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Advanced Polymer Architectures with Stimuli-Responsive Properties Starting from Inimers

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ABSTRACT: Novel, well-defined, temperature- and/or pH-sensitive copolymer architectures were prepared by atom transfer radical (co)polymerization (ATRP) of a temperature-sensitive poly(methyl vinyl ether) (PMVE) macromonomer, obtained via living cationic polymerization of MVE initiated with inimer 3,3-diethoxypropyl acrylate. Temperature-sensitive comb architectures were obtained by ATRP homopolymerization (Me₆TREN/CuBr in toluene) of the PMVE macromonomer. ATRP copolymerization of the PMVE macromonomer with *tert*-butyl acrylate, a hydrolyzable precursor for pH-sensitive acrylic acid (AA), gives statistical graft copolymers. Palm-tree block copolymers containing a linear P*t*BA (PAA after hydrolysis) block and a branched block based on PMVE macromonomers were also prepared and fully characterized. Using turbidimetry, dynamic light scattering, FT-IR, and NMR, the temperature and/or pH responsiveness of those (co)polymer architectures are compared with the properties of previously synthesized linear block copolymers containing PMVE and P*t*BA or PAA.

Introduction

Recently, much attention has been paid to stimuli-responsive polymers that can respond reversibly to small changes in the environment (temperature, pH, ionic strength, light, electric or magnetic field, etc.), thereby resulting in a large change of a physical property (volume, structure, elasticity, etc.).¹ Those stimuli-responsive systems are of interest for various potential applications:² in biomedical and pharmaceutical industry (drug delivery), (bio)separations, intelligent switches and valves, sensors and actuators, etc.

In the literature, many references describe polymers sensitive to only one stimulus.^{3,4} Here, we will focus on water-soluble polymers sensitive to temperature or a combination of temperature and pH. Most studies concerning pH- and temperature-sensitive multicomponent materials are concentrated on block, graft, and statistical copolymers, blends, or hydrogels of poly(meth)acrylic acid as pH-sensitive component and poly(*N*-isopropylacrylamide) or *N*-substituted poly(acrylamides) as temperature-sensitive segment.^{5–8}

In our work, poly(acrylic acid) (PAA) was chosen as the pH-sensitive fragment and poly(methyl vinyl ether) (PMVE) as the temperature-sensitive polymer segment. PAA is a weak acidic polymer with ionizable groups ($pK_{a,apparent} = 4.75^9$), which responds to changes in pH and ionic strength by changing coil dimensions and solubility. The electrostatic repulsion between the negatively charged carboxylic acid groups results in an increase of the hydrodynamic volume of the polymer compared to the uncharged chains at low pH. PMVE is a temperature-sensitive polymer showing reversible phase separation (lower critical solution temperature behavior, LCST) in water around body temperature (37 °C). At low temperatures, the polymer is hydrophilic and the chains extended into the aqueous solution (water-soluble). Above the cloud point temperature (T_{cp}), the polymer becomes hydrophobic, with the chains forming a compact coil and being insoluble in water.

By combining PAA and PMVE into different architectures, it is possible to vary the LCST of PMVE in a controlled manner as a function of the pH, the composition of the copolymer, and the polymer architecture. This allows to adjust the T_{cp} of the material for specific applications. However, this combination is not straightforward from a synthetic point of view because each monomer can only be polymerized via its specific mechanism.

For the polymerization of *tert*-butyl acrylate (*t*BA) (precursor for pH-sensitive acrylic acid) atom transfer radical polymerization (ATRP) was applied.^{10,11} The polymerization of MVE¹² typically occurs via a living cationic mechanism starting from an acetal functionalized initiator.^{13,14} Controlled polymerization techniques were selected in order to gain control over the composition, molecular weights, polydispersities, end functionalities, and thus the polymer properties.

In order to combine both living radical and living cationic polymerization, two types of heterofunctional initiators, respectively dual initiators and inimers, were used, with each type giving rise to different polymer architectures. As highlighted in a recent review,¹⁵ a dual initiator^{3,14–17} contains two initiation functions that can initiate different polymerization mechanisms selectively and independently, in such a way that the dual initiator stays attached to the growing chain. Linear block copolymers are obtained with this strategy. An inimer is characterized by the presence of an initiation function and a polymerizable group. In this paper, the synthesis and use of inimer 3,3-diethoxypropyl acrylate for the combination of ATRP and living cationic polymerization of MVE are described. First of all, the acetal initiation function will initiate living cationic polymerization of MVE in order to prepare a well-defined PMVE macromonomer, functionalized with an acrylate polymerizable group. These PMVE macromonomers will subsequently be (co)polymerized by ATRP, resulting in branched polymer architectures like comb-shaped polymers, palm-tree¹⁸/tadpole-shaped¹⁹ block copolymers, and statistical graft copolymers.

In the literature, many publications about ATRP of macromonomers expressing a wide range in chemical properties^{19–29}

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are available, but in many other cases it concerns copolymerizations between a normal monomer and poly(ethylene oxide) macromonomers.^{30–34} In this work ATRP of PMVE macromonomers is considered, which should result in a temperature-responsive copolymer in combination with PtBA and a birefractive polymer (pH and temperature) in combination with the hydrolyzed form of PtBA (PAA). The temperature- and/or pH-sensitive behavior of different polymer architectures with similar composition will be compared in this study using techniques such as turbidimetry, dynamic light scattering, nuclear magnetic resonance spectroscopy (NMR), and Fourier-transform infrared spectroscopy (FT-IR). Literature reports on such dual responsive behavior of PMVE and PAA have been scarce (only for blends^{35–37} and hydrogels⁶) which motivates the present study.

Experimental Part

Materials and Methods. *Synthesis of Inimer 3,3-Diethoxypropyl Acrylate.* To a well-stirred solution of 3,3-diethoxy-1-propanol (10.86 mL, 69.0 mmol), 4-(dimethylamino)pyridine (0.0421 g, 0.34 mmol), and Et₃N (14.4 mL, 0.10 mol) in 250 mL of CH₂Cl₂, acryloyl chloride (5.88 mL, 72.4 mmol) was added dropwise at 0 °C. After 15 min, the reaction mixture was allowed to warm to room temperature and was subsequently stirred for 24 h. The precipitate obtained was filtered off, and the product was successively extracted with acidic ice–water (0.5 M HCl), NaHCO₃ (3×), brine (2×), and water (1×). After evaporation of the collected CH₂Cl₂ phases, the product was purified by column chromatography with 18:2 cyclohexane:ethylacetate as the eluent. This procedure yields 9.61 g of a transparent liquid (69% yield). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 1.20 (t, 6H, (CH₃CH₂O)₂CH–, J = 7.16 Hz), 1.98 (q, 2H, –CHCH₂–, J = 6.41 Hz), 3.51 and 3.66 (m, 4H, CH(OCH₂CH₃)₂), 4.25 (t, –(C=O)OCH₂–, J = 6.40 Hz), 4.64 (t, 1H, –CH(OCH₂CH₃)₂, J = 5.84 Hz), 5.84 (dd, 1H, ³ J = 10.36 Hz and ² J = 1.51 Hz), 6.13 (dd, 1H, ³ J = 10.55 Hz and ³ J = 17.33 Hz) and 6.37 (dd, 1H, ³ J = 17.39 Hz and ² J = 1.50 Hz). APT-NMR (CDCl₃, 75 MHz) δ (ppm): 15.28 (2C, (CH₃CH₂O)₂CH–), 33.07 (1C, –CH₂CH–), 61.02 (1C, –(C=O)OCH₂CH₂–), 61.46 (2C, CH(OCH₂CH₃)₂), 100.18 (1C, –CH–), 128.46 (1C, CH₂=CH–), 130.62 (1C, CH₂=CH–), 166.10 (1C, –(C=O)O–). GC-MS (m/z): 157 [M – OCH₂CH₃]⁺; 103; 85; 57; 55; 47. Thin-layer chromatography with 18:2 cyclohexane:ethylacetate as eluent gives a ratio to front of 0.28 (developed with I₂ on silica). Anal. Calcd for C₁₀H₁₈O₄ (202.248 g/mol): C (59.39%) H (8.97%) O (31.64%). Found: C (59.62%) H (8.82%) Br (31.29%).

Synthesis of Acrylate-Functionalized PMVE Macromonomer (PMVE-A). A typical polymerization procedure for [monomer]₀/[initiator]₀ = 15.3 is given below: 5.38 mL (26.2 mmol) 3,3-diethoxypropyl acrylate and 4.48 mL (31.5 mmol) trimethylsilyl iodide (TMSI) were added to 230 mL of dry toluene under a nitrogen atmosphere at –40 °C. After 10 min, an initial amount of MVE (1.50 g, 0.025 mol) was added. The polymerization was started by the addition of activator ZnI₂ (279 mg, 0.874 mmol, dissolved in 10 mL diethyl ether). At the same moment, the addition of MVE gas was continued at a rate of 50 g/h until the desired [monomer]₀/[initiator]₀ ratio was achieved (total 23.3 g, 0.401 mol). After 55 min, the reaction (still at –40 °C) was terminated by the addition of LiBH₄ (2 M in THF) (15.7 mL, 31.5 mmol), and the excess of LiBH₄ was destroyed by the addition of water. The polymer solution was washed three times with 10% aqueous Na₂S₂O₃ and then three times with deionized water and dried over MgSO₄. Next, the solution is filtered and toluene was removed using a cold trap and under vacuum (oil pump). The resulting yellow viscous oil (yield: 79%) was stored in a freezer, protected from the light by aluminum foil in order to avoid autopolymerization. $M_{n, \text{GPC}}(\text{PMVE-A})$ = 1300 g/mol and M_w/M_n = 1.12 (CHCl₃ as eluent, polystyrene standards); $M_{n, \text{NMR}}$ = 1100 g/mol; $M_{n, \text{MALDI}}$ = 1050 g/mol. The average polymerization degree of MVE is 16, which is represented by a subscript: PMVE₁₆-A. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.18 (t, 3H, –OCH₂CH₃), 1.34–2.04

Table 1. Data for Br-Terminated PtBA Obtained by ATRP

code ^b	$M_{n, \text{GPC}}$ (g/mol) ^c	M_w/M_n ^a	$M_{n, \text{NMR}}$ (g/mol)
PtBA ₂₃	2850	1.10	3100
PtBA ₅₁	6900	1.08	6700

^a M_n = number-average molecular weight; M_w = weight-average molecular weight; M_w/M_n = polydispersity index. ^b Subscripts represent the degree of polymerization. ^c GPC with refractive index detection in CHCl₃, calibrated with polystyrene standards.

(2H_{polymer} namely CH₂ protons of PMVE and 2H_{inimer} –CH₂CH₂CH–), 3.14–3.74 (broad, 4H_{polymer} namely CH– and CH₃ protons of PMVE and 3H_{inimer}, namely –CH₂CH(OCH₂CH₃)–), 4.28 (t, 2H, –OCH₂–), 5.83 (dd, 1H CH₂=CH–), 6.13 (dd, 1H CH₂=CH–), 6.37 (dd, 1H CH₂=CH–). FT-IR (KBr, CH₂Cl₂) ν (cm^{–1}): 2950–2820 (s), 1726 (m) (C=O, ester of initiator), 1636 (w) (ν C=C), 1458 (w), 1378 (w), 1294 and 1272 (w), 1190, 1106, and 1078 (s) (ν_{as} C–O–C), 983 and 813 (w) (CH-bending double bond).

