Penultimate Effects in the Copolymerization of Maleic Anhydride with Electron-Rich Styrene Derivatives

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ABSTRACT: The (controlled) free-radical copolymerization of maleic anhydride and styrene or derivatives thereof is often thought to provide nearly perfect alternating copolymers. Here, the RAFT copolymerization of electron-rich styrene derivatives with maleic anhydride is reported. This copolymerization shows distinct penultimate effects, resulting in polymers with increased incorporation of styrene monomers, that is, where a tendency toward periodic (S-S-MA) copolymers exists. This work could be a first step towards periodic copolymers based on maleic anhydride and styrene derivatives. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *00*, 000–000

KEYWORDS: copolymerization; microstructure; reversible addition fragmentation chain-transfer (RAFT)

INTRODUCTION The microstructure, that is, the tacticity and monomer sequence, of polymers strongly influences their properties. Highly iso- or syndiotactic polymers, for example, form much more crystalline materials than do atactic polymers.[1] Monomer sequence is among others known to influence the glass-transition temperature, crystallinity, pK_a and pK_b of polyions and the luminescent properties of copolymers.[2] The differences in the properties of periodic versus random copolymers is mainly due to the alignment and differences in the spacing of functional groups. These effects are found for very simple periodic copolymers, primarily for alternating copolymers, and it can reasonably be expected that more dramatic changes in material properties can be achieved if more complex monomer sequences are introduced, a fact that is supported by the properties of many biopolymers.[3–8]

Whereas alternating copolymers are relatively commonplace,[9–11] the creation of synthetic polymers, especially through chain-growth polymerization methods, with complex monomer sequences is currently highly challenging. A number of methods have been developed for the creation of somewhat more complex periodic copolymers though, such as the (regioselective) ring-opening metathesis polymerization of substituted cyclooctene monomers[12] and the cyclopolymerization of trifunctional monomers,[13] but these methods still rely on the tedious synthesis of suitable monomers. A more modular path towards ABA-periodic copolymers is provided by the copolymerization of maleimides with bulky nonconjugated olefins (e.g., β-pinene or D-limonene).[14–17]

In this work, we focus on the copolymerization of maleic anhydride (MA) with styrene (S) derivatives, which is often thought to yield nearly perfectly alternating copolymers. The copolymer of styrene and maleic anhydride, *a.k.a.* SMA, or close derivatives thereof, are widely used as thermoplasts, as dispersing agents, in adhesives and many other applications. The free-radical copolymerization of MA and S or derivatives of these monomers proceeds in an alternating fashion because of the electron-deficient and -rich nature of the vinyl groups in the monomers respectively. This leads to favorable energy levels of the reacting species as well as to the formation of charge–transfer complexes. The degree of alternation is additionally enhanced by the inability of MA to homopolymerize under normal conditions.[18]

EXPERIMENTAL

Materials

4-Vinylaniline (Fluorochem, 97%), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (ABCR, 97%), 4-acetoxystyrene (ABCR, 98%), di-*tert*-butyl dicarbonate (Iris Biotec, 99.2%), acetic anhydride (Roth, 99%), hexanoyl chloride (Fluka, 98%), methyl iodide (Sigma Aldrich, 99.5%), potassium hydroxide (Fluka, 85%), sodium acetate (Acros Organics, 99%), sodium chloride (Baker, 99.5%), sodium bicarbonate (Roth, 99%),

Additional Supporting Information may be found in the online version of this article.

pivaloyl chloride (Alfa Aesar, 98%), hydrochloric acid (Baker, 37–38%), and triethylamine (ABCR, 99%) were used as received.

Azobisisobutyronitrile (AIBN) was recrystallized from methanol before use. Maleic anhydride was sublimated at 70 °C under reduced pressure. *N,N*-Dimethylformamide (DMF, VWR, 99.9%) was used as received. Dry THF was obtained from a Pure Micro Solv, PS-Micro solvent purification system (Innovative Technology, Oldham, United Kingdom). 1,4-Dioxane (Ferac, 99%) was passed through an Allox plug to remove the radical inhibitor. All other organic solvents were distilled before use.

Characterization

NMR Spectroscopy

NMR spectra were recorded on a Bruker Avance III-500 Spectrometer (Rheinstetten, Germany). ^{1}H-NMR spectra were recorded at 500 MHz while ^{13}C-NMR spectra were measured at 126 MHz. Additional ^{1}H-NMR spectra were measured on a Bruker Avance III-300 Spectrometer (Rheinstetten, Germany) at 300 MHz.

