Supporting Info

A Nondestructive, Statistical Method for Determination of Initiation Efficiency:
Dipentaerythritol-Aided Synthesis of Ternary ABC₃ Miktoarm Stars using a Combined “Arm-First” and “Core-First” Approach

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Experimental Materials
Poly(propylene glycol) (Mₙ = 4000 g/mol according to the manufacturer’s data; Dₐ,MSEC = 1.1 and Mₐ,MALDI = 4170 g/mol, Dₐ,MALDI = 1.01) was delivered by Polysciences, Warrington, PA, USA. N,N-dimethylaminoethyl methacrylate (DMAEMA; purified by filtration over basic alumina), silica and N,N-dimethyl-4-pyridinamine (DMAP) were purchased from Acros Organics, Geel, Belgium. Poly(ethylene glycol) monomethyl ether (Mₙ = 5000 g/mol according to the manufacturer’s data; Dₐ,MSEC = 1.1 and Mₐ,MALDI = 4950 g/mol, Dₐ,MALDI = 1.01; dried in vacuo after precipitation twice in anhydrous diethyl ether and then hexane respectively), methanesulfonyl chloride, anhydrous tetrahydrofuran (THF; destabilized; for anionic polymerization) were removed and the solution was cooled with ice before precipitation in diethylether, filtrated, washed with heptanes again precipitated in diethylether, filtrated, washed with heptanes and methanol and dialyzed against methanol over night. Then it was acquired and used as delivered (except where otherwise stated).

Syntheses
Monotelechelic Poly(ethylene oxide) with dipentaerythritoldiacetal-endgroup (PEO₁₄₋(OH))ₐ

The monomesylated poly(ethylene glycol) (4.55 g, 9.10⁻³ mol) was dissolved in 35 mL THF under nitrogen counterflow by carefully heating with a fan. The dipentaerythritoldiacetonketal (1.51 g; 4.52⁻³ mol) and sodium hydride (100 mg 50% NaH, 2.08⁻² mol) were suspended in 15 mL THF under nitrogen-counterflow and refluxed at 75°C. Then, the PEO solution was slowly added with a syringe under nitrogen counterflow and refluxed at 75°C over night. The next day, further NaH (450 mg 50% NaH, 9.4⁻¹ mol) was added under N₂-counterflow and stirring was allowed for another 5 h. The mixture was centrifuged and the supernatant was acidified by addition of acetic acid until well pH paper shows neutral pH. The mixture was centrifuged and the supernatant was reprecipitated in diethyl ether and the precipitated polymer was dissolved in methanol and dialyzed against methanol over night. Then it was again precipitated in diethyl ether, filtrated, washed with heptanes and hexane and dried in vacuo to yield 2.8 g (60%) PEO-block-Bismesylated Mes-PPO₆₂-Mₐ,MSEC = 1.1) was prepared according to reference [3] and sodium hydride (100 mg 50% NaH, 2.08⁻² mol) was suspended in 15 mL THF under nitrogen-counterflow and refluxed at 75°C. Then, the PEO solution was slowly added with a syringe under nitrogen counterflow and refluxed at 75°C over night. The next day, further NaH (450 mg 50% NaH, 9.4⁻¹ mol) was added under N₂-counterflow and stirring was allowed for another 5 h. The mixture was centrifuged and the supernatant was acidified by addition of acetic acid until well pH paper shows neutral pH. The mixture was centrifuged and the supernatant was reprecipitated in diethyl ether and the precipitated polymer was dissolved in methanol and dialyzed against methanol over night. Then it was again precipitated in diethyl ether, filtrated, washed with heptanes and hexane and dried in vacuo to yield 2.8 g (60%) PEO-block-dipentaerythritoldiaketal with a conversion of more than 92 % according to NMR (comparing methyl signal at 3.38 ppm and methyl signal at 1.4 ppm). SEC (DMF, 1 g/L LiBr; PMMA calibration): M₉ = 11700 g/mol, D₉ = 1.05; MALDI-ToF MS (DCTB): M₉ = 5290 g/mol, D₉ = 1.01; δ(400 MHz; CDCl₃; Me₂Si) 3.85-3.4 (s, PEO-H; 16H, overlapping peaks of dipentaerythritol unit -R-C₃H₆-O-) 3.38 (3H, s, CH₃-O-PEO), 1.4-1.0 (12H, s, ketal-R-CH₃).