ATRP Homopolymerization of PMVE-A Macromonomer (Poly(PMVE₁₆)₂₃ in Table 2). 0.60 g of PMVE₁₆-A (0.55 mmol), 1.77 μ L of ethyl-2-bromopropionate (1.36 $\times 10^{-2}$ mmol), 3.49 μ L of Me₆TREN (1.36 $\times 10^{-2}$ mmol), and 0.35 mL of toluene were mixed in a test tube using a stirring bar. The reaction mixture was degassed via three freeze–pump–thaw cycles, and 2.00 mg (1.36 $\times 10^{-2}$ mmol) of CuBr was added to the frozen reaction mixture under nitrogen. The tube was subsequently sealed with a septum, and all residual oxygen was removed under vacuum. The reaction mixture was allowed to thaw and put under nitrogen, and the reaction was started by immersing the tube in a preheated oil bath at 90 °C. The reaction was terminated in liquid nitrogen after 225 min (58% conversion). After dilution with THF, the catalyst was removed with Al₂O₃. In order to remove unreacted macromonomer (42%), the THF solution was dialyzed against water with a Spectra/Por 7 dialysis membrane (molecular weight cutoff of 1000 g/mol) for 10 days, with replacement of the water at regular time intervals. The final polymer (light yellow, viscous) is obtained after lyophilization of the aqueous solution present inside the dialysis membrane. GPC analysis confirms that the unreacted macromonomer has disappeared (no more low molecular weight peak). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.16 (broad, 12H, –C(CH₃)₂ and 2 \times CH₃CH₂O–), 1.40–2.10 (4H_{polymer} namely CH₂ protons of PMVE and CH₂ protons of the acrylate backbone of the polymacromonomer; 2H_{inimer} –CH₂CH₂CH–), 2.23 (broad, 1H, CH protons of the acrylate backbone of the polymacromonomer), 3.14–3.73 (broad, 4H polymer namely CH– and CH₃ protons of PMVE and 3H_{inimer}, namely –CH₂CH(OCH₂CH₃)–), 4.12 (broad, 2H_{polymer} and 2H_{inimer} –OCH₂–). FT-IR (KBr, CH₂Cl₂) ν (cm^{–1}): 2950–2821 (s), 1732 (s) (C=O, ester), 1463 (m), 1455 (m), 1380 (m), 1261 (m), 1186 (m), 1103 and 1023 (s) (ν_{as} C–O–C), 867 (w), 800 (s). $M_{n, \text{GPC}}$ = 13 800 g/mol and M_w/M_n = 1.15 (CHCl₃ as solvent, polystyrene standards).

Synthesis of PtBA-Br Macroinitiators by ATRP. PtBA-Br macroinitiators were prepared by ATRP using methyl-2-bromopropionate/Me₆TREN/CuBr, as described by Du Prez et al.³⁸ (see Table 1).

Statistical Graft Copolymers Poly(tBA-co-PMVE₁₆-A) by ATRP Copolymerization of tBA and PMVE₁₆-A. For poly(tBA-co-PMVE₁₆), **8** (see Table 3), with an initial monomer mixture of 90/10 mol % tBA/PMVE₁₆-A (DP_{tBA} = 270), 0.425 g (0.387 mmol) of PMVE₁₆-A was weighed in a test tube containing a magnetic stirring bar. 0.505 mL (3.48 mmol) of tBA, 1.67 μ L (0.0129 mmol) of ethyl 2-bromopropionate initiator, 6.59 μ L (2.58 $\times 10^{-2}$ mmol) of Me₆TREN ligand, and 2.47 mL of toluene were added. The reaction mixture was degassed by five freeze–pump–thaw cycles, and 3.70 mg (2.58 $\times 10^{-2}$ mmol) of CuBr was added under a nitrogen atmosphere to the frozen reaction mixture. Next, the tube was sealed with a septum, and residual oxygen above the frozen reaction mixture was removed by pumping. The reaction mixture was allowed to thaw and was immersed in a preheated oil bath at 90 °C. After 120 min (% conversion tBA = 94 and % conversion PMVE₁₆-A = 83), the reaction was terminated by cooling in liquid

Table 2. Results of the ATRP Homopolymerization of PMVE-A Macromonomers in Toluene, Initiated with Ethyl 2-Bromopropionate

code ^a	PMVE ₁₆ -A/ EtBrPr/CuBr/Me ₆ TREN	T (°C)	toluene (wt %)	time (min)	% conversion ^b	M _{n,conv} ^c (g/mol)	M _{n,GPC} ^d (g/mol)	M _w /M _n ^d
poly(PMVE ₁₄) ₁₂	20:1:0.7:0.7	90	38	279	62	12 300	9 500	1.09
poly(PMVE ₁₆) ₁₇	40:1:1:1	50	33	275	44	19 200	14 100	1.08
poly(PMVE ₁₆) ₂₃	40:1:1:1	90	33	225	58	25 300	13 800	1.15

^a Subscripts represent the degree of polymerization (DP) obtained by $DP_{PMVE-A} = DP_{theoretical} \times \% \text{ conversion}$. ^b % conversion from refractive index vs retention time via GPC (CHCl₃, polystyrene standards) (see Supporting Information, Figure S1). ^c $M_{n,conv} = DP_{theoretical} \times M_n(\text{PMVE-A}) \times (\% \text{ conversion})$. ^d GPC with refractive index detection in CHCl₃, calibrated with polystyrene standards.

Table 3. Results for the ATRP Copolymerizations of *t*BA with PMVE₁₆-A (MM) in Toluene at 90 °C

poly(<i>t</i> BA-co-PMVE ₁₆)	<i>t</i> BA/ PMVE ₁₆ -A/ EtBrPr/ CuBr/ Me ₆ TREN	<i>f</i> ^a <i>t</i> BA/MM (mol %)	<i>F</i> ^a <i>t</i> BA/MM (mol %) ^b	conc. monomer (mol/L)	wt % toluene	time (min)	% conversion <i>t</i> BA/ PMVE	M _{n,GPC} (g/mol) ^c	M _w /M _n ^e
1	13/38/1/0.75/0.75	25/75	37/63	1.5	39	180	58/52 ^c	12 950	1.13
2	25/25/1/0.75/0.75	50/50	56/44	1.4	47	90	75/67 ^c	12 100	1.16
3	25/25/1/1/1	50/50	58/42	2.2	35	60	94/88 ^c	14 500	1.21
4	38/13/1/0.75/0.75	75/25	79/21	1.3	60	165	89/80 ^c 87/81 ^d	9 600	1.26
5	30/270/1/2/2	10/90	18/82	1.5	36	260	78/65 ^c 80/67 ^d	17 300	1.21
6	30/270/1/2/2	10/90	15/85	2.6	24	74	43/32 ^c	13 000	1.07
7	270/30/1/2/2	90/10	— ^f	1.4	69	169	36/28 ^c 36/28 ^d	19 800	1.15
8	270/30/1/2/2	90/10	92/8	5.1	20	120	94/83 ^c	44 200	1.33

^a *f* = molar fraction of comonomers in the feed; *F* = molar fractions of monomers in the copolymer. ^b From ¹H NMR: mol % *t*BA = $[9H_{PrBA}(\delta = 1.4 \text{ ppm})/9]/[4H_{PMVE}(\delta = 3.4 \text{ ppm})/(4DP_{PMVE-A})] \times 100$ and mol % PMVE = $100 - \text{mol \% } t\text{BA}$. ^c % conversion for *t*BA from GC and % conversion for the macromonomer from GPC after correction for the contribution of *t*BA via Gladstone–Dale. ^d % conversion from ¹H NMR by comparison of a monomer peak ($\delta = 5.79\text{--}5.86 \text{ ppm}$ for PMVE-A and $\delta = 5.69\text{--}5.77 \text{ ppm}$ for *t*BA) with toluene as an internal standard (3H at 7.12–7.22 ppm). ^e Determined via GPC (CHCl₃, refractive index detection, polystyrene standards). ^f Not determined.

Table 4. Results for the ATRP of PMVE₁₆-A Macromonomers in Toluene, Initiated with *Pr*BA-Br-Macroinitiators

code ^a	PMVE ₁₆ -A/ <i>Pr</i> BA-Br/ Me ₆ TREN/ CuBr/CuBr ₂	T (°C)	solvent (wt %)	time (min)	% conversion ^b	M _{n,conv} ^c (g/mol)	mol % <i>Pr</i> BA ^d	M _{n,GPC} ^e (g/mol)	M _w /M _n ^e
<i>Pr</i> BA ₂₃ - <i>b</i> -poly(PMVE ₁₆) ₁₄	40/1/1/1/0	50	33% acetone	330	36	19 200	62	12 700	1.07
<i>Pr</i> BA ₂₃ - <i>b</i> -poly(PMVE ₁₆) ₁₈	40/1/1/1/0	90	33% toluene	279	46	22 900	56	13 000	1.11
<i>Pr</i> BA ₂₃ - <i>b</i> -poly(PMVE ₁₆) ₃₂	40/1/2/2/0	90	33% acetone	256	80	38 300	46	17 900	1.19
<i>Pr</i> BA ₂₃ - <i>b</i> -poly(PMVE ₁₆) _{7.5}	10/1/2/2/0.1	90	33% toluene	38	75	11 400	76	8 600	1.19
<i>Pr</i> BA ₅₁ - <i>b</i> -poly(PMVE ₁₆) ₁₇	40/1/2/2/0	90	33% toluene	173	42	25 200	75	15 000	1.16
<i>Pr</i> BA ₅₁ - <i>b</i> -poly(PMVE ₁₆) ₂₆	30/1/3/3/0	90	33% toluene	172	65	28 000	74	15 100	1.18

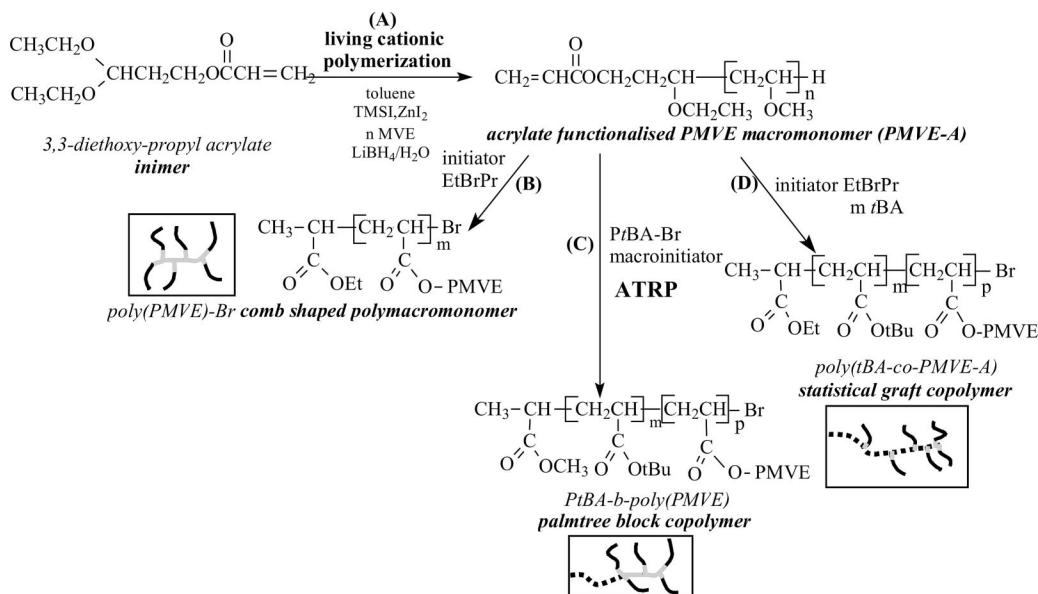
^a $DP_{PMVE-A} = DP_{theoretical} \times \% \text{ conversion}$. ^b % conversion from ¹H NMR by comparison of a macromonomer peak ($\delta = 5.79\text{--}5.86 \text{ ppm}$) with toluene (3H at 7.12–7.22 ppm) as an internal standard. ^c $M_{n,conv} = DP_{theoretical} \times (\% \text{ conversion}) \times M_n(\text{PMVE-A})$. ^d mol % *Pr*BA from ¹H NMR. ^e Determined by GPC with CHCl₃ as an eluent, refractive index detection, and calibration with polystyrene standards.