All chemical shifts (δ) were measured relative to proton residual signals of the deuterated solvents [$CDCl_3$ (Roth, 99.8%), CD_3OD (Deutero, 99.8%) or DMSO-d_6 (Deutero, 99.8%)]. Assignment of the peaks is shown in the Supporting Information.

Size Exclusion Chromatography

SEC measurements using THF as the eluent were performed on a WEG Dr. Bures system (WEG Dr. Bures GmbH & Co. KG, Dallgow-Döberitz, Germany) equipped with a UV-detector (Knauer UV 2500) operating at $\lambda = 255$ nm. Measurements were performed at 60 °C with a flow rate of 1 ml/min using PS columns (50–1000 Å).

SEC measurements in *N,N*-dimethylacetamide (DMAc) were performed on a Tosoh EcoSEC HLC-8320GPC system equipped with UV- and RI-detectors. RI data is reported. Measurements were performed at 50 °C with a flow rate of 1 ml/min using PS columns (30–1000 Å).

Commercial polystyrene standards were used for calibration.

MALDI-TOF-MS

MALDI-TOF MS measurements were performed on an Autoflex III Smartbeam system from Bruker (Billerica). A solution containing 7 mg of α-cyano-4-hydroxycinnamic acid or 7 mg of 2,5-dihydroxybenzoic acid in 1 ml of a 50:50:0.1 acetonitrile-water-trifluoroacetic acid solution was used as a matrix solution. 2 mg of the polymers were dissolved in 1 ml of a 50:50:0.1 acetonitrile-water-trifluoroacetic acid solution. 1 µl of the polymer solution was mixed with 1.5 µl of the matrix solution on the substrate. 1 µl of this solution was taken and diluted with another 1.5 µl of the matrix solution. The samples were dried at room temperature. The measurements were performed in positive mode.

UV-Vis-Spectroscopy

UV-Vis measurements were performed using an Eon microplate spectrophotometer from BioTek (Bad Friedrichshall, Germany) with Polystyrene 96 microwell plates with flat bottoms from Greiner Bio-One GmbH (Frickenhausen, Germany).

UPLC-ESI-MS

UPLC-ESI-MS measurements were performed on an Acquity-UPLC H-Class CM Core system with a C18 reversed-phase column (Acquity UPLC BEH C18 1.7 µm, 2.1 mm × 50 mm) at 40 °C, an Acquity-UPLC PDA detector and an Acquity-UPLC QDA detector from Waters (Eschborn, Germany). The measurements took place over the course of 4 min with an acetonitrile-water gradient with an increasing water content of 30 to 90 vol %.

Elemental Analysis

Elemental analysis was performed on a CHNS 932 machine from LECO (St. Joseph).

Monomer Synthesis

4-Methoxystyrene (MOS)

4-Acetoxystyrene (7.0 ml, 45.5 mmol, 1.0 eq.) and potassium hydroxide (7.688 g, 137.0 mmol, 3.0 eq.) were dispersed in 37 ml of water and were stirred for 3 h. A solution of methyl iodide (4.25 ml, 68.3 mmol, 1.5 eq.) in 90 ml of acetone was added dropwise over the period of an hour while the temperature was kept constant at rt using a water bath. The resulting yellow suspension was stirred at rt for 2 days after which the volatiles were removed *in vacuo*. The remaining aqueous phase was extracted four times with chloroform, the combined organic phases were filtered over cotton wool and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using 100:6 vol/vol cyclohexane: ethyl acetate. The product was obtained as a colorless oil (5.856 g, 43.7 mmol, 96% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 7.37–7.34 (m, 2 H), 6.89–6.85 (m, 2H), 6.66 (dd, 1H), 5.62 (d, 1 H), 5.13 (d, 1H), 3.81 (s, 3 H).

N-(4-Vinylphenyl)Acetamide (VAAc)

VAAc was synthesized according to a slightly adapted literature procedure[19]:

4-Vinylaniline (3.4 ml, 29.0 mmol, 1 eq.) was dissolved in a 2 M aqueous solution of hydrochloric acid (32 ml) under argon and cooled to 0 °C. A solution of 37 g of sodium acetate in 116 ml water was added as well as acetic anhydride (37 ml, 390 mmol, 13.4 eq.). The mixture was allowed to slowly heat to rt and was stirred for 62 h. The slightly yellow precipitate was collected by filtration and washed with distilled water. The solid was redissolved in 400 ml of ethyl acetate and filtered through a silica plug. The solvent was removed *in vacuo*, yielding the product as a slightly yellow solid. (3.905 g, 24.2 mmol, 83% yield).