Bismesylated Mes-PPO₆₂-Mes B

Hydroxy-telechelic PPO with one OH-group on each terminus (60 g, Mₙ = 4000 g/mol, 0.015 mol) was dissolved in dichloromethane (200 g) and triethylamine (11g, 0.11 mol) and mixed with 20 grams of molecular sieve. After 3h, the gins were removed and the solution was cooled with ice before methansulfonylchloride (6 g, 5 mL, 0.052 mol) was added dropwise with help of syringe through a septum (30 min). Then, the solution was allowed to warm up overnight under stirring.
The mixture was filtered over silica and concentrated, before the polymer was dissolved in dioxane (~100 mL) and dialyzed against dioxane for 10 days (MWCO 3500). Then, the solution was again concentrated by freeze-drying and vacuum (30 g). SEC (DMF, 1 g/L LiBr; PMMA calibration): $M_n = 6200$ g/mol, $D_M = 1.13$; $\delta_C(400$ MHz; CDCl$_3$; Me$_2$Si): 4.79 (2H, m, CH$_2$SO-\(\text{-CHCH}_{-}\text{CH}_{-}\text{CH}_{-}\)); 3.6-3.45 (m, O-\text{-CHCH}_{-}\text{CH}_{-}\text{CH}_{-}\)); 3.4-3.3 (m, O-\text{-CHCH}_{-}\text{CH}_{-}\text{CH}_{-}\)); 3.02 (6H, ds, CH$_2$SO$_2$-), 1.34 (6H, dd, CH$_2$SO$_2$-\text{-CHCH}_{-}\text{CH}_{-}\text{CH}_{-}\)); 1.2-1.0 (m, O-\text{-CHCH}_{-}\text{CH}_{-}\text{CH}_{-}\)).

Poly(ethylene oxide)-block-poly(propylene oxide) with inner dipentaerythritol (PEO$_{114}$-(OH)$_2$PPO$_{69}$) $D$, prepared with bismesylated poly(propylene oxide) (Mes-PPO$_{10}$-Mes)

The mesylated poly(propylene oxide) ($B$, 3.0 g, 1.1 $10^{-4}$ mol) was dissolved in 5 mL dry, inhibitor-free THF and dried over molecular sieves. The solution was added with a syringe into the setup that was equipped with a nitrogen-flushed condenser / water trap (CaCl$_2$) and heated at 65°C. A mixture of PEO-dipentaerythritolidketal ($A$, freshly precipitated in anhydrous diethyl ether and hexane from dichloromethane solution; dried in vacuum; 0.5 g, 9.4 $10^{-7}$ mol) and NaH (100 mg, 50% NaH, 2.1 $10^{-3}$ mol) in 5 mL dry THF was slowly added with a syringe under nitrogen counterflow and stirring, before it was refluxed for 2 h at 75°C. Then, the left-over precipitate of non-reacted NaH was washed with 5 mL dry THF and added to the reaction mixture, before it was refluxed under stirring at 65°C over the weekend. Then it was refluxed at 75°C. After 1 h, 400 mg NaH were added under N$_2$-counterflow, stirring and reflux. After hour, sodium butanol (1 g butanol was mixed with 0.6 g of 50% NaH in 10 mL dry THF) was added under N$_2$-counterflow, stirring and the mixture was refluxed for further 2 h. Then, the mixture was acidified by addition of acetic acid until the pH paper shows neutral pH. The mixture was centrifuged at 40°C and 5000 rpm in order to remove non-dissolved sodium salts and the supernatant was concentrated. It was dissolved in 10 mL hot THF and precipitated in the freezer overnight. The next day, hexane was added and the suspension was centrifuged at 5°C and 5000 rpm in order to remove non-bound PPO. The precipitate was dried in vacuum before it was dissolved in water and dialyzed for 16 h against water (MWCO 3500) and freeze dried to yield 0.54 g (60 %) with 50% conversion to dipiblock according to NMR. The polymer was dissolved in 10 mL of a concentrated NaCl solution and dialyzed for 4 days at 40°C against a 3 M NaCl solution (MWCO 12000) in order to reduce the amount of non-reacted PEO (no full removal of PEO possible in that way). Then, 1.5 g acetic acid and 0.15 g formic acid were added to 30 mL of the polymer solution (pH 3). The mixture was stirred for 20 h at RT. Then it was dialyzed for 8 h against water. When a pH of 6 was reached, it was freeze dried to get 0.47 g PEO/PPO mixture with 95 % conversion in deprotection of the ketol and a conversion to diblock of ~ 50 mol % according to NMR. One part of this mixture was directly used for the synthesis of the macronitiator. Another part was used for the full removal of non-bound PEO.

