information was elucidated from NMR by comparison of the PMA or PS signal at 2.30 ppm respectively, 6.24–7.24 ppm with the PMVE signal at 3.30 ppm. Block copolymer formation with MA or styrene has also been confirmed by ^1H NMR. The peak at 1.93 ppm for $–C(CH_3)_2–$ in the PMVE-Br macroinitiator shifts to 1.14 or 0.91 ppm after the attachment of respectively, MA and styrene.

Finally, one of the block copolymers (PMVE-*b*-PS, entry 9 in Table 1) was analyzed with MALDI-TOF (Fig. 9). MALDI-TOF in linear mode allows determination of the absolute molar mass and MALDI-TOF in reflectron mode further confirms the polymeric fine structure. The molecular

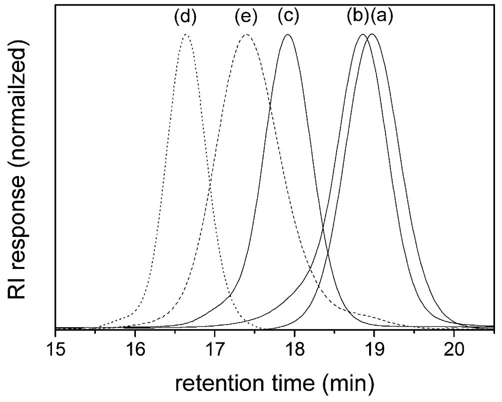


Fig. 8. GPC traces (RI detection) of (a) PMVE-Br macroinitiator, (b) PMVE-*b*-PS (entry 9 in Table 1), (c) PMVE-*b*-PS (entry 11 in Table 1), (d) PMVE-*b*-PMA (entry 8 in Table 1) and (e) PMVE-*b*-PS-*b*-ptBA (entry 16 in Table 2).

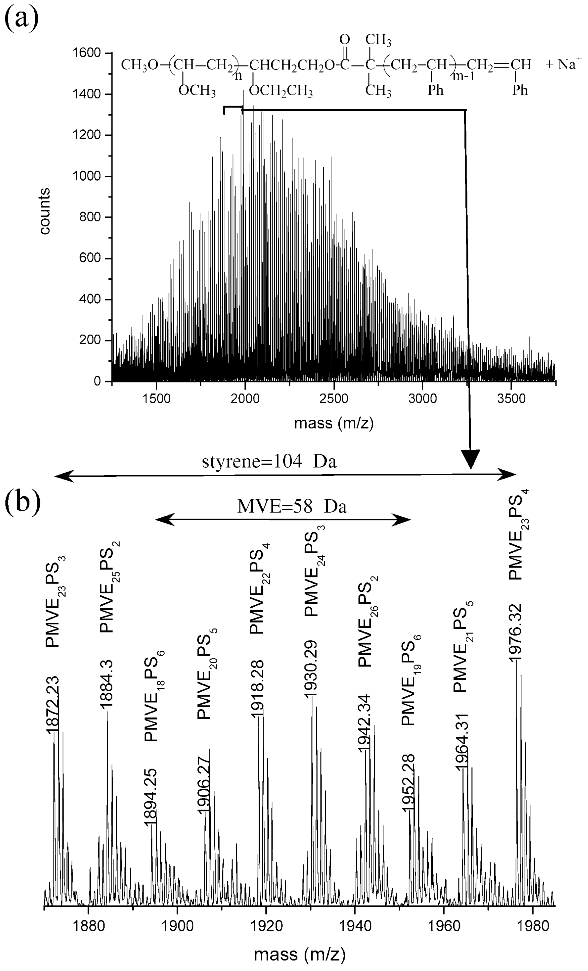


Fig. 9. Reflectron mode MALDI-TOF of PMVE-*b*-PS (entry 9 in Table 1) with dithranol/NaTFA (a) complete spectrum and (b) detail of $m/z = 1870$–1985 Da. The subscripts in the labels represent the degree of polymerization of each block.