^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.48–7.35 (m, 4 H), 7.20 (s, 1 H), 6.67 (dd, 1 H), 5.67 (d, 1 H), 5.19 (d, 1 H), 2.18 (s, 3 H).

N-(4-Vinylphenyl)Hexanamide (VAHex)

5.0 ml of 4-vinylaniline (42.7 mmol, 1.0 eq.) was added to a solution of 9.8 ml of triethylamine (70.5 mmol, 1.5 eq.) in 100 ml ethyl acetate under argon at 0 °C. Hexanoyl chloride (7.7 ml, 59.4 mmol, 1.4 eq.) was added dropwise. After complete addition the solution was diluted with an additional 30 ml of ethyl acetate and stirred at rt for 24 h. The solution was washed three times with a 2:1 mixture of brine and 1 M sodium hydroxide solutions. The organic phase was filtered over cotton wool and the solvent is removed *in vacuo* to yield the product as a white solid (8.108 g, 37.3 mmol, 88%).

^{1}H-NMR (500 MHz, CD_3OD, δ, ppm): 7.52 (d, 2 H), 7.37 (d, 2 H), 6.69 (dd, 1 H), 5.70 (d, 1 H), 5.15 (d, 1 H), 2.36 (t, 2 H), 1.70 (m, 2 H), 1.25-1.4 (m, 4 H), 0.94 (t, 3 H). ^{13}C-APT-NMR (125 MHz, CD_3OD, δ, ppm): 174.7 (C, 1 C), 139.6 (C, 1 C), 137.6 (CH, 1 C), 134.9 (C, 1 C), 127.6 (CH, 2 C), 121.1 (CH, 2 C), 113.0 (CH2, 1 C), 38.0 (CH_2, 1 C), 32.6 (CH_2, 1 C), 26.6 (CH_2, 1 C), 23.5 (CH_2, 1 C), 14.3 (CH_3, 1 C). ESI-MS (m/z): calcd. for $C_{14}H_{20}NO^+$, 218.154, found, 218.22 $[M + H]^+$. Elemental analysis calcd. for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found C, 77.357; H, 9.107; N, 6.421.

N-(4-Vinylphenyl)Pivalamide (VAPiv)

VAPiv was prepared following a slightly modified literature procedure[19]:

3.6 ml of 4-vinylaniline (30 mmol, 1.0 eq.) was added to a solution of 4.6 ml of triethylamine (33.0 mmol, 1.1 eq.) in 70 ml ethyl acetate under argon at 0 °C. Pivaloyl chloride (4.4 ml, 36.0 mmol, 1.2 eq.) was added dropwise. After complete addition the solution was diluted with an additional 30 ml of ethyl acetate and stirred at rt for 24 h. The solution was washed three times with a 2:1 mixture of brine and saturated sodium bicarbonate solutions (3 × 50 ml). The organic phase was filtered over cotton wool and the solvent was removed *in vacuo*. The product was further purified by column chromatography using 4:1 vol/vol cyclohexane: ethyl acetate as the eluent. The product was obtained as a white solid (5.690 g, 28.0 mmol, 93% yield).

^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 7.52-7.48 (m, 2 H), 7.39–7.35 (m, 2 H), 7.31 (s, 1 H), 6.67 (dd, 1 H), 5.68 (d, 1 H), 5.19 (d, 1 H), 1.32 (s, 9 H).

Boc-Protected 4-Vinylaniline (VABoc)

VABoc was prepared following a slightly modified literature procedure[20]:

4-Vinylaniline (0.44 ml, 3.77 mmol, 1.0 eq.) and di-*tert*-butyl dicarbonate (0.990 g, 4.54 mmol, 1.2 eq.) were dissolved in 10 ml dry THF and the solution was refluxed under argon overnight. The solvent was removed *in vacuo* and the crude product was redissolved in dichloromethane (20 ml). The organic phase was washed twice with a 10 wt % sodium bicarbonate solution and subsequently with distilled water. The combined aqueous solutions were extracted three times with dichloromethane after which the organic phases were combined and filtered over cotton wool. The solvent was removed *in vacuo* and the product was further purified by column chromatography using 100:12 vol/vol cyclohexane: ethyl acetate as eluent. The product was obtained as a white solid (0.682 g, 3.11 mmol, 82% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 7.35–7.31 (m, 4 H), 6.65 (dd, 1 H), 6.48 (s, 1 H), 5.65 (d, 1 H), 5.16 (d, 1 H), 1.52 (s, 9 H).