nitrogen, the polymer was diluted with THF, and the catalyst was removed with neutral Al₂O₃. In order to remove unreacted (macro-)monomer (6% unreacted *t*BA, 17% unreacted PMVE₁₆-A), the colorless THF solution was dialyzed against water (replaced repeatedly) with a Spectra/Por 7 dialysis membrane with a molecular weight cutoff of 1000 g/mol (at room temperature for 10 days). The polymer was finally isolated as a colorless, transparent, viscous polymer by lyophilization of the aqueous solution. GPC analysis confirmed that the unreacted macromonomer was efficiently removed. ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 1.16 (broad, 9H, $2 \times \text{CH}_3\text{CH}_2\text{O}-$, $-\text{O}(\text{C}=\text{O})\text{CH}(\text{CH}_3)-$), 1.43 (s, 9H, C(CH₃)₃ protons of *Pr*BA), 1.49–2.01 (broad, 6H_{polymer} namely CH₂ protons of PMVE, CH₂ protons of *Pr*BA and CH₂ protons of the acrylate backbone of the polymacromonomer; 2H_{inimer} $-\text{CH}_2\text{CH}_2\text{CH}-$), 2.27 (s, 2H_{polymer} namely CH protons of *Pr*BA and CH protons of the acrylate backbone of the polymacromonomer, 1H_{initiator} $-\text{O}(\text{C}=\text{O})\text{CH}(\text{CH}_3)-$), 3.13–3.73 (broad, 4H_{polymer} namely CH and CH₃ protons of PMVE, 3H_{inimer} namely $-\text{CH}_2\text{CH}(\text{OCH}_2\text{CH}_3)-$ and CH₃CH₂O $-\text{}$), 4.12 (s, CH₂O(C=O) $-\text{}$ of the inimer and initiator and R₂CHBr). FT-IR (KBr, CH₂Cl₂) ν (cm⁻¹): 2975–2820 (m), 1729 (s) (C=O, ester), 1456 (w), 1392 and 1367 (m) (asymmetric doublet for tertiary butyl groups), 1256 (w), 1150 and 1108 (s) (ν_{as} C–O–C). $M_{n,GPC}[\text{poly}(\text{PrBA-co-PMVE}_{16}\text{-A}) \textbf{8}] = 44\,200 \text{ g/mol}$ and $M_w/M_n = 1.33$; mol % *Pr*BA by ¹H NMR is 92%.

Synthesis of *Pr*BA₅₁-*b*-poly(PMVE₁₆)₁₇ via ATRP of PMVE₁₆-A Starting from a Br-Terminated *Pr*BA Macroinitiator (Table 4). 0.585 g of PMVE₁₆-A (0.532 mmol), 1.33×10^{-2} mmol of macroinitiator (0.0891 g of *Pr*BA₅₁-Br), 6.80 μL of Me₆TREN (2.66×10^{-2} mmol), and 0.37 mL of solvent (toluene) were added to a test tube with stirring bar. The reaction mixture was degassed by three

freeze–pump–thaw cycles, and 2.60 mg of CuBr (2.65×10^{-2} mmol) was added to the frozen reaction mixture. The tube was subsequently sealed with a septum, and all residual oxygen was removed under vacuum. The reaction mixture was allowed to thaw and put under nitrogen, and the reaction was started by immersing the tube in a preheated oil bath at 90 °C. After the desired reaction time (173 min and 42% conversion for *Pr*BA₅₁-*b*-poly(PMVE₁₆)₁₇), the reaction mixture was terminated by cooling in liquid nitrogen and by dilution with THF. Catalyst was removed over Al₂O₃, and the THF solution was dialyzed against water with Spectra/Por 7 dialysis membranes (molecular weight cutoff of 1000 g/mol) for 10 days in order to remove unreacted macromonomer (58%). The water was replaced at regular time intervals. The final polymer (colorless, transparent, viscous) was isolated by lyophilization of the water inside the dialysis membrane. GPC analysis confirms that the unreacted macromonomer was efficiently removed. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.16 (broad, 6H, $-\text{C}(=\text{O})\text{CH}(\text{CH}_3)-$ and CH₃CH₂O $-\text{}$), 1.44 (broad, 9H, $-\text{C}(\text{CH}_3)_3$ protons of *Pr*BA), 1.48–2.02 (6H_{polymer} namely CH₂ protons of PMVE, CH₂ protons of the acrylate backbone of the polymacromonomer and CH₂ protons of *Pr*BA; 2H_{inimer} $-\text{CH}_2\text{CH}_2\text{CH}-$), 2.24 (broad, 2H_{polymer}, CH protons of the acrylate backbone of the polymacromonomer and CH protons of *Pr*BA), 3.12–3.63 (broad, 4H_{polymer} namely CH and CH₃ protons of PMVE and 3H_{inimer}, namely $-\text{CH}_2\text{CH}(\text{OCH}_2\text{CH}_3)-$), 4.11 (broad, R₂CHBr, 2H_{polymer} $-\text{OCH}_2-$ and 3H_{initiator} $-\text{OCH}_3$). FT-IR (KBr, CH₂Cl₂) ν (cm⁻¹): 2974–2820 (s), 1731 (vs) (C=O, ester), 1455 (m), 1383 and 1368 (asymmetric doublet for tertiary butyl groups), 1254 (m), 1141 (s), 1102 and 1085 (s) (ν_{as} C–O–C), 843 (w), 792 (s). $M_{n,GPC}[\text{PrBA}_{51}\text{-b-poly}(\text{PMVE}_{16})_{17}] = 15\,000 \text{ g/mol}$ and $M_w/M_n = 1.16$ (CHCl₃ as

Scheme 1. Schematic Representation of the Inimer Strategy To Combine Living Cationic Polymerization and ATRP (A) Living Cationic Polymerization of MVE with Inimer 3,3-Diethoxypropyl Acrylate, (B) ATRP Homopolymerization of PMVE-A, (C) ATRP Block Copolymerization of PMVE-A Initiated with PtBA-Br Macroinitiator, and (D) Statistical ATRP Copolymerization of PMVE-A and *t*BA^a



^a Legend: gray = inimer, black = PMVE, dotted line = PtBA.

eluent, polystyrene standards); mol % PtBA by ¹H NMR is 75%.

Hydrolysis of PtBA in PtBA-*b*-polyPMVE and Poly(*t*BA-co-PMVE). Statistical graft copolymers (poly(*t*BA-co-PMVE)) and palm-tree block copolymers (PtBA-*b*-poly(PMVE)) were hydrolyzed with a 5-fold excess of MeSO₃H relative to the *tert*-butyl ester groups for 1 h in CH₂Cl₂ (1 mL per g of copolymer). This procedure is exemplified for the hydrolysis of poly(*t*BA-co-PMVE₁₆) **8**.

0.70 g of poly(*t*BA-co-PMVE₁₆) **8** with 56 wt % PtBA (Table 3) was hydrolyzed in 7 mL of CH₂Cl₂ at room temperature for 1 h with a 5-fold excess of MeSO₃H with respect to the *tert*-butyl ester groups (0.989 mL, 15.2 mmol). The reaction mixture was subsequently purified by dialysis in water with a Spectra/Por 7 dialysis membrane with a molecular weight cutoff of 1000 g/mol (at room temperature for 2 days). Poly(AA-co-PMVE₁₆) **8** was finally isolated as a yellow to brown polymer (0.47 g) by lyophilization of the aqueous solution. Full conversion of PtBA to PAA was obtained, as confirmed by ¹H NMR (disappearance of the typical *tert*-butyl resonance at 1.44 ppm) and FT-IR data (disappearance of the typical *tert*-butyl asymmetric doublet at 1392 and 1367 cm⁻¹ (m)). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 1.17 (3H_{inimer} CH₃CH₂O–, and 6H_{initiator} namely CH₃O– and –O(C=O)CH(CH₃)–), 1.45–2 (broad, 6H_{polymer} namely CH₂ protons of PAA, CH₂ protons of PMVE and CH₂ protons of the acrylate backbone of the polymacromonomer; 2H_{inimer} –CH₂CH₂CH–), 2.40 (s, 2H_{polymer}, CH protons of PAA and CH protons of polymacromonomer backbone; 1H_{initiator} –O(C=O)CH(CH₃)–), 3.02–3.70 (broad, 4H_{polymer}, CH and CH₃ protons of PMVE; 3H_{inimer}, namely –CH(OCH₂CH₃)–), 4.14 (s, 5H, 2 × –CH₂OC=O– and R₂CHBr). FT-IR (KBr pellets pressed) ν (cm⁻¹): 3700–2300 (broad) (complexed COOH), 1732 (vs), 1450 (m), 1365 (w), 1244–1176 (m) (ν_{as} C–O–C), 1109 (w), 1054 (m), 954, 924, and 884 (w).

Results and Discussion

The combination of living cationic polymerization of MVE and controlled radical polymerization using an inimer is based on a two-step strategy (Scheme 1). In a first step (Scheme 1A), the acetal function of the inimer 3,3-diethoxypropyl acrylate is used to initiate MVE polymerization, giving rise to PMVE with a polymerizable acrylate end group (PMVE macromonomer,

PMVE-A). The macromonomer obtained is subsequently polymerized by ATRP. Comb-shaped polymers are the result of the homopolymerization of the macromonomers (Scheme 1B). Statistical copolymerization of PMVE-A with *t*BA leads to graft copolymers with an acrylate backbone and PMVE grafts (Scheme 1D). When a linear polymer such as PtBA-Br, obtained by ATRP, is used as a macroinitiator for the polymerization of a macromonomer, a block copolymer arises with a branched second block. These types of block copolymers are also called palm-tree block copolymers¹⁸ or tadpole-shaped¹⁹ block copolymers (Scheme 1C).

Synthesis of Acrylate-Functionalized Poly(methyl vinyl ether) Macromonomer (PMVE-A) by Living Cationic Polymerization of MVE. An acrylate-functionalized PMVE macromonomer (PMVE-A) was prepared by living cationic polymerization of MVE in toluene with 3,3-diethoxypropyl acrylate/trimethylsilyl iodide (TMSI) as initiating system and ZnI₂ as activator at –40 °C, which is known to produce living vinyl ether polymers^{13,14} (Scheme 1A). The polymerization was deactivated by adding LiBH₄ in order to convert the α-iodo ether ends into nonreactive proton groups. Functional initiator 3,3-diethoxypropyl acrylate containing both an initiation function for living cationic polymerization of MVE (acetal) and a polymerizable vinyl group (acrylate monomer) (inimer) was used to introduce the polymerizable group in the macromonomer. The results for the synthesis of the PMVE-A macromonomer are given in the Experimental Part. Since the PMVE-A will be used as macromonomer, the preservation of the acrylate functionality during living cationic polymerization is essential. The end-group functionality was verified by MALDI-TOF. The molecular weight difference between two consecutive peaks in the MALDI spectrum (Figure 1a) is 58 Da, which corresponds to the mass of one MVE monomer unit. Figure 1b presents the *m/z* = 819–882 Da range of this spectrum in more detail. The MALDI-TOF spectrum is used for determination of chain-end structures, by comparison of experimental (top) and simulated (bottom) isotope distributions (Figure 1b). The good correspondence of the shape of both isotopical patterns and of the *m/z* values confirms that the desired fully acrylate-

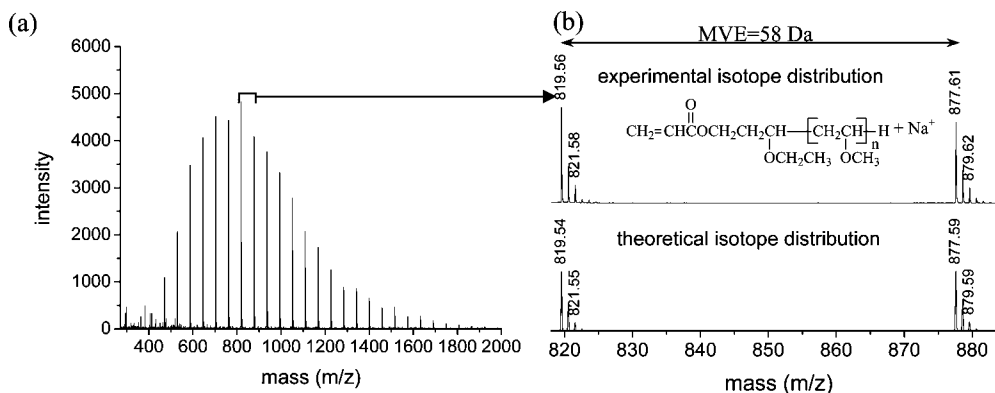


Figure 1. (a) Reflectron mode MALDI-TOF of PMVE₁₆-A and (b) determination of end groups for PMVE₁₆-A, by comparison of experimental (top) and theoretical (bottom) isotope distributions.

functionalized PMVE was synthesized, without any trace of side product.