This was achieved by dissolution of 210 mg of the polymer mixture in ~ 10 mL acetone and a successive fractionated precipitation by a careful and dropwise addition of diethyl ether. When the solution turned hazy, the addition was stopped. After removal of the precipitated PEO by filtration with a syringe filter (0.45 µm, PTFE membrane), the dissolved fraction was dried in vacuo and analyzed by NMR in order to assess the block ratio. This precipitation procedure was repeated, until the block ratio did not change anymore and the pure diblock copolymer was obtained (75 mg). SEC (DMF, 1 g/L LiBr; PMMA calibration): $M_n = 15800$ g/mol, $D_M = 1.12$; MALDI-ToF MS (DCTB): $M_M = 9400$ g/mol, $D_M = 1.01$; $\delta_C(400$ MHz; CDCl$_3$; Me$_2$Si): 3.64 (s, PEO-H); 3.6-3.45 (m, O-CH$_2$-CH$_2$-CH$_2$-O); 3.45-3.35 (m, O-CH$_2$-CH$_2$-CH$_2$-O); 1.2-1.05 (m, O-CH$_2$-CH$_2$-CH$_2$-O).

Macronitiator with four ATRP initiation sites PEO$_{114}$Br$_2$-PPO$_{10}$ (poly(ethylene oxide) - block - 2,2,6,6-tetramethyl(methyl-2-bromo-2'-methylpropanoate)-4-oxa-1,7-heptanoldiol - block - poly(propylene oxide)) $E$

1.6 g chloroform and triethylamine (0.8 g, 7.9 $10^{-3}$ mol) have been dried for one hour over molecular sieves and were added to the deprotected diblock PEO-block-PPO mixture ($D$, 100 mg, ~ 50 mol % diblock) with inner dipentaerythritol moiety (~ 6 $10^{-3}$ mol OH Groups) and 1.3 mg N,N-dimethyl-4-pyridinamine (DMAP) and then cooled with ice under stirring. Then 2-bromo-2-methylpropanoyl bromide (26 mg; 1.1 $10^{-3}$ mol) was added and the mixture was stirred for 2.5 h, before another 80 mg of bromide (3.5 $10^{-4}$ mol) were added. The temperature was allowed to slowly increase to RT overnight under stirring. The next day, the flask was equipped with a condenser and the mixture was refluxed at 75°C for 2 h. When the mixture was cooled down, chloroform was added and the mixture was filtrated. The mixture was concentrated, before it was dissolved in hot THF and centrifuged. The solution was cooled in the freezer. At the next day, after adding hexane, the mixture was centrifuged and the precipitate was dried in vacuo. The precipitate was dissolved in methanol and dialyzed for 3 days against methanol (MWCO 3500) and then for 10 h against water before it was freeze dried. It was dissolved in 5 mL aceton and the side product PEO(-Br)$_2$ was precipitated. This was achieved by a careful and dropwise addition of diethyl ether. When the solution turned hazy, the addition was stopped. After removal of the precipitated PEO by filtration with a syringe filter (0.45 µm, PTFE membrane), the dissolved fraction was dried in vacuo and analyzed by NMR in order to assess the block ratio. This precipitation procedure was repeated, until the block ratio did not change anymore. Finally, the supernatant was concentrated, dissolved in water and freeze dried in order to obtain pure macronitiator (22 mg, 33 % yield relative to pure diblock). SEC (DMF, 1 g/L LiBr; PMMA calibration): $M_n = 18100$ g/mol, $D_M = 1.07$; MALDI-ToF MS (DCTB): $M_M = 9670$ g/mol, $D_M = 1.01$; $\delta_C(400$ MHz; CDCl$_3$; Me$_2$Si): 4.22 (8H, s, -CH$_2$-O-C=O-), 3.64 (s, PEO-H); 3.6-3.45 (m, O-CH$_2$-CH$_2$-CH$_2$-O); 3.45-3.35 (m, O-CH$_2$-CH$_2$-CH$_2$-O); 1.92 (24H, s, -O-C=O-(CH$_2$)$_n$-Br); 1.18-1.07 (m, O-CH$_2$-CH$_2$-CH$_2$-O).