Polymer Synthesis

Maleic anhydride and the styrene derivative (total ~40 eq.) were dissolved in stock solutions of the chain-transfer agent (4-cyano-4-(phenylcarbonothioylthio)pentanoic acid, 1 eq.) and AIBN (0.1 eq.) and some extra solvent (1,4-dioxane or DMF) according to tables shown in the Supporting Information. A sample was taken and characterized by ^{1}H-NMR spectroscopy to determine the exact ratio of monomers. The solutions were degassed by three freeze-pump-thaw cycles after which the flasks were backfilled with argon and heated to 65 °C.

Conversion of the monomers was monitored by drawing aliquots at regular intervals and measuring ^{1}H-NMR spectra for these samples. Spectra were recorded diluted in $CDCl_3$ or CD_3OD. One of the signals where the monomer and polymer signals overlap (a signal from the group in para-position to the vinyl group of the styrene derivative) was used as an internal standard by which the decrease in signal intensity of the vinyl signals of MA and the styrene derivative can be determined which is assumed to be due solely to the polymerization. Often two signals are found for MA: the anhydride and the hydrolyzed product, the sum of which is used to determine the conversion of MA.

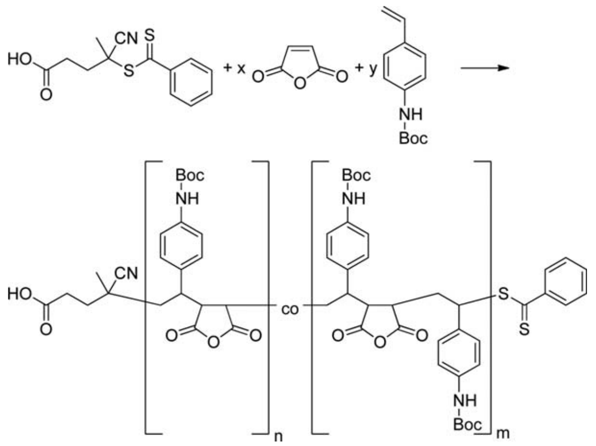
For each series of copolymerizations one polymer (from a 5:3 mixture of the styrene derivative and MA) was purified after polymerization at higher conversions. The polymers were purified by dialysis in acetone followed by freeze-drying from 1,4-dioxane.

^{1}H-NMR and SEC elugrams of the purified polymers are shown in the Supporting Information.

Job's Plot

Stock solutions with a concentration of 0.1 M were prepared for all monomers in both 1,4-dioxane and in DMF. The stock solutions were mixed in varying ratios in a 96-wells plate. Three (or in some cases six) solutions were prepared for each ratio to exclude errors in the mixing. The plates were shaken for 10 sec and UV-Vis spectra were subsequently recorded (range: 300–500 nm, $\Delta\lambda = 1$ nm)

UV-Vis spectra were also recorded for the stock solutions. The absorption attributed to charge–transfer complexes was



SCHEME 1 Periodic RAFT copolymerization of maleic anhydride with Boc-protected 4-vinylaniline

found by subtracting the weighted (based on the ratio of the two monomers) absorption found for the pure monomers from the measured absorption.

RESULTS AND DISCUSSION

RAFT Copolymerization of Maleic Anhydride and Boc-Protected 4-Vinylaniline

To our great surprise such a strictly alternating copolymer was not formed when maleic anhydride (MA) is copolymerized with *Boc*-protected 4-vinylaniline (VABoc) in a reversible addition-fragmentation chain-transfer (RAFT) copolymerization in 1,4-dioxane. For an alternating copolymerization a 1:1 ratio of the monomers is expected in the polymer. Instead, MA and VABoc are incorporated into the polymer in a ratio of about 2:3. Since this ratio is found almost independently of the feed ratio of the monomers (also see Supporting Information) this strongly suggests that this finding is not due to the presence of access VABoc but rather due to a tendency towards a periodic copolymerization, where, besides the typical alternating sequence of VABoc and MA also ABA-sequences [(VABoc-MA–VABoc)$_n$] are incorporated into the polymer (Scheme 1).