ATRP Homopolymerization of PMVE-A Macromonomer. Before proceeding to the ATRP synthesis of (block) copolymers starting from PMVE-A macromonomer, the reaction conditions are investigated for the ATRP homopolymerization of PMVE-A initiated with ethyl 2-bromopropionate (Scheme 1B). As the PMDETA/CuBr catalyst systems did not result in any polymerization, we switched to the more active Me₆TREN/CuBr catalyst system (giving a higher equilibrium constant),³⁹ often used for ATRP of acrylates (Table 2). A more active catalyst system was required because the concentration of reactive sites in the solution is relatively low since the macromonomer itself is of relatively high molecular weight.

Using the reaction conditions in Table 2, it was not possible to achieve full conversion (determined by GPC, see Supporting Information, Figure S1) of the macromonomer. The highest conversion could be obtained when the lowest degree of polymerization was targeted. This since the radical concentration is the highest, the viscosity limited and the effect of steric hindrance around the growing radical are less pronounced. If a higher degree of polymerization (DP = 40) is targeted, the reaction stops at slightly lower conversions, although a higher catalyst concentration was used to increase the concentration of radicals in the solution and enhance the rate of the polymerization. The results in Table 2 and the first-order kinetic plot in Figure 2a further show that the system reactivity (and thus the conversion) could be influenced by the reaction temperature: an increase of the temperature from 50 °C (poly(PMVE₁₆)₁₇) to 90 °C (poly(PMVE₁₆)₂₃), corresponds to an increase of the conversion from 44% to 58%. The kinetic study further shows that the reaction is controlled up to a certain conversion, after which deviation in the first-order kinetic plot is observed (Figure 2a). Nevertheless, the polymers obtained have a narrow molecular weight distribution and *M_n* evolves linearly as a function of the conversion (Figure 2b). Similar deviations of the first-order kinetics were already mentioned earlier in literature for the radical polymerization of macromonomers. They were ascribed to the increasing viscosity of the reaction medium and/or to increasing steric hindrance around the propagating species, rather than to irreversible termination reactions like the recombination of growing radicals.²⁰

It has been reported previously for the controlled radical polymerization of sterically hindered 4-acetoxystyrene⁴⁰ and for the controlled homopolymerization of macromonomers (poly(isobutyl vinyl ether),²⁰ poly(tetrahydrofuran),²¹ poly(lactic acid),²² poly(dimethylsiloxane),^{24–26} etc.) that, as the polymerization proceeds and the viscosity of the medium increases, the propagation mechanism can change from a chemically controlled

to a diffusion-controlled process. However, Roos et al.⁴¹ indicated that for controlled radical (co)polymerization the diffusion phenomenon was less pronounced than for free radical polymerization because the time interval for monomer addition to a polymer chain is much larger (seconds or minutes) than for conventional radical systems (milliseconds).

However, more recently, Ohno et al.¹⁹ ascribed the limited degree of polymerization of macromonomers to progressively increasing steric congestion for macromonomers in approaching the growing chain ends of densely grafted polymers. High segment density around the propagating chain end makes it more difficult for the active site to approach the polymerizable end group of the macromonomers. The effect of steric hindrance increases as the number of branches around the propagating active place increases.⁴² As the segment density around the propagating radical increases at high conversion, bimolecular termination becomes more difficult. By consequence, initial termination reactions are more important with the polymerization of macromonomers.⁴³

Statistical Graft Copolymers Based on PMVE-A Macromonomers and *t*BA: Poly(PMVE-A-co-*t*BA). ATRP copolymerization of two acrylates, namely *t*BA and PMVE-A macromonomer, was performed with EtBrPr as an initiator, in toluene as a solvent (Scheme 1C). The results of the copolymerizations are shown in Table 3.

The conversion of the PMVE-A macromonomer was determined by GPC from the peak area of the original macromonomer compared to the peak area of the copolymer (after deconvolution when appropriate). The apparent GPC peak areas were corrected for the contribution of the *t*BA conversion (measured by GC). This procedure was derived from the relationship between polymer concentrations and their relative intensities in the GPC signal. If the densities of the polymers are comparable ($\rho_{20\text{ °C}}(\text{PMVE}) = 1.058\text{ g/cm}^3$; $\rho(\text{PrBA}) = 1.022\text{ g/cm}^3$),⁴⁴ the signal intensities of PMVE and of the PMVE/PrBA copolymers can be approximated in GPC, using the Gladstone–Dale equation (1),^{45,46} which states the additivity of the refractive indices of the constituent components in copolymers.

$$\frac{\text{GPC area}_{\text{PMVE}_{16}\text{-A}}}{\text{GPC area}_{\text{copolymer}}} = \frac{\{[\text{PMVE}_{16}\text{-A}]_0 \text{MW}_{\text{PMVE}_{16}\text{-A}} (1 - \text{conversion}_{\text{PMVE}_{16}\text{-A}}) R_1\}}{\{([\text{PMVE}_{16}\text{-A}]_0 \text{MW}_{\text{PMVE}_{16}\text{-A}} \cdot \text{conversion}_{\text{PMVE}_{16}\text{-A}} \cdot R_1) + ([t\text{BA}]_0 \text{MW}_{t\text{BA}} \cdot \text{conversion}_{t\text{BA}} \cdot R_2)\}} \quad (1)$$

with $R_1 = n_D(\text{PMVE}) - n_D(\text{CHCl}_3)$, $R_2 = n_D(\text{PrBA}) - n_D(\text{CHCl}_3)$, $n_D(\text{CHCl}_3) = 1.444$, $n_D(\text{PMVE}) = 1.467$, and

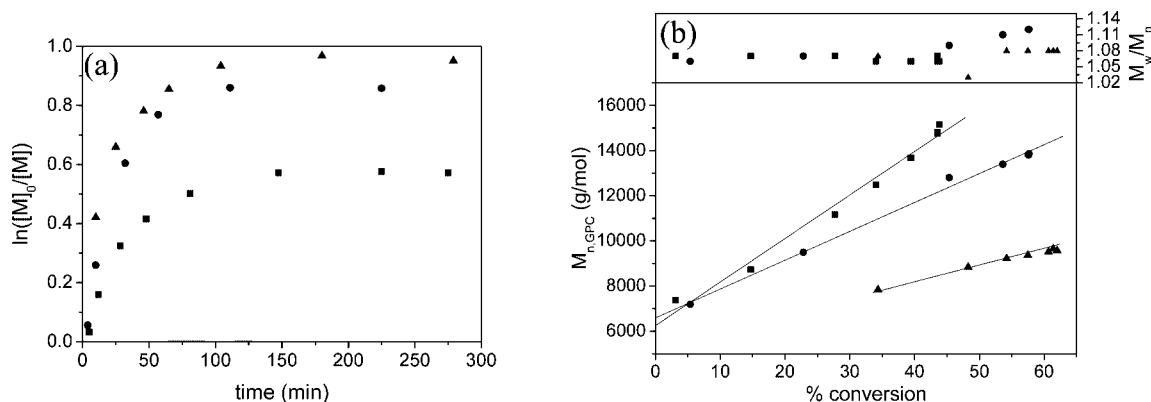


Figure 2. Kinetic curves of (a) $\ln([M]_0/[M])$ vs reaction time and (b) dependence of $M_{n, GPC}$ (bottom) and molecular weight distributions (top) of the monomer conversion for ATRP of PMVE-A: poly(PMVE₁₄)₁₂ (▲), poly(PMVE₁₆)₁₇ (■), and poly(PMVE₁₆)₂₃ in Table 2 (●).

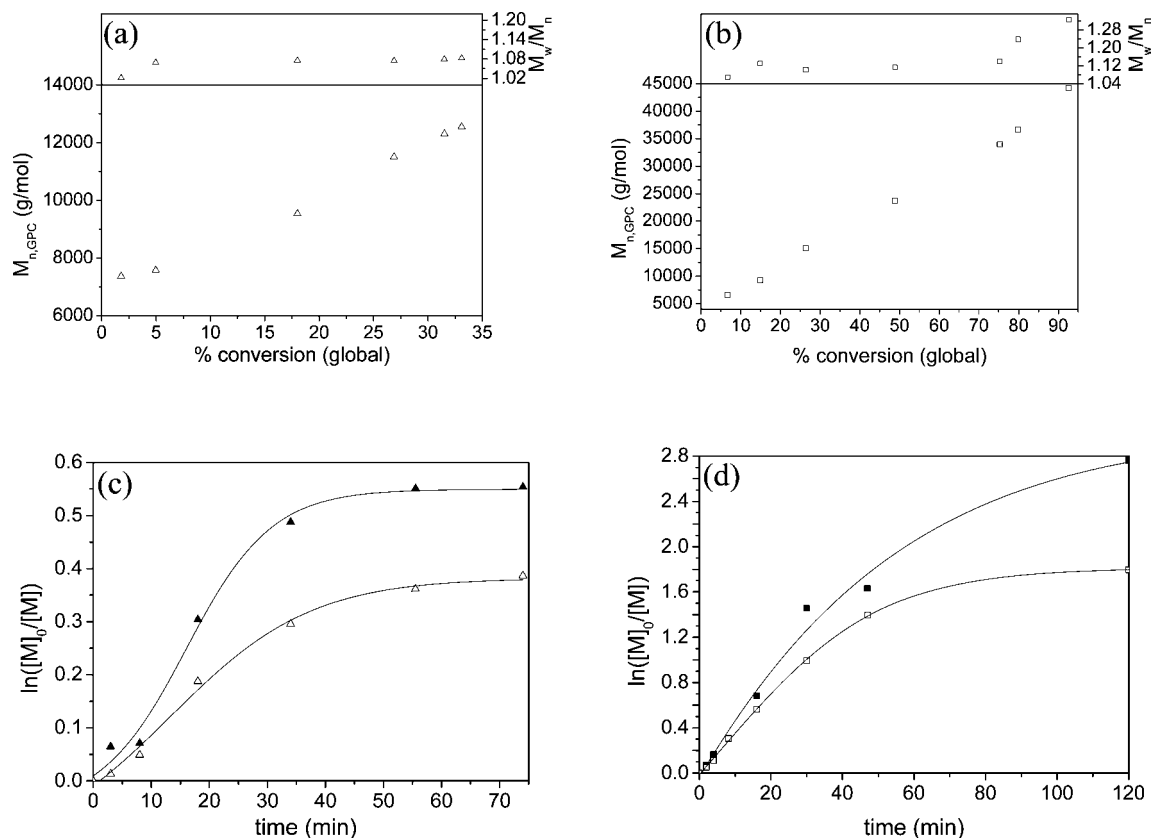


Figure 3. (a) M_n (bottom) and M_w/M_n (top) vs % global conversion for poly(*t*BA-co-PMVE₁₆-A) **6** (Δ). (b) M_n (bottom) and M_w/M_n (top) vs % global conversion for poly(*t*BA-co-PMVE₁₆-A) **8** (□). (c) First-order kinetic plot for the ATRP copolymerization of 10/90 mol % *t*BA/PMVE₁₆-A in the feed for poly(*t*BA-co-PMVE₁₆-A) **6** (▲, Δ). (d) First-order kinetic plot for the ATRP copolymerization of 90/10 mol % *t*BA/PMVE₁₆-A in the feed for poly(*t*BA-co-PMVE₁₆-A) **8** (■, □). Filled symbols: data for *t*BA; open symbols: data for PMVE₁₆-A.