Miktoarm star with 1 PEO arm, 1 PPO arm and ~ 4 PDMAEMA arms (PEO$_{114}$-(PDMAEM$_{69}$)$_3$)-PPO$_{10}$ $F$

A mixture of the macronitiator PEO$_{114}$-Br$_2$-PPO$_{10}$ ($E$, 15 mg; $M_n \sim 10200$ g/mol; 5.88 $10^{-6}$ mol Br groups), copper(I)chloride (CuCl; 0.7 mg; 7.11 $10^{-6}$ mol) and copper(I)chloride (CuCl$_2$; 0.2 mg; 1.5 $10^{-6}$ mol) were mixed in anisole (filtrated over basic alumina; 0.57 g) and deoxygenated by purging with nitrogen.
Then, the ligand \(N,N,N',N''-\)hexamethyldihydriliramine (HMTETA; 20.8 mg; 9.0 \(10^{-5}\) mol) and the monomer \(N,N\)-dimethylaminomethanol methacrylate (DMAEMA; 1.256 g; 8.0 \(10^{-3}\) mol; filtered over basic alumina) were also mixed and deoxygenated. 134 mg of this solution (0.132 g DMAEMA, 8.4 \(10^{-3}\) mol; 2.1 mg HMTETA, 9.1 \(10^{-6}\) mol) was introduced to the macroinitiator mixture at 80°C under stirring and nitrogen counterflow. After 3 h, the reaction was terminated by injection of chloroform and contact with air. The conversion was 49% according to NMR (\(M_{\text{calcd}}(\text{total}) = 55000 \text{ g/mol}\); theoretical formula: PEO\(_{114}\)-PDMAEMA\(_{30}\)-PPO\(_{69}\)). Then the polymer solution was filtered through silica and then concentrated, before it was dissolved in dioxane and precipitated from hexane. Then the precipitate was dissolved in dioxane and dialyzed against dioxane for several days (MWCO 3500 g/L) before it was freeze dried to yield 70 mg of miktoarm star. SEC (DMF, 1 g/L LiBr, PMMA calibration): \(M_n = 58900 \text{ g/mol}, D_M = 1.39; \text{MALDI-ToF MS (CHCA)}: M_n = 60000 \text{ g/mol}, D_M = 1.19; \delta_1(400 MHz; CDCl}_3; \text{MeSi}) = 4.2 - 3.9 (O-CH\_2CH\_2N, PDMAEMA), 3.64 (s, PEO-H), 3.6-3.45 (m, O-C\_2H\_5CH\_2O, PPO), 3.45-3.25 (m, O-CH\_2CH\_2OCH\_2-CH\_2, PPO), 2.65-2.5 (O-CH\_2CH\_2N, PDMAEMA), 2.35 - 2.25 (-N(C\_6H\_4), PDMAEMA), 2.0 - 1.7 (PDMAEMA backbone CH\_2), 1.17-1.1 (m, O-CH\_2CH\_2OCH\_2O, PPO), 1.1 - 0.85 (PDMAEMA backbone CH\_2).  

### Cleavage of the arms

Different samples of the miktoarm star, which were collected after the respective experiment in order to gain conversion was 49% according to NMR (\(P_{\text{calcd}}(\text{arm}) = 70\)). 50 µL of the t-BuP\(_4\) base solution (1 M in hexane, 4 \(10^{-5}\) mol, 2 eq.) were added under nitrogen counter flow and the mixture was stirred for 30 min at 55°C. The reaction was started by adding the monomer ethyl glycidyl ether (0.15 mL, 150 mg, 1.5 \(10^{-3}\) mol, 70 eq.). The reaction was stopped after 90 h (100% conversion according NMR) by adding excess of methyl iodide (0.1 mL, 0.2 g, 1.6 \(10^{-3}\) mol \(-80\) eq.). The solvent was removed in vacuum. The product was dissolved in hot THF and precipitated upon cooling in the freezer over night. The next day, the precipitate was separated by centrifugation at -10°C and 5000 rpm from the supernatant. Finally the precipitate was dissolved in 1.4 dioxane and the product was recovered by freeze-drying (yield 109 mg).