weight obtained with MALDI-TOF in linear mode ($M_{n,MALDI}=2600$ Da) is in very good agreement with the molecular weight obtained by NMR ($M_{n,NMR}=2700$ Da). MALDI-TOF in reflectron mode gives a symmetrical peak (Fig. 9(a)) with well resolved isotope patterns (Fig. 9(b)). Different series of peaks can be observed, with a mass difference of 58 Da (MVE repeating unit) or 104 Da (styrene repeating unit). It turns out that each PMVE-*b*-PS chain has an acetal end group at one side, a part of the dual initiator in the middle and an unsaturated end group instead of a Br end group at the other end (see structure in Fig. 9). It has been reported that the unsaturation is due to the fact that the covalent bromo linkage on a PS chain is susceptible to fragmentation during the process of MALDI analysis [50]. Those results confirm that well-defined PMVE-*b*-PS block copolymers can be made from dual initiator BrDEP. As MALDI-TOF cannot be used to check for the Br end group functionality of the AB diblock copolymer, a chain extension experiment was performed. ATRP of tBA was performed from a PMVE-*b*-PS-Br chain end, under similar conditions as the PMVE-*b*-ptBA block copolymerizations. GPC analysis of the triblock copolymer in Fig. 8(e) provides clear evidence that the PMVE-*b*-PS-Br block copolymer (entry 9 in Table 1, Fig. 8(b)) is almost completely Br functionalized (only a small low molecular weight shoulder). More data about the triblock copolymer PMVE-*b*-PS-*b*-ptBA can be found in Table 2 (entry 16).

5. Conclusion

A novel dual initiator was synthesized and successfully used in the preparation of PMVE containing block copolymers via combination of ATRP and living cationic routes. First, both ptBA-acetal and PMVE-Br have been successfully prepared and used as macroinitiators for living cationic polymerization of MVE and ATRP of the protected acrylic acid monomer tBA, respectively. The dual initiator can thus be used from both sides to prepare the desired block copolymers containing PMVE and ptBA. After hydrolysis of the ptBA block, PMVE-*b*-PAA block copolymers have been obtained. Chain extension of the Br terminated AB diblock copolymers by ATRP of styrene or MMA, leads to well defined ABC triblock copolymers. It is clear that the use of dual initiators in the preparation of tailor-made polymers and copolymers offers interesting opportunities for the creation of new macromolecular architectures. Indeed, the versatility of this strategy was proved by ATRP of other monomers like styrene and MA from PMVE-Br as a macroinitiator for the synthesis of PMVE-*b*-PS and PMVE-*b*-PMA.

Acknowledgements

K. Bernaerts thanks the FWO (Fund for scientific research-Flanders, Belgium) for a PhD scholarship. The FWO and the Belgian Programme on Interuniversity Attraction Poles initiated by the Belgian State, Prime Minister's office, are acknowledged for financial support.

References

[1] Fadet A. Coupling reactions in polymer synthesis. In: Aggarwal SL, Russo S, editors. Comprehensive polymer science, 2nd Suppl. London: Pergamon Press; 1996. p. 133–62.

[2] Quirk RP, Kinning DJ, Fetters LJ. Block copolymers. In: Aggarwal SL, editor. Comprehensive polymer science, vol. 7. London: Pergamon Press; 1989. p. 1.

[3] Schué F. Synthesis of block copolymers by transformation reactions. In: Allen G, Bevington JC, editors. Comprehensive polymer science, vol. 6. Oxford: Pergamon Press; 1989. p. 359–67.

[4] Bernaerts KV, Schacht EH, Goethals EJ, Du Prez FE. J Polym Sci, Part A: Polym Chem 2003;41(21):3206–17.

[5] Tunca U, Karliga D, Ertekin S, Ugur AL, Sirkecioglu O, Hizal G. Polymer 2001;42(20):8489–93.

[6] Tunca U, Erdogan T, Hizal G. J Polym Sci, Part A: Polym Chem 2002;40(12):2025–32.

[7] Mecerreyes D, Atthoff B, Boduch KA, Trollsås M, Hedrick JL. Macromolecules 1999;32(16):5175–82.

[8] Mecerreyes D, Moineau G, Dubois P, Jérôme R, Hedrick JL, Hawker CJ, et al. Angew Chem Int Ed 1998;37(9):1274–6.

[9] Meyer U, Palmans ARA, Loontjens T, Heise A. Macromolecules 2002;35(8):2873–5.

[10] Weimer MW, Scherman OA, Sogah DY. Macromolecules 1998; 31(23):8425–8.

[11] Puts RD, Sogah DY. Macromolecules 1997;30(23):7050–5.

[12] Hawker CJ, Hedrick JL, Malmström EE, Trollsås M, Mecerreyes D, Moineau G, et al. Macromolecules 1998;31(2):213–9.

[13] Haucourt NH, Goethals EJ, Schappacher M, Deffieux A. Makromol Chem Rapid Commun 1992;13(6):329–36.