$n_D(\text{PrBA}) = 1.46$.⁴⁷ By rearranging eq 1, it is possible to calculate the conversion of the macromonomer with the formula

$$\text{conversion}_{\text{PMVE-A}} = \frac{1 - AB \cdot \text{conversion}_{t\text{BA}}}{A + 1} \quad (2)$$

with $A = \text{GPC area}_{\text{PMVE-A}} / \text{GPC area}_{\text{copolymer}}$ and $B = ([t\text{BA}]_0 \text{MW}_{t\text{BA}R_2}) / ([\text{PMVE-A}]_0 \text{MW}_{\text{PMVE-A}R_1})$. For some of the reactions in Table 3, the conversion calculation by combination of GC and GPC via the Gladstone–Dale formula was cross-checked by ¹H NMR. As can be seen from the data, the results are comparable within the experimental error margin.

The kinetic study of reactions **6** ($[t\text{BA}]:[\text{PMVE}_{16}\text{-A}] = 10:90$) and **8** ($[t\text{BA}]:[\text{PMVE}_{16}\text{-A}] = 90:10$) is shown in Figure 3. Low polydispersities and a linear evolution of M_n as a function of the global conversion are observed.

Together with the first-order kinetic plots (Figure 3c,d), it can be concluded that the ATRP copolymerization of *t*BA with PMVE₁₆-A macromonomer is controlled up to certain conversions, after which the linearity in the first-order plot is lost due to increased steric hindrance and viscosity. As could be expected, this effect is more pronounced for the reaction with the highest amount (90 mol %) of PMVE₁₆-A macromonomer in the feed (poly(*t*BA-co-PMVE₁₆-A) **6** in Figure 3c). Furthermore, the first-order kinetic plots of both reactions demonstrate faster consumption of *t*BA than the PMVE₁₆-A macromonomer.

Since reactions **6** and **8** involve the use of a large excess of one monomer relative to the other one, the Mayo and Lewis method⁴⁸ simplified by Jaacks⁴⁹ was preferentially applied to estimate the relative reactivity of *t*BA and PMVE₁₆-A. The

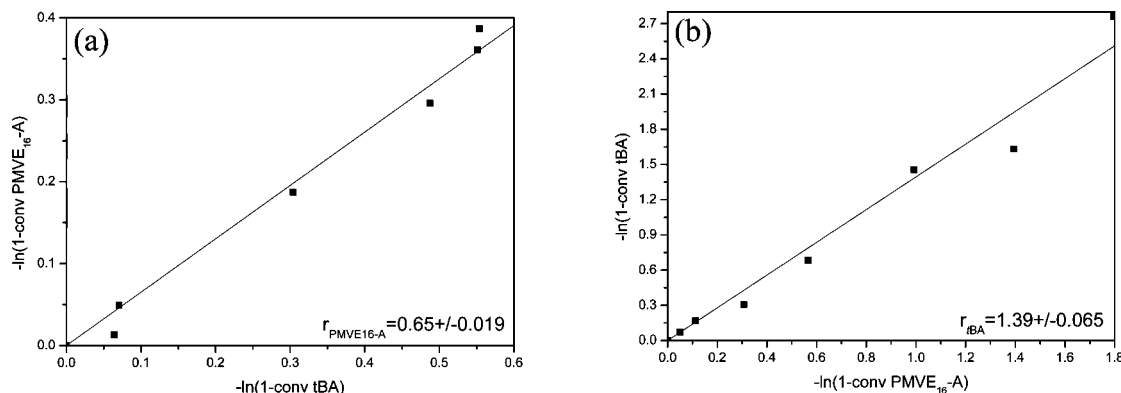


Figure 4. Jaacks plots for the ATRP copolymerization ($DP_{\text{total}} = 300$) of (a) 10/90 mol % tBA/PMVE₁₆-A for poly(tBA-co-PMVE₁₆-A) **6** and (b) 90/10 mol % tBA/PMVE₁₆-A for poly(tBA-co-PMVE₁₆-A) **8**.

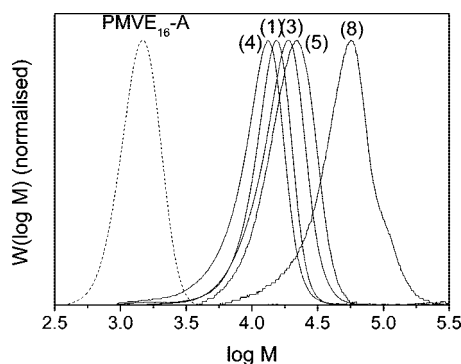


Figure 5. GPC traces (refractive index detection) for PMVE₁₆-A macromonomer (---) and poly(tBA-co-PMVE₁₆-A) **4**, **1**, **3**, **5**, and **8** (—) in Table 3.

reactivity ratio of the monomer in excess is obtained from the linear logarithmic plot of comonomer conversions:

$$\ln \frac{[M_1]_t}{[M_1]_0} = r_1 \ln \frac{[M_2]_t}{[M_2]_0} \quad (3)$$

If the conversions of M_1 and M_2 at the time t are C_1 and C_2 , respectively, eq 3 can be written as

$$\ln(1 - C_1) = r_1 \ln(1 - C_2) \quad (4)$$

Figure 4a,b shows double-logarithmic plots of fractional comonomer conversions C_{tBA} and $C_{\text{PMVE}_{16}\text{-A}}$: their slopes provide reactivity ratios $r_{\text{PMVE}_{16}\text{-A}} = 0.65 \pm 0.019$ (Figure 4a) and $r_{\text{tBA}} = 1.39 \pm 0.065$ (Figure 4b). This indicates the formation of copolymers poly(tBA-co-PMVE₁₆-A) with a slight gradient in composition along the backbone of the copolymer, which means that PMVE₁₆-A side chains are less concentrated at the beginning of the polymer chain. The reactivity parameters obtained are apparent values, which enclose different experimental parameters, like the inherent reactivity of the vinyl function of the macromonomer, the diffusion of the macromonomer in the reaction medium, and the thermodynamic incompatibility between the growing polymer chain and the macromonomer.^{23–25,33}

The GPC curves of some copolymers, after removal of the unreacted (macro)monomer by dialysis against water, are presented in Figure 5. Well-defined copolymers were formed with narrow polydispersities, which indicates that every polymer chain has about the same number and distribution of the grafts. From Table 3, it can further be concluded that copolymerizations with a low targeted degree of polymerization (DP 50 vs DP 300) need less catalyst in order to achieve an acceptable conversion. Indeed, at higher DP , there is increased steric

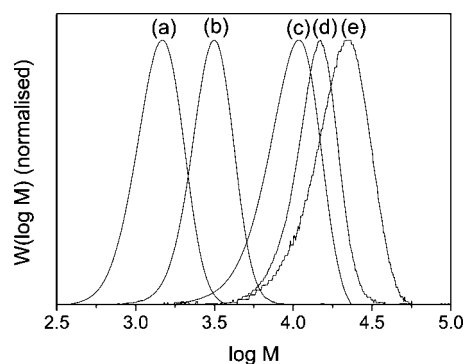


Figure 6. GPC traces (refractive index detection) for (a) PMVE₁₆-A macromonomer, (b) PrBA₂₃ macroinitiator, (c) PrBA₂₃-*b*-poly-(PMVE₁₆)_{7.5}, (d) PrBA₂₃-*b*-poly-(PMVE₁₆)₁₈, and (e) PrBA₂₃-*b*-poly-(PMVE₁₆)₃₂.

hindrance and a lower radical concentration in the reaction mixture. This reduced reactivity was compensated by the use of a higher catalyst concentration.³²

Palm-Tree Architectures Based on a PrBA and PMVE-A Macromonomer. Not only statistical graft copolymers, but also block copolymers, were prepared with tBA and PMVE-A macromonomer. Therefore, well-defined PrBA-Br macroinitiators were first prepared by ATRP³⁸ and subsequently used to initiate ATRP of PMVE-A in a next step (Scheme 1C). This strategy results in the formation of so-called palm-tree block copolymers,¹⁸ also called tadpole-shaped¹⁹ block copolymers. The right reaction conditions for the synthesis of palm-tree block copolymers consisting of PrBA and PMVE₁₆-A were established using the knowledge buildup during the homopolymerization of PMVE₁₆-A and the statistical copolymerization. As the macromonomer is slightly less reactive than a low molecular weight acrylate monomer (see copolymerization parameters), a high reactivity has to be ensured. Therefore, on one hand, the strong ligand Me₆TREN is used and, on the other hand, the catalyst concentration is increased.

As can be concluded from Table 4, palm-tree block copolymers with varying compositions and narrow polydispersities can be prepared by variation of the molecular weight of the PrBA macroinitiator, namely PrBA₂₃ ($M_n = 3100$ g/mol) and PrBA₅₁ ($M_n = 6700$ g/mol), and/or variation of the targeted DP 's and the catalyst amounts. The GPC traces in Figure 6 show that the signal of the palm-tree block copolymer quantitatively shifts to higher molecular weights compared to the PrBA macroinitiator and that all unreacted macromonomer can be successfully removed by dialysis against water.

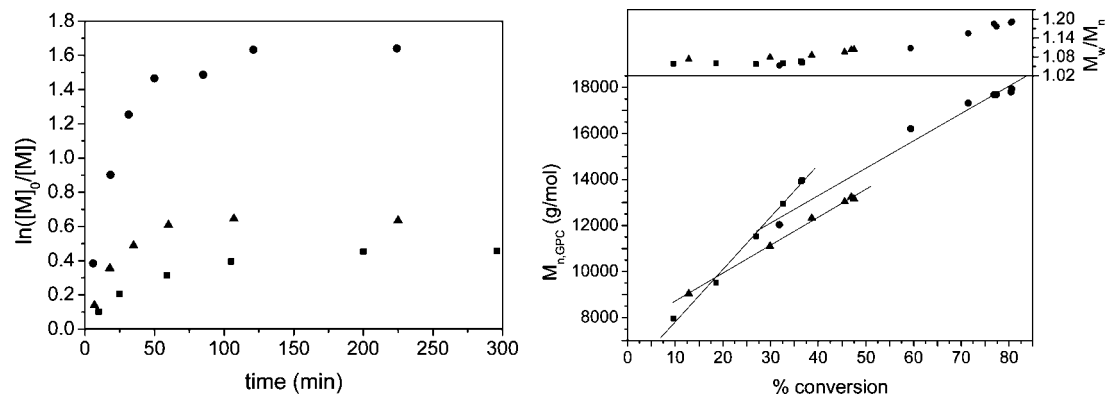


Figure 7. kinetic plots of (a) $\ln([M]_0/[M])$ vs reaction time and (b) dependence of molecular weights (bottom) and molecular weight distributions (top) of the monomer conversion for ATRP of PMVE₁₆-A with PtBA-Br as a macroinitiator: PtBA₂₃-b-poly(PMVE₁₆)₁₄ (■); PtBA₂₃-b-poly(PMVE₁₆)₁₈ (▲), and PtBA₂₃-b-poly(PMVE₁₆)₃₂ (●).