SEC (THF, 1 g/L; PMMA calibration): \(M_n = 9400 \text{ g/mol}, D_M = 1.09; \delta_1(400 MHz; CDCl}_3; \text{MeSi}) = 3.8-3.6 (PEO-H, s), 3.53-3.33 (PEGO\(_{14}\)-CH\_2CH\_2CH\_2OCH\_2) m, 3.31 (3H, PEGO\(_{14}\)-CH\_2), 3.30 (3H, PEGO\(_{14}\)-CH\_2, bs), 1.33 (12H, acetal -CH\_2-CH\_2, s), 1.16-1.08 (PEGO\(_{14}\)-CH\_2-CH\_2, m).

### Poly(ethylene oxide)-block-poly(ethyl glycidyl ether) with inner dipentaerythritol (PEO\(_{114}\)(OH)\(_2\)-PEGE\(_{17}\))

Acetic acid was added to an aqueous polymer solution (G, 0.09 g in 10 mL) until a pH of 3 was reached. Then it was dialyzed for 16 h against water with acetic acid (pH 5). Finally it was dialyzed for 3 days against millipore water and freeze dried to yield 0.08 g (final formula: PEO\(_{114}\)-PDMAEMA\(_{30}\)-PPO\(_{69}\)). Then the polymer solution was filtrated over basic alumina (50 µL of the t-BuP\(_4\) base solution (1 M in hexane, 4 \(10^{-5}\) mol, 2 eq.) were added under nitrogen counter flow and the mixture was stirred for 30 min at 55°C. The reaction was started by adding the monomer ethyl glycidyl ether (0.15 mL, 150 mg, 1.5 \(10^{-3}\) mol, 70 eq.). The reaction was stopped after 90 h (100% conversion according NMR) by adding excess of methyl iodide (0.1 mL, 0.2 g, 1.6 \(10^{-3}\) mol \(-80\) eq.). The solvent was removed in vacuum. The product was dissolved in hot THF and precipitated upon cooling in the freezer over night. The next day, the precipitate was separated by centrifugation at -10°C and 5000 rpm from the supernatant. Finally the precipitate was dissolved in 1.4 dioxane and the product was recovered by freeze-drying (yield 109 mg).

### Poly(ethylene oxide)-block-poly(ethyl glycidyl ether) with inner dipentaerythritol (PEO\(_{114}\)(OH)\(_2\)-PEGE\(_{17}\))

Acetic acid was added to an aqueous polymer solution (G, 0.09 g in 10 mL) until a pH of 3 was reached. Then it was dialyzed for 16 h against water with acetic acid (pH 5). Finally it was dialyzed for 3 days against millipore water and freeze dried to yield 0.08 g with 96% conversion in dehydration.

SEC (THF, 1 g/L; PMMA calibration): \(M_n = 12800 \text{ g/mol}, D_M = 1.10; \delta_1(400 MHz; CDCl}_3; \text{MeSi}) = 3.8-3.6 (PEO-H, s), 3.53-3.33 (PEEGO\(_{14}\)-CH\_2CH\_2CH\_2OCH\_2) m, 3.31 (3H, PEGO\(_{14}\)-CH\_2, s), 3.30 (3H, PEGO\(_{14}\)-CH\_2, bs), 1.2-1.11 (PEEGO\(_{14}\)-CH\_2-CH\_2, m).
Macrominitiator with four ATRP initiation sites $\text{PEO}_{114}\text{-Br}_{2}\text{-PEGE}_{17}$] $\text{PEO}_{114}\text{-Br}_{2}\text{-PEGE}_{17}$ \text{[poly(ethylene oxide) - block - 2,2,6,6-tetrais(2'-bromo-2'-methylpropionato)-4-oxa-1,7-heptanidol - block - poly(ethyl glycidyl ether)]} $I$

A mixture of the macrominitiator $\text{PEO}_{114}\text{-Br}_{2}\text{-PEGE}_{17}$ ($I$, 9.6 mg; $M_n \approx 7600$ g/mol; 5.11 $10^6$ mol Br groups), copper(I)chloride (CuCl; 0.7 mg; 7.11 $10^6$ mol) and copper(II)chloride (CuCl$_2$; 0.1 mg; 7.10$^7$ mol) were mixed in anisole (filtrated over basic alumina; 0.555 g) and deoxygenated by purging with nitrogen.