The RAFT copolymerization of MA and VABoc in 1,4-dioxane was performed using different feed ratios. The conversion of both monomers was monitored by taking aliquots and the composition of the polymer was determined from the monomer conversion as determined by ^{1}H-NMR spectroscopy. The composition of the formed polymers at low conversion (~20%) was used to determine reactivity ratios using both the terminal model and the penultimate model. The terminal model is applicable when only the last monomer in the growing chain influences the addition of monomers. Penultimate models can be used to describe systems where both the last and the second-to-last (penultimate) monomer in the chain determine the rate of addition of subsequent monomers. A number of different methods have been developed to determine reactivity ratios, especially for the terminal model. Of these methods the linear-least-square (LLS) method, Joshi–Joshi (J–J),[21] Fineman–Ross (F–R),[22] inverted Fineman-Ross (inv. F–R, where the definition of Monomer 1 and 2 is reversed), Yezrielev–Brokhina–Roskin (Y–B–R),[23] Kelen–Tüdős (K–T),[24] extended Kelen–Tüdős (ext. K–T),[25] Tidwell–Mortimer (T–M),[26] and Mao–Huglin (M–H)[27] methods were used here. Though all of these methods are based on the original copolymerization equations by Mayo and Lewis,[28] some differences apply. All except the last three are only suited for very low conversions since they only consider the immediate polymer composition. Additionally the weighting of data points is different.

The reactivity ratios that were found using the terminal model for the copolymerization of MA and VABoc were often significantly negative for either r_1 or r_2 (Table 1, the various styrene derivatives in this manuscript are defined as Monomer 1, MA as Monomer 2), which is physically impossible. In addition, the found reactivity ratios do not accurately predict the composition of the polymers that is found experimentally. Both of these facts indicate that this copolymerization is not accurately described by the terminal model.

The penultimate model assumes that the last two monomers, rather than only the last one, in a growing chain determine the rate of addition of the following monomers. This results in four chain-ends that need to be considered and accordingly four reactivity ratios (r_{11}, r_{12}, $r_{21,}$ and r_{22}). Fortunately the inability of MA to homopolymerize (except under very extreme conditions) simplifies the problem by allowing the presumption that two of these reactivity ratios (r_{12} and r_{22}) are 0. The remaining reactivity ratios (r_{11} and r_{21}) can, for example, be determined by a modified Kelen-Tüdős procedure or by a linear least square method. In both cases the values found for r_{11} are close to 0, whereas r_{21} is determined to be around 0.6 [0.67 (K–T) or 0.53 (LLS)]. The fact that $r_{11} \sim 0$ means that $k_{111} \ll k_{112}$, meaning that homopolymerization of VABoc onto a chain-end consisting of two VABoc moieties (as terminal and penultimate moieties) is negligible. r_{21} values around 0.6 mean that k_{211} is only slightly lower than k_{212}, indicating that the addition of MA is slightly preferred for a chain with VABoc terminal and with

TABLE 1 Reactivity Ratios Found for the Copolymerization of MA and VABoc Using Various Methods Based on the Terminal Model

	LLS	J–J	F–R	Inv. F–R	Y–B–R	K–T	Ext. K–T	T–M	M–H
r_1	0.14	0.16	0.12	0.34	0.13	0.14	−0.01	0.05	0.17
r_2	−0.06	−0.12	−0.15	0.01	−0.07	−0.12	−0.14	0.00	−0.01
$r_1.r_2$	−0.01	−0.02	−0.02	0.00	−0.01	−0.02	0.00	0.00	−0.00

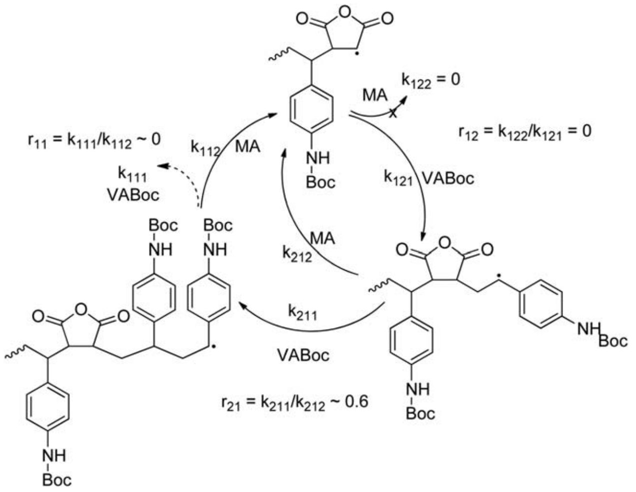


FIGURE 1 Scheme of the various steps that are significant in the copolymerization of VABoc and MA. Dashed arrows show less preferable pathways.