As for the synthesis of polymacromonomers and for statistical copolymerizations, a deviation from linearity in the first-order kinetic plot occurs (Figure 7a). By increasing the reactivity of the system, it is possible to push the reaction to higher conversions. This could be achieved via several methods: (i) increase of the reaction temperature from 50 to 90 °C; (ii) increase of the catalyst concentration from 1 to 2 equiv ($P = tBA_{23}$ -b-poly(PMVE₁₆)₁₈ vs PtBA₂₃-b-poly(PMVE₁₆)₃₂); (iii) increase of the radical concentration by starting from a lower $[M]_0/[I]_0$ ratio, in combination with 2 equiv of catalyst. In order to avoid termination reactions by the high radical concentration at the beginning of the reaction, 5 mol % Cu(II)Br₂ was added (PtBA₂₃-b-poly(PMVE₁₆)_{7.5}). Moreover, the effect of steric hindrance around the growing radical is smaller for lower initial DP's. (iv) The solvent was varied (acetone or toluene). Solvents have a major influence on the polymerization rate and the degree of control in ATRP.^{50–53} This is ascribed to the formation of different complex structures, but also to the different solubility of activator and deactivator in several solvents.⁵⁴ The more polar solvent acetone promotes the solubility of the catalyst system compared to toluene, such that higher conversions are achievable. The high conversion for PtBA₂₃-b-poly(PMVE₁₆)₃₂ can thus probably be attributed not only to the amount of catalyst but also to the use of a polar solvent. Those effects are clearly visible in the first-order kinetic plots (Figure 7a) for the first three reactions in Table 4. Figure 7b shows that M_n evolves linearly as a function of the conversion and that the polydispersities are low. It can thus be concluded that the reactions are controlled up to a certain conversion.

Similarly to the PtBA₂₃ macroinitiator, an increased conversion can be achieved for the PtBA₅₁ macroinitiator by increasing the catalyst and radical concentration by starting with a lower targeted DP (PtBA₅₁-b-poly(PMVE₁₆)₁₇ vs PtBA₅₁-b-poly(PMVE₁₆)₂₆).

Hydrolysis of PtBA to PAA. The polymer architectures containing PtBA were converted via hydrolysis of the *tert*-butyl groups to pH-sensitive PAA copolymers. Hydrolysis was done with 5 equiv of MeSO₃H relative to the *tert*-butyl ester functions. It was first verified whether the PMVE–ether bonds and the ester linkage between the PMVE chains and the backbone survive those hydrolysis conditions. To this end, the PMVE₁₆-A macromonomer was subjected to a model reaction, which consists in the addition of a large excess of MeSO₃H (5 equiv per MVE unit, i.e., 80 equiv per ester linkage). The mixture was stirred for 1 h in CH₂Cl₂ at room temperature. GPC analysis (see Supporting Information, Figure S2a) gives a signal at the same molecular weight as before hydrolysis. Also in MALDI-TOF and ¹H NMR no side products are observed (see Supporting Information, Figure S2b). Successful hydrolysis of the

Table 5. T_{cp} Values of PolyPMVE (1 wt % Aqueous Solutions, Heating at 0.2 °C/min)

code	$M_{n,exp}$ (g/mol)	T_{cp} (°C)
PMVE ₁₆ -A	1 100	24.9
poly(PMVE ₁₆ -A) ₁₇	19 200	24.9
poly(PMVE ₁₆ -A) ₂₃	25 300	23.8

PMVE/PtBA copolymers is proven in the same way as previously for the linear block copolymers.¹⁴ In FT-IR the typical asymmetric doublet caused by the *tert*-butyl groups at 1368 and 1393 cm^{−1} disappears, and a broad carboxylic acid band appears in the region 3700–2300 cm^{−1}. In ¹H NMR the *tert*-butyl signal at 1.44 ppm disappears after hydrolysis (see Supporting Information, Figure S3). In order to make GPC analysis of PAA containing copolymers feasible, GPC was measured with *N,N*-dimethylacetamide (with 0.21% LiCl and 0.6% HOAc) as the eluent, following the procedure of Pasch et al.⁵⁵ This method allows to reduce ionic and adsorption effects of PAA on the column. The polydispersity index of the samples before and after hydrolysis remains nearly unchanged, which indicates that the characteristics of the polymers are preserved during reaction with 5 equiv of MeSO₃H (see Supporting Information, Figure S4).

Properties

Temperature-Sensitive (Co)polymers. PMVE-A Macromonomer and Poly(PMVE) Polymacromonomer. The temperature-responsive behavior of the PMVE macromonomer and of the poly(PMVE) homopolymers was studied (Table 5). Compared to nonfunctionalized PMVE with a cloud point temperature (T_{cp}) around body temperature (37 °C), PMVE₁₆-A shows a lower T_{cp} (24.9 °C), measured by turbidimetry (UV–vis). As published earlier,⁵⁶ terminal modification by hydrophobic end groups (coming from the inimer in this case) lowers T_{cp} . In fact, PMVE-A can be considered as an amphiphilic structure composed of a long hydrophilic PMVE block (with narrow polydispersity) and a short hydrophobic block (monodisperse, 14.4 wt %) coming from the inimer. As the molar ratio of the end groups relative to PMVE remains identical in the graft copolymer compared to the PMVE macromonomer, the T_{cp} will also be influenced by the hydrophobic end groups composing the backbone. As can be seen from Table 5, the T_{cp} of the polymacromonomer is of the same order of magnitude as the one of the macromonomer. The influence of the molecular weight ($M_{n,exp}$) on the T_{cp} is according to the expectations for a type III LCST polymer:⁵⁶ a higher molecular weight polymer results in a lower T_{cp} .

PtBA-b-PMVE, PtBA-b-poly(PMVE), and Poly(tBA-co-PMVE). In the next section, the influence of the hydrophobic PtBA segment on the thermoresponsive properties of PMVE is

Table 6. T_{cp} Values for Different Copolymer Architectures Based on P r BA and PMVE

code ^a	mol % P r BA	wt % P r BA	T_{cp} (°C)
linear block copolymers			
PMVE ₅₀ -Br	0	0	27
P r BA ₁₆ - <i>b</i> -PMVE ₇₄	17	32	26.9
P r BA ₁₆ - <i>b</i> -PMVE ₅₀	24	41	<3 °C ^b
P r BA ₁₆ - <i>b</i> -PMVE ₃₃	32	51	not soluble
palm-tree block copolymers			
PMVE ₁₆ -A	0	0	24.9
P r BA ₂₃ - <i>b</i> -poly(PMVE ₁₆ -A) ₃₂	46	9	24.3
P r BA ₂₃ - <i>b</i> -poly(PMVE ₁₆ -A) ₁₈	56	13	24.3
P r BA ₂₃ - <i>b</i> -poly(PMVE ₁₆ -A) ₁₄	62	16	25.2
P r BA ₂₃ - <i>b</i> -poly(PMVE ₁₆ -A) _{7.5}	76	27	21.8
statistical graft copolymers			
PMVE ₁₆ -A	0	0	24.9
poly(<i>t</i> BA- <i>co</i> -PMVE ₁₆) 5	19	2.6	22.0
poly(<i>t</i> BA- <i>co</i> -PMVE ₁₆) 1	37	6.5	17.3
poly(<i>t</i> BA- <i>co</i> -PMVE ₁₆) 3	58	14	16.0
poly(<i>t</i> BA- <i>co</i> -PMVE ₁₆) 4	79	31	14.5
poly(<i>t</i> BA- <i>co</i> -PMVE ₁₆) 8	92	56	not soluble

^a Subscripts represent DP. ^b The polymer is dissolved, but it gives a milky solution in the fridge at 3 °C, rendering the measurement of T_{cp} impossible.

described. The T_{cp} values measured for different copolymer architectures with varying compositions of P r BA and PMVE are presented in Table 6. The linear block copolymer P r BA₁₆-*b*-PMVE₇₄¹⁴ shows a lower T_{cp} (27 °C) compared to the value expected for pure PMVE (37 °C). Pure PMVE₅₀ prepared with dual initiator 2-bromo-(3,3-diethoxypropyl)-2-methylpropanoate (represented as PMVE₅₀-Br; 7.9 wt % hydrophobic end groups) shows a similar T_{cp} decrease. In the block copolymer, however, PMVE has a higher DP, namely DP = 74. This means that for PMVE₇₄-Br homopolymer a slightly higher T_{cp} can be expected (than for PMVE₅₀-Br) due to the higher ratio of hydrophilic PMVE vs hydrophobic end group. The incorporation of 32 wt % hydrophobic P r BA only marginally decreases the LCST of PMVE₇₄-Br. However, linear block copolymers P r BA-*b*-PMVE with higher fractions of P r BA are too hydrophobic and not water-soluble anymore above 3 °C.

For palm-tree block copolymers, the same phenomenon is observed as for the linear block copolymers: incorporation of P r BA has, within the experimental error margins, nearly no influence on the T_{cp} of the PMVE-A macromonomer. In the case of a statistical graft copolymer, however, copolymer poly(*t*BA-*co*-PMVE₁₆-A) **4** with a comparable P r BA content (31 wt %) gives a much larger T_{cp} decrease (± 10 deg) compared to the T_{cp} of the PMVE macromonomer. Similar results for block and graft copolymers based on poly(*N*-isopropylacrylamide) as temperature-sensitive polymer with a hydrophobic segment (C₁₈H₃₅, polystyrene, or methacrylic acid stearyl ester) were reported in the literature.^{57–59}

The fact that the T_{cp} for the amphiphilic block copolymers (linear and palm tree) is nearly independent of the comonomer fraction can be explained by the fact that the P r BA chains are not directly interacting with the PMVE chains in aqueous medium. Micelle formation (see further, Figure 8b,d) occurs through self-aggregation of the hydrophobic segments of the block copolymer, excluding the water molecules from the hydrophobic core of the micelle.^{60,61} As P r BA in the core of the micelle is protected from the water by PMVE, the P r BA segments give (nearly) no hydrophobic contribution to the LCST.^{57–59,62} On the contrary, for the statistical graft copolymers, no micelle formation is expected as hydrophobic aggregation of the comonomer causes partial entanglement of the temperature sensitive polymer⁶³ (Figure 8f). Consequently, the hydrophobic aggregates remain partially exposed to water and influence the T_{cp} value more strongly. This phenomenon was already observed earlier by Patrickios et al.⁶³ for a statistical

terpolymer of hexa(ethylene glycol) methacrylate, *N,N'*-(di-methylamino)ethyl methacrylate, and methyl methacrylate. In order to verify whether this micellar aggregation theory is correct, the micellization of block and statistical copolymers was compared via ¹H NMR in selective solvents. This technique is a common method to observe micellar aggregation, as demonstrated by Spevacek,⁶⁴ Armes,^{65–67} and others.^{68–70} As a point of reference, ¹H NMR spectra are measured in a good solubilizing solvent (CDCl₃) for both P r BA and PMVE. D₂O was used as a selective solvent for PMVE. Since micelles can only be formed if the block copolymers are amphiphilic, ¹H NMR spectra have to be measured below the T_{cp} of PMVE (5 °C was chosen). If micellization occurs with the formation of a hydrophobic P r BA core, protected from D₂O by the surrounding hydrophilic PMVE corona, a disappearance, or at least a decrease in relative intensity (compared to ¹H NMR in the good solvent CDCl₃), of the P r BA signals should be observed. The ¹H NMR spectra confirm the assumption that the block copolymers (linear and palm tree) form micelles, while the statistical copolymers do not. Indeed, for the linear and palm-tree block copolymers the typical P r BA peaks disappear in D₂O at 5 °C (Figure 8a–d). In the case of statistical copolymers, there is no indication of micelle formation because the signals of P r BA remain clearly visible in the selective solvent, with approximately the same relative integrations as in the common solvent CDCl₃ (Figure 8e,f).

pH- and Temperature-Sensitive Copolymers. In order to study the bireponsive behavior, some of the P r BA/PMVE containing copolymers were hydrolyzed to the corresponding polymers composed of PAA/PMVE (Table 7).