[14] Reyntjens WGS, Goethals EJ. Des Monomers Polym 2001;4(2): 195–201.

[15] Van Meirvenne D, Haucourt N, Goethals EJ. Polym Bull 1990;23(2): 185–90.

[16] Goethals EJ, Haucourt NH, Peng LB. Macromol Symp 1994;85: 97–113.

[17] Goethals EJ, Reyntjens W, Lievens S. Macromol Symp 1998;132: 57–64.

[18] Goethals EJ, Reyntjens W, Zhang X, Verdonck B. Macromol Symp 2000;157:93–9.

[19] Wang JS, Matyjaszewski K. Macromolecules 1995;28(23): 7901–10.

[20] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117(20): 5614–5.

[21] Matyjaszewski K, editor. Controlled radical polymerization. ACS Symposium Series, vol. 685. Washington, DC: American Chemical Society; 1998.

[22] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28(5):1721–3.

[23] Hoffman AS. Macromol Symp 1995;98:645–64.

[24] Schilli CM, Zhang M, Rizzardo E, Thang SH, Chong BYK, Edwards K, et al. Macromolecules 2004;37(21):7861–6.

[25] Chen G, Hoffman AS. Nature 1995;373(6509):49–52.

[26] Gan L-H, Cai W, Tam KC. Eur Polym J 2001;37(9):1773–8.

[27] Salgado-Rodriguez R, Licea-Claverie A, Arndt KF. Eur Polym J 2004;40(8):1931–46.

[28] Yoo MK, Sung YK, Lee YM, Cho CS. Polymer 2000;41(15):5713–9.

[29] Nishi T, Kwei K. Polymer 1975;16(4):285–90.

[30] Gerard H, Higgins JS. Phys Chem Chem Phys 1999;1(13):3059–64.

[31] Kwei TK, Nishi T, Roberts RF. Macromolecules 1974;7(5):667–74.

[32] Ohmura T, Sawamoto M, Higashimura T. Macromolecules 1994; 27(14):3714–20.

[33] Hashimoto T, Hasegawa H, Hashimoto T, Katayama H, Kamigaito M, Sawamoto M. Macromolecules 1997;30(22):6819–25.

[34] Ciampolini M, Nardi N. Inorg Chem 1966;1:41–4.

[35] Bednarek M, Biedron T, Kubisa P. Macromol Chem Phys 2000; 201(1):58–66.

[36] Katayama H, Kamigaito M, Sawamoto M. J Polym Sci, Part A: Polym Chem 2001;39(8):1249–57.

[37] Katayama H, Kamigaito M, Sawamoto M. J Polym Sci, Part A: Polym Chem 2001;39(8):1258–67.

[38] Rahman MS, Hashimoto T, Kodaira T. J Polym Sci, Part A: Polym Chem 2000;39(24):4362–72.

[39] D'Agosto F, Charreyre MT, Delolme F, Dessalces G, Cramail H, Deffieux A, et al. Macromolecules 2002;35(21):7911–8.

[40] Bennevault V, Larrue F, Deffieux A. Macromol Chem Phys 1995; 196(10):3075–90.

[41] Cramail H, Schappacher M, Deffieux A. Polym Adv Technol 1994;5: 568–74.

[42] Matyjaszewski K, Shipp DA, Wang J-L, Grimaud T, Patten TE. Macromolecules 1998;31(20):6836–40.

[43] Matyjaszewski K, Wang J-L, Grimaud T, Shipp DA. Macromolecules 1998;31(5):1527–34.

[44] Mori H, Seng DC, Lechner H, Zhang M, Müller AHE. Macromolecules 2002;35(25):9270–81.

[45] Zhang M, Breiner T, Mori H, Müller AHE. Polymer 2003;44(5): 1449–58.

[46] Tsolakis PK, Kallitsis JK, Tsitsilianis C. J Macromol Sci, Pure Appl Chem 2002;A39(3):155–69.

[47] Queffelec J, Gaynor SG, Matyjaszewski K. Macromolecules 2000; 33(23):8629–39.

[48] Teodorescu M, Matyjaszewski K. Macromol Chem, Rapid Commun 2000;21(4):190–4.

[49] Carlmark A, Vestberg R, Jonssen EM. Polymer 2002;43(15): 4237–42.

[50] Shen X, He X, Chen G, Zhou P, Huang L. Macromol Rapid Commun 2000;21(16):1162–5.