MA penultimate monomers. Nevertheless, VABoc is added to this chain-end to a significant degree, so that two subsequent VABoc moieties are regularly incorporated. The relevant steps in the copolymerization are shown in Figure 1.

RAFT Copolymerization of Maleic Anhydride with Other Electron-Rich Styrene Derivatives

To investigate the reason for the increased incorporation of this styrene derivative a number of other activated styrene derivatives were prepared and copolymerized with MA. Different electron-donating substituents were introduced in the *para*-position. Both the nature of the group (ether, carbamate or amide) was varied as well as the size of the groups. The monomers are shown in Figure 2.

All *para*-substituents are electron-donating, but ethers are most strongly so, while amide groups are weaker donors. The carbamate group in VABoc has an intermediate effect. This is also confirmed by the positions of the peaks corresponding to the vinyl groups of the monomers in ^{1}H-NMR spectra, which relates to the electron density of the ring and vinyl group. Three monomers with amide groups are chosen with different steric properties, ranging from small (VAAc) to bulky (VAPiv). Originally also the copolymerization of *N,N*-dimethyl-4-vinylaniline was envisioned, which is even more electron-rich, but this monomer could not be used since it was very poorly soluble in 1,4-dioxane.

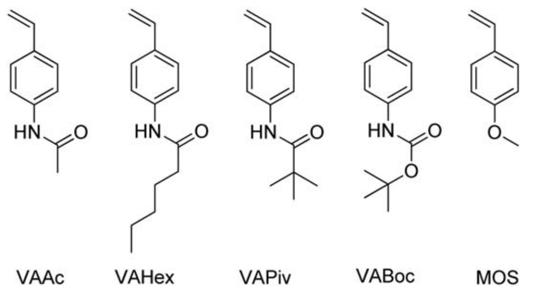


FIGURE 2 Chemical structures of the various styrene derivatives used in this work.

TABLE 2 Chemical Shift (ppm) of Vinyl Signals in the Monomers that were Used in this Work

Monomer	δ_1 (ppm)	δ_2 (ppm)	δ_3 (ppm)
S	5.22	5.74	6.65
VAAc	5.19	5.67	6.66
VAHex	5.19	5.67	6.66
VAPiv	5.19	5.68	6.66
VABoc	5.16	5.65	6.65
MOS	5.13	5.61	6.66

Styrene (S) is shown as a reference.

RAFT copolymerizations of the various styrene derivatives with maleic anhydride were, unless mentioned otherwise, performed in 1,4-dioxane at 65 °C using AIBN as the radical initiator and 4-cyano-4-(thiobenzoylthio)pentanoic acid as the chain-transfer agent (CTA); the same conditions used for the copolymerization of VABoc and MA. The RAFT process provides a good control over the copolymerizations (Đ between 1.08 and 1.40 in all cases). For the copolymerization of MA with VAPiv the evolution of the molecular weight and dispersity with conversion is shown in the Supporting Information. As is typical for many controlled polymerizations Đ decreases (from 1.34 to 1.22) with increasing conversion.

For all combinations of styrene derivatives with MA copolymerizations were performed with different monomer feed-ratios (ranging from 7:1 to 1:7) and the conversion of the monomers was followed by ^{1}H-NMR spectroscopy. Because of the poor solubility of VAAc in 1,4-dioxane it was not possible to complete this entire series: the two copolymerizations with the highest fraction of VAAc could not be performed, so that only four data points were attained, making the reactivity ratios that were calculated from this data somewhat less reliable. The same methods of calculating the reactivity ratios as mentioned before were used. The full list of reactivity ratios that were determined is shown in the Supporting Information, but an excerpt showing the results for the extended Kelen–Tüdős, Tidwell–Mortimer, and Mao–Huglin methods, those methods best suited for higher conversions for the terminal model, is shown in Table 2.