T_{cp} Study as a Function of pH by Turbidimetry (UV-vis). As PAA is pH-sensitive and PMVE temperature-sensitive, the influence of the pH on the ionization of PAA has to be considered for the study of the LCST of PMVE. Therefore, the different samples were dissolved in buffers of pH 2–10, and the T_{cp} of those 1 wt % aqueous solutions was determined by turbidimetry (UV-vis). Figure 9a shows the typical course of the variation in light absorbance at 540 nm as a function of the temperature for 1 wt % buffered PAA₁₆-*b*-PMVE₇₄ solutions (pH 2–9). A T_{cp} is observed at all pH values and the absorbance curves shift to a higher temperature starting from a pH between 4 and 5. The T_{cp} values of those linear block copolymers are shown as a function of the pH in Figure 9b. Similar to the shift of the absorbance curves to higher temperatures in Figure 9a, a T_{cp} jump occurs between pH 4 and 5 in Figure 9b, which can be correlated with the pK_a of PAA. Below the pK_a value, a decrease in the T_{cp} of the block copolymers is observed compared to the T_{cp} of pure PMVE-Br (~ 30 °C for DP = 50–74, see Table 6). If the pH decreases, the ratio of nonionized COOH groups vs the ionized acid groups (COO[−]) in PAA increases, which makes the formation of inter- and intramolecular hydrogen bonds between PAA and PMVE¹⁴ more probable. This results in a decrease of the PMVE–water interactions, and as a consequence in a decrease of the hydrophilic nature of the copolymers (thus a T_{cp} decrease). Logically, it can be expected that this T_{cp} decrease will be larger if the polymer becomes more hydrophobic, i.e., if the polymer contains more PAA that can form hydrogen bonds with PMVE. This is indeed observed when the results at pH 4 for both block copolymer samples in Figure 9b are compared.

At lower pH however, the T_{cp} values of both samples are close to each other. This is ascribed to the fact that the samples are not completely water-soluble at this low pH due to complexation, and the fraction of insoluble polymer increases for larger PAA fractions. From the type III phase diagram of PMVE,⁵⁶ it can be deduced that the T_{cp} is higher for lower polymer concentrations. Indeed, a higher water content induces

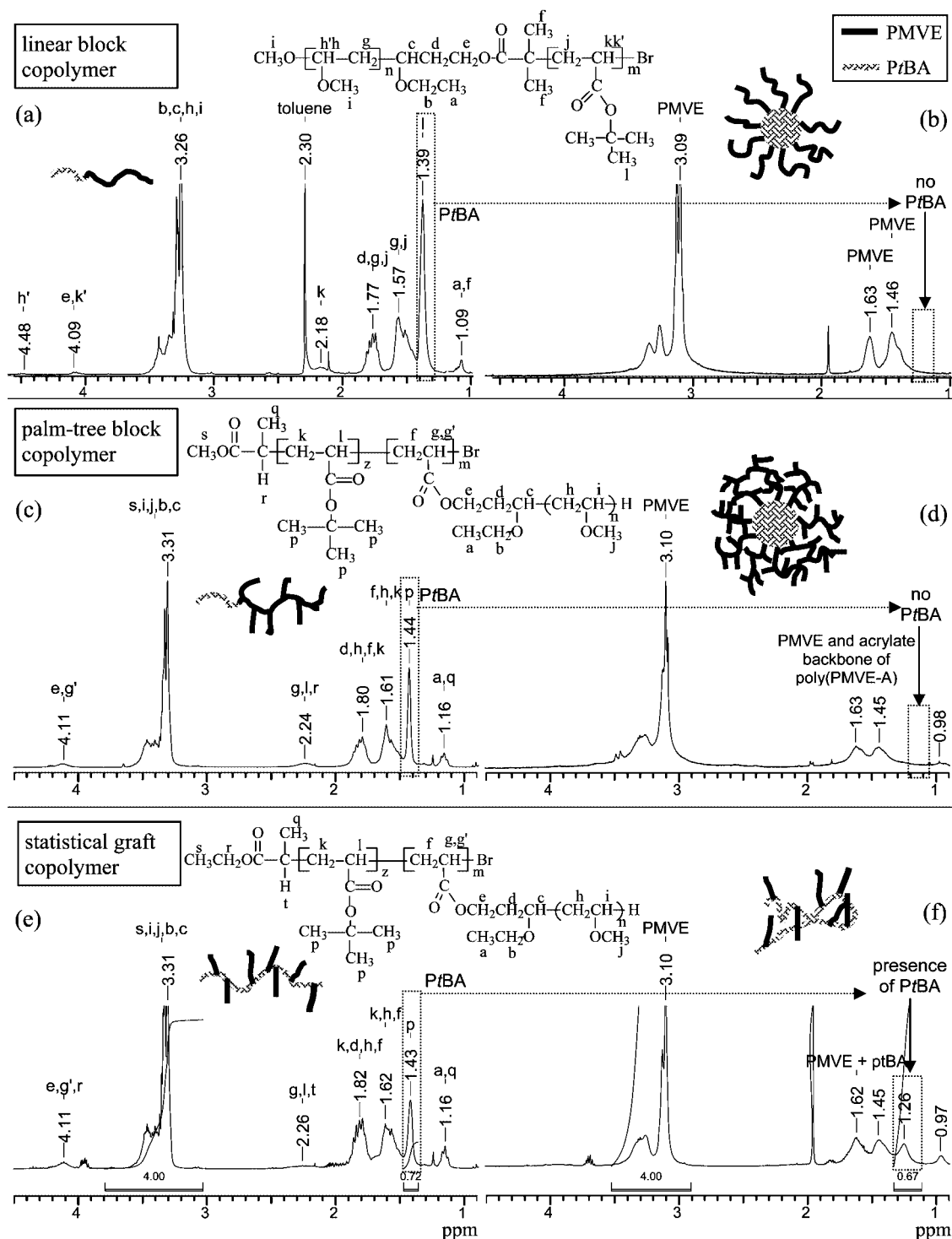


Figure 8. ^1H NMR in different solvents: (a) $\text{PrBA}_{16}\text{-}b\text{-PMVE}_{74}$ in CDCl_3 (300 MHz), (b) $\text{PrBA}_{16}\text{-}b\text{-PMVE}_{74}$ in D_2O at 5 °C (500 MHz), (c) $\text{PrBA}_{23}\text{-}b\text{-poly}(\text{PMVE}_{16}\text{-A})_{14}$ in CDCl_3 (300 MHz), (d) $\text{PrBA}_{23}\text{-}b\text{-poly}(\text{PMVE}_{16}\text{-A})_{14}$ in D_2O at 5 °C (500 MHz), (e) $\text{poly}(\text{rBA-co-PMVE}_{16}\text{-A})$ **3** in CDCl_3 (300 MHz), and (f) $\text{poly}(\text{rBA-co-PMVE}_{16}\text{-A})$ **3** in D_2O at 5 °C (500 MHz).

more polymer/water interactions, and by consequence more thermal energy is required in order to break the water structure, such that hydrophobic polymer/polymer interactions (i.e., precipitation) can dominate over polymer/water interactions.⁷¹ The constant T_{cp} at low pH values could also be due to micelle formation as in the case of the PrBA -PMVE copolymers, where it was shown that the weight fraction of PrBA does not influence much the T_{cp} .

With increasing pH, the $\text{COOH}:\text{COO}^-$ ratio decreases, which causes a decrease of the hydrogen-bonding contribution and an increase in the hydrophilicity of the PMVE/PAA copolymers.

Above its pK_{a} , PAA is fully ionized (hydrophilic), and the carboxylic acid groups repel each other electrostatically. This results in a T_{cp} increase, proportional to the hydrophilicity (wt % PAA) of the copolymers: at pH 9 the T_{cp} of $\text{PAA}_{16}\text{-}b\text{-PMVE}_{74}$ with 21 wt % PAA (\blacksquare) is smaller than the T_{cp} of $\text{PAA}_{16}\text{-}b\text{-PMVE}_{50}$ with 28 wt % PAA (\triangle). Müller et al. did similar observations for another biresponsive block copolymer, namely $\text{poly}(\text{N-isopropylacrylamide-}b\text{-acrylic acid})$.⁵

The transition between complexed COOH groups and free carboxylate (COO^-) at increasing pH was confirmed for different polymer architectures via FT-IR at pH 3 and pH 10

Table 7. Data for the PAA/PMVE Containing Copolymer Architectures Derived from the Corresponding PzBA/PMVE Precursors in Table 6

code	mol % PAA	wt % PAA
linear block copolymers		
PAA ₁₆ - <i>b</i> -PMVE ₇₄	17	21
PAA ₁₆ - <i>b</i> -PMVE ₅₀	24	28
statistical copolymers		
poly(AA- <i>co</i> -PMVE ₁₆) 1	37	4
poly(AA- <i>co</i> -PMVE ₁₆) 3	58	8
poly(AA- <i>co</i> -PMVE ₁₆) 4	79	20
poly(AA- <i>co</i> -PMVE ₁₆) 8	92	42
palm-tree block copolymers		
PAA ₂₃ - <i>b</i> -poly(PMVE ₁₆ -A) ₃₂	46	5
PAA ₂₃ - <i>b</i> -poly(PMVE ₁₆ -A) ₁₈	56	8
PAA ₂₃ - <i>b</i> -poly(PMVE ₁₆ -A) _{7.5}	76	17

(Figure 10). At pH 3, the peak around 1738 cm⁻¹ demonstrates that the COOH groups form hydrogen bonds. Upon increase of the pH, this peak diminishes and a carboxylate peak around 1575 cm⁻¹ appears, indicating that the hydrogen bonds are broken at high pH.

Among the statistical graft copolymers obtained by copolymerization of PMVE₁₆-A macromonomer, only the copolymers with high PAA content (20 and 42 wt %) contain a precipitate at low pH. The expected T_{cp} decrease with increasing PAA content (and thus increasing complexation) is now clearly observed at low pH (Figure 9c). At high pH the general rule holds that copolymers of PMVE with hydrophilic comonomers have a higher T_{cp} compared to the PMVE₁₆-A macromonomer. A larger hydrophilic part allows the copolymer to stay in solution up to a higher temperature. For poly(AA-*co*-PMVE₁₆-A) **8** with 42 wt % PAA, a T_{cp} could only be measured at pH 4. At a lower pH the polymer is not water-soluble anymore, and at higher pH no T_{cp} was observed up to 80 °C, which means

that the T_{cp} at pH 4 must be situated in the pH jump. From these observations, it can be concluded that the temperature-sensitive behavior of PMVE is lost above a critical amount of PAA.

The aqueous samples of the palm-tree block copolymers based on PMVE₁₆-A macromonomer (Figure 9d) with a small amount of PAA are fully water-soluble over the whole pH range, but PAA₂₃-*b*-poly(PMVE₁₆-A)_{7.5} with 17 wt % PAA (■) gives precipitate formation at pH 2 and pH 3. Nevertheless, at low pH the expected trend is visible: T_{cp} decreases as the polymer contains more PAA (Figure 9d). At high pH, however, T_{cp} does not increase as a function of the number of PAA units in the copolymer, as was the case for the linear block copolymers and statistical copolymers. At high pH the T_{cp} of the palm-tree block copolymers is of the same order of magnitude than the T_{cp} of the PMVE₁₆-A macromonomer.

The fact that polymers with comparable compositions but different architecture (PAA₁₆-*b*-PMVE₇₄, PAA₂₃-*b*-poly(PMVE₁₆-A)_{7.5}, and poly(AA-*co*-PMVE₁₆-A) **4** with ~20 wt % PAA) show fundamentally different phase separation behavior suggests that their supramolecular structures differ. The common point between the different copolymer architectures is that a T_{cp} jump occurs as a function of pH and that it occurs at lower pH (closer to the pK_a value of pure PAA) for higher PAA contents. Moreover, the T_{cp} jump covers a larger temperature range for copolymers with a larger PAA fraction.