Then, the ligand $\text{N,N,N',N''-hexamethylytriethyltriamine}$ (HMTETA; 25.5 mg; 1.11 $10^4$ mol) and the monomer $\text{N,N-dimethylaminomethyl methacrylate}$ (DMAEMA; 2.232 g; 1.42 $10^2$ mol) were mixed with basic alumina (filtered over basic alumina) and deoxygenated. 150 mg of this solution (0.148 g PE) was added.

The mixture was heated to 55 °C. After another 5 h, the mixture was cooled down, chloroform was added and the mixture was filtered. The mixture was reconcentrated before it was dissolved in hot THF and dialyzed for 1 week against THF (MWCO 1000) and then for 16 h against 1,4-dioxane before it was freeze dried to yield 42 mg product.

The NMR spectra were measured with a 400-MHz Bruker DRX 400 NMR spectrometer at 23 °C. Unless otherwise stated, CDCl$_3$ was used as solvent (usually 10 mg mL$^{-1}$). The chemical shifts are presented in parts per million downfield from the TMS standard. As reference the proton signal of residual CHCl$_3$ was used.

Osmometry

A membrane osmometer (Osmomat 009, Gonotec GmbH, Berlin, Germany) with regenerated cellulose membrane (Gonotec two layer membrane 90.9.0010; cut off 20000 dalton) was used for the determination of the molecular weight of miktoarm stars. Solutions with different concentrations in THF were injected to extrapolate to zero concentration. The cell was kept at 30 °C. To rinse the measurement cell with a new sample, approximately 0.7 mL of sample solution were injected three times.

Size exclusion chromatography (SEC)

SEC analyses were performed at room temperature using a high-pressure liquid chromatography pump (Bischoff 2250) and a refractive index detector (Jasco 2031plus) and in some cases with a PSS viscosity detector. The eluting solvent was dimethylformamide (DMF) with 1 g/L LiBr and a flow rate of 1.0 mL/min (polymer concentration 1 g/L). Five columns with PSS GRAM material were applied. The length of the precolumn was 50 mm and the diameter 8 mm (30 Å). The remaining four columns had a length of 300 mm, diameter of 8 mm, particle size of 10 µm, and the nominal pore widths were 30, 100, 1000 and 3000 Å. Narrow-dispersed poly(methyl methacrylate) samples (PSS, Mainz, Germany) were used for (universal) calibration and the software package PSS WinGPC Unity (PSS, Mainz, Germany) was used for the evaluation.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-ToF) Mass Spectrometry

MALDI-TOF mass spectrometry was performed on a Bruker ultrafleXtreme equipped with a 337 nm smartbeam laser in the reflective and linear mode. THF solutions of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (5 µL of 20 mg/ mL), sodium trifluoroacetate (0.1 µL of 10 mg/ mL) and analyte (5 µL of 10 mg/ mL linear polymers) were injected to MALDI-ToF MS (CHCA) was used as matrix (45 µL of 10 g/ mL in DMSO) mixed with polymer solution in THF (5 µL of 10 g/ mL). This mixture was applied on a sample plate and dried in vacuo (1 µL; measurement in linear mode). The spectra acquisition and spectra handling was performed with software Bruker Daltonics flexControl and Bruker Daltonics flexAnalysis (both vers. 3.3), before the spectra were exported to the program OriginPro 9.0 for further analysis. For determination of the molar mass obtained by...
MALDI-ToF, the spectra were directly evaluated by integration in order to obtain $M_n$ and $M_w$. In case of overlapping peaks, Gaussian fitting in the region above $3 \times 10^4$ g/mol was performed for the miktoarm stars, taking then the whole Gaussian distribution above 0 g/mol for integration. In Origin, the spectra were compared with simulated ones. The detailed procedure for extraction of the arm number (initiation site efficiency) is presented in the Results and Discussion section.

References