As with the copolymerization of VABoc and MA many of these ratios are, impossibly, negative, and the other values do not accurately describe the composition of the copolymers, which again plateau at about 60% of the styrene derivative. Only for the copolymerization of VAHex and MA more or less decent fits are achieved, indicating that penultimate effects are probably limited in this copolymerization.

The least-square method of fitting the data with the penultimate model seems much more reliable. This method gives fits that are in much better agreement with experimental data for the copolymerizations of VAAc, VAPiv, and MOS with

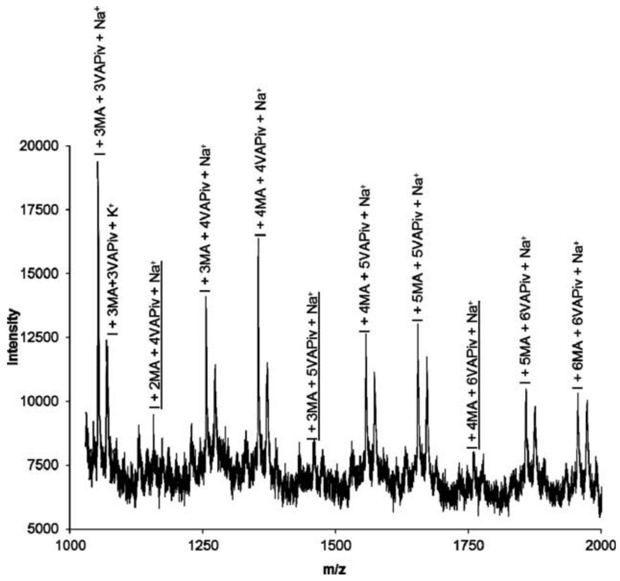


FIGURE 3 MALDI-TOF MS spectrum of the copolymer of VAPiv and MA synthesized in 1,4-dioxane. Only a selection of the peaks are assigned, for example, only one of the counterions is labeled (Na^+, whereas in most cases also the corresponding H^+ and K^+ peaks are observed). "I" represents the R-group of the CTA: the dithioester is not found. The underlined assignments indicate species with increased SD content.

MA than any of the fits with the terminal model. For VAHex the reactivity ratios attained are in good agreement with the values found using the terminal model. Though we will not discuss the copolymerization of VAAc with MA in detail because of the limited number of data points for this copolymerization due to limited solubility of VAAc in 1,4-dioxane. Both VAPiv and MOS show $r_{11} \sim 0$ and $r_{21} \sim 1$, indicating that the chance of two styrene moieties between MA moieties is as high as only one.

The increased incorporation of styrene derivatives could also be confirmed by MALDI-TOF MS, where peaks corresponding to both alternating copolymers and oligomers with larger numbers of styrene derivatives were found (the spectra for the copolymer of VAPiv and MA is shown in Figure 3, all other MALDI spectra are shown in the Supporting Information, though no peaks at all were found for the MALDI spectra of the copolymer of VABoc and MA, possibly because the molecular weight of this polymer was too high). Although the ^{1}H-NMR spectra of the polymers clearly show aromatic signals corresponding to the Z-group of the CTA, the dithioester Z-group is not found in most MALDI spectra, possibly because this group is labile under the ionization conditions. This quantitative removal of this one end-group significantly simplifies the assignment of the peaks. Various species of oligomers are found: (1) oligomers with equal amounts of MA and SD, (2) species with n MA and $n+1$ SD and (3) n MA and $n+2$ SD residues. The first two could form also for an alternating copolymer, but the third series can only occur when SD dimers are incorporated in the polymer chain.

^{13}C-NMR spectra of the various polymers were also recorded. For the copolymers of VAAc with MA and VAPiv with MA spectra were recorded both for the polymers prepared in 1,4-dioxane and in DMF, the former solvent resulting in distinct penultimate effects whereas in DMF alternating sequences seem to prevail. For comparison a homopolymer of VAPiv was also synthesized. All spectra are shown in the Supporting Information. While the spectra of the VAPiv homopolymer and its copolymers differ strongly, the copolymers prepared in 1,4-dioxane and DMF are very similar, though minor differences are present. Larger differences are apparent between the spectra of the copolymers of VAAc and MA synthesized in different solvents, possibly because the penultimate effect is much more pronounced in this monomer system (Table 3). Especially the MA carbonyl-C and aryl-C signals differ significantly. Any differences that might be present in the backbone signals are hard to distinguish because of the strong broadening of these signals, likely due to the rather rigid backbone. These differences in