Dynamic Light Scattering (DLS). Dilute solutions (concentration ≈ 1.6 g/L) of selected copolymers (poly(PMVE₁₆)₁₇, PAA₁₆-*b*-PMVE₇₄, poly(AA-*co*-PMVE) **3**, and PAA₂₃-*b*-(PMVE₁₆)₇) have been prepared in buffered water. Details about sample preparation can be found in the Experimental Part. Because of technical problems (water condensation at low temperature), no reliable DLS measurements could be obtained

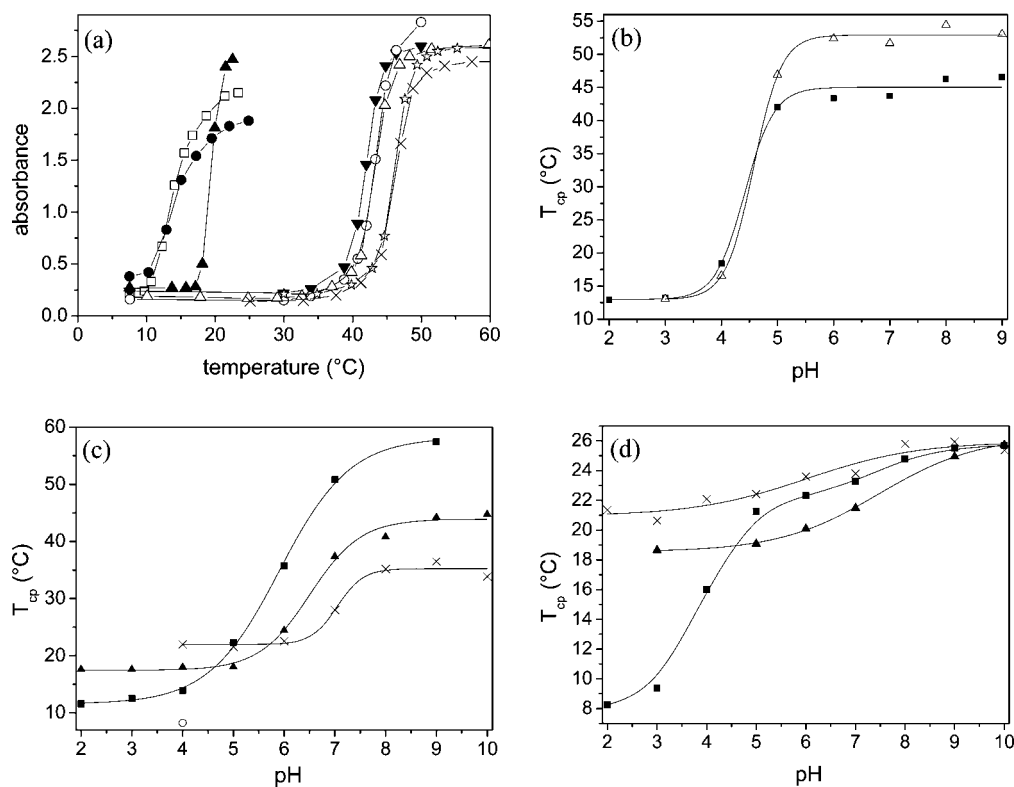


Figure 9. (a) UV-vis absorbance curves as a function of temperature for 1 wt % buffered PAA₁₆-*b*-PMVE₇₄ solutions at pH 2 (□), pH 3 (●), pH 4 (▲), pH 5 (▼), pH 6 (○), pH 7 (△), pH 8 (✱), and pH 9 (×). (b) T_{cp} vs pH for linear block copolymers PAA₁₆-*b*-PMVE₇₄ with 21 wt % PAA (■) and PAA₁₆-*b*-PMVE₅₀ with 28 wt % PAA (△). (c) T_{cp} vs pH for statistical graft copolymers poly(AA-*co*-PMVE₁₆-A) with 4 wt % PAA (×), 8 wt % PAA (▲), 20 wt % PAA (■), and 42 wt % PAA (○). (d) T_{cp} vs pH for palm-tree block copolymers PAA₂₃-*b*-poly(PMVE₁₆-A)₃₂ with 5 wt % PAA (×), PAA₂₃-*b*-poly(PMVE₁₆-A)₁₈ with 8 wt % PAA (▲), and PAA₂₃-*b*-poly(PMVE₁₆-A)_{7.5} with 17 wt % PAA (■).

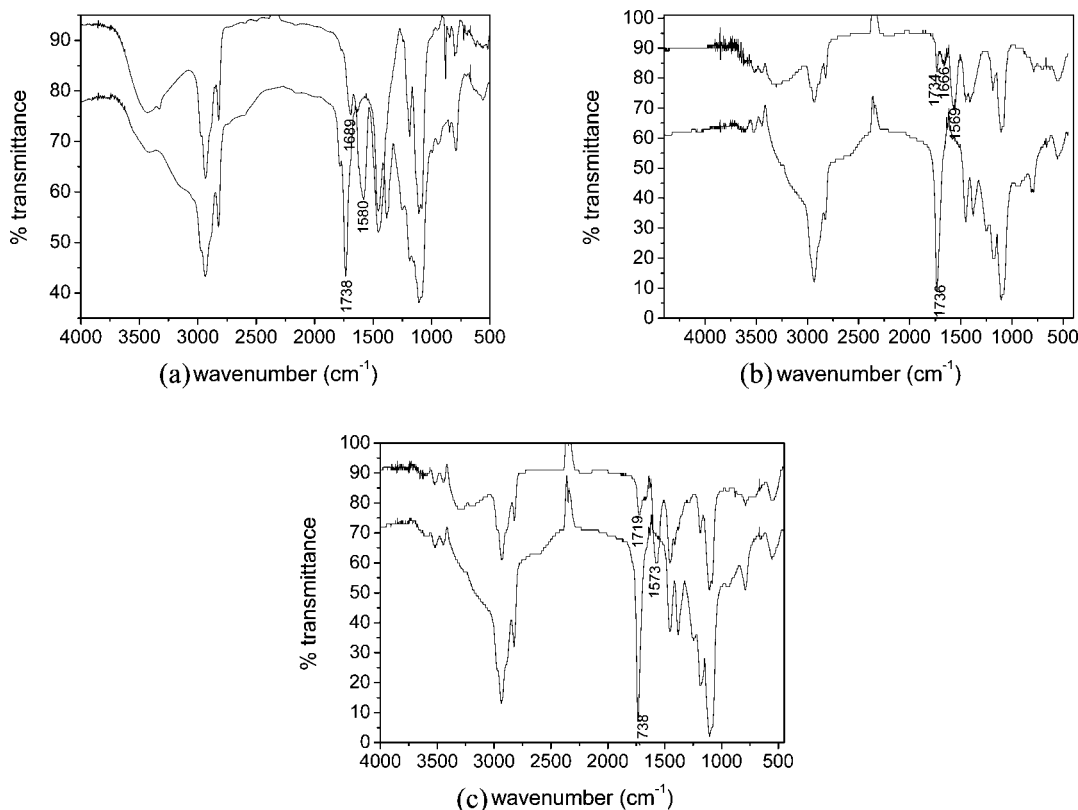


Figure 10. FT-IR spectra at pH 10 (top) and pH 3 (bottom) for (a) PAA₁₆-*b*-PMVE₇₄, (b) PAA₅₁-*b*-poly(PMVE₁₆-A)₂₆, and (c) poly(AA-*co*-PMVE₁₆-A) **4** with 20 wt % PAA.

Table 8. Dynamic Light Scattering Results of the Different Buffered (pH 10) Solutions of Copolymers below and above the Cloud Point^a

polymer	R_h (nm) at 20 °C	R_h (nm) at 55 °C
poly(PMVE ₁₆) ₁₇ comb-shaped	17 (0.50)	768 (0.30)
PAA ₁₆ - <i>b</i> -PMVE ₇₄ linear block copolymer	54 (0.48)	258 (0.31)
PAA ₂₃ - <i>b</i> -poly(PMVE ₁₆) _{7.5} palm-tree block copolymer	71 (0.10)	324 (0.50)
poly(AA- <i>co</i> -PMVE) 3 statistical graft copolymer	63 (0.35)	123 (0.20)

^a The PDI are given in parentheses.

for the samples at pH 3 at low temperature. The results for pH 10 are summarized in Table 8.

First of all, it should be noted that aggregates have been detected in all the starting solutions at 20 °C, although all samples should exist as unimers at this temperature since they only contain hydrophilic groups. The hydrodynamic radius (R_h) of these aggregates is about 17 nm for the poly(PMVE₁₆)₁₇ sample while it is ca. 60 nm for the copolymers containing PAA blocks (Table 8). The formation of aggregates in poly(PMVE₁₆)₁₇ could be attributed to defects in the hydrogen-bonded network of water molecules around PMVE blocks, which could create hydrophobic microenvironments acting as association points. The crowded brushlike structure with the acrylate backbone of the poly(PMVE₁₆)₁₇ sample could also be in part responsible of these defects. In the case of PAA-containing copolymers, the aggregation could be due to the well-known and earlier explained polyelectrolyte effect since the PAA is charged at this pH.⁷² After crossing the cloud point, very large particles were observed (more than 700 nm) in the case of the poly(PMVE₁₆)₁₇ sample, in agreement with the observed macroscopic precipitation. For the PAA-containing samples,

objects with a R_h of about 150–300 nm were observed (Table 8). Such huge R_h 's are not in agreement with the formation of block copolymer micelles but rather indicate the formation of stable colloidal aggregates. The reversible formation of those aggregates has been confirmed by DLS for all systems under investigation.

Conclusions

This paper describes the combination of living cationic polymerization and controlled radical polymerization (ATRP) to generate several (co)polymer architectures using the inimer strategy. Acrylate-functionalized PMVE macromonomer was successfully prepared by living cationic polymerization of MVE with inimer 3,3-diethoxypropyl acrylate. PMVE macromonomers were homo and (block) copolymerized with *tert*-butyl acrylate (precursor for acrylic acid) via ATRP, yielding comb polymers, statistical graft copolymers, and palm-tree block copolymers. Palm-tree block copolymers were successfully prepared starting from a *Pr*BA-Br (made by ATRP) macroinitiator. Copolymerization of PMVE-A with a monomer such as *t*BA results in statistical graft copolymers. Finally, the *Pr*BA-segments were transformed via hydrolysis into the pH-responsive PAA.

The influence of the copolymer composition (*Pr*BA, PAA) and architecture (comb polymers, linear and palm-tree block copolymers, statistical graft copolymers) on the thermosensitive behavior of the PMVE segments has been studied. Thermosensitive copolymers composed of *Pr*BA and PMVE show a T_{cp} behavior that depends on the polymer architecture. Linear and palm-tree block copolymers have a T_{cp} that is nearly independent of the content of hydrophobic *Pr*BA, while for statistical graft copolymers the T_{cp} decreases as a function of increasing *Pr*BA content. The different behavior of those architectures can be related to the fact that amphiphilic block copolymers (i.e., below

T_{cp}) are able to form micelles, while statistical graft copolymers are not.

For the PAA-containing copolymers, the influence of the pH on the T_{cp} was studied. For both the block copolymers (linear and palm tree) and the statistical graft copolymers, increasing PAA content decreases T_{cp} at low pH compared to the T_{cp} of the PMVE building block due to complexation (hydrogen bonding). At high pH, the T_{cp} seems to depend on the copolymer architecture. Linear block copolymers and statistical graft copolymers show an increase in T_{cp} as the PAA-COO⁻ content increases (i.e., increasing hydrophilicity). However, for the palm-tree block copolymers the T_{cp} seems not to depend on the PAA content and is comparable to the T_{cp} found for the PMVE macromonomer.

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Supporting Information Available: Materials and methods; GPC curves for the ATRP homopolymerization of PMVE₁₆-A; model reaction between MeSO₃H and PMVE₁₆-A; ¹H NMR and GPC analysis of PMVE/PrBA before and after hydrolysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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