TABLE 3 Reactivity Ratios Found for Various Copolymerizations Using Either the Terminal or the Penultimate Model

		Ext. K–T		T–M		M–H	
Mon 1	Mon 2	r_1	r_2	r_1	r_2	r_1	r_2
Terminal model							
VAAc	MA	−0.003	−0.152	0.986	−0.010	1.417	−0.002
VAHex	MA	−0.001	−0.058	0.046	−0.023	0.255	−0.005
VAPiv	MA	−0.003	−0.205	0.134	0.019	0.310	−0.004
MOS	MA	−0.002	−0.013	0.081	−0.008	0.175	−0.011
Mon 1	Mon 2	r_{11}	r_{21}				
Penultimate model							
VAAc	MA	0.000	6.424				
VAHex	MA	0.000	0.235				
VAPiv	MA	0.018	1.041				
MOS	MA	−0.003	1.029				

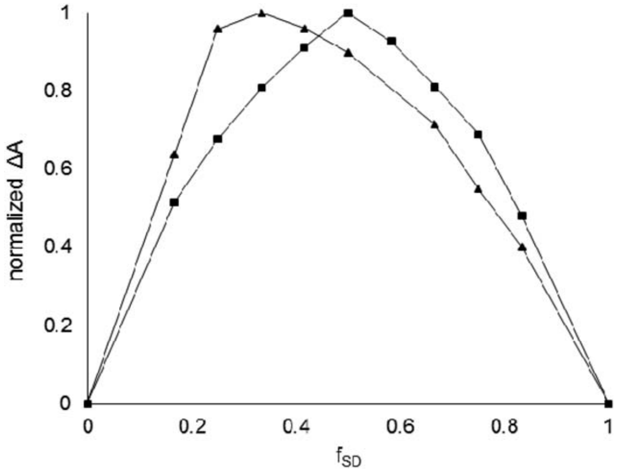


FIGURE 4 Job's plot of the formation of charge–transfer complexes between VAPiv and MA in 1,4-dioxane (triangles, from $\lambda = 316$ nm) and in *N,N*-dimethylformamide (squares, from $\lambda = 321$ nm).

the ^{13}C-NMR spectra might be another indication that the monomer sequence differs for these polymers.

Charge–Transfer Interactions

The charge–transfer complex that is known to form between styrene derivatives and MA[29] appears to be strongly involved in the observed penultimate effect. First indications for this were gained from the copolymerization of VAAc and MOS with MA in DMF. In these cases good fits were achieved with the terminal model, which yielded reactivity ratios close to 0, indicative of a strictly alternating copolymerization.

The charge–transfer complexes between electron-rich styrene derivatives (SD) and MA was further studied by preparing Job's plots using UV-Vis spectroscopy. The UV-Vis spectra of solutions (in 1,4-dioxane at room temperature) containing both styrene derivatives and MA show a new adsorption band between 300 and 320 nm which is attributed to the formation of charge–transfer complexes. A series of spectra was recorded with constant total concentrations of monomers and the corrected (against the absorption of the monomers at this wave length) absorption at the wave length where the complex absorbs strongest was plotted against the fraction of the styrene derivative (f_{SD}). For all monomers a maximum intensity of the new band is found at $f_{SD} = 0.33$, indicating that the highest concentration of charge–transfer complexes is formed at this ratio, which indicates that the complexes likely contain twice as much MA as SD. This is only the case for the electron-rich styrenic monomers used in this study though: styrene itself shows a maximum at $f_{MA} = 0.5$. In DMF most monomers show a single peak at $f_{SD} = 0.5$, indicating a 1:1 ratio of MA and SD in the complexes. Only for VAAc a second peak at $f_{SD} \sim 0.25$ is observed reproducibly, possibly indicating a second species of complexes with a 3:1 ratio of MA and SD. The Job's plots for VAPiv and MA in 1,4-dioxane and DMF are shown in Figure 4, respectively.

DISCUSSION

This difference in complexation stoichiometry is likely related to the polarity of the solvents: due to its higher polarity DMF is better able to stabilize the charge generated in the charge–transfer complex, therefore, allowing for higher charge densities than in 1,4-dioxane. The formation of 2:1 MA SD complexes nevertheless does not explain the tendency toward the incorporation of more SD in the copolymer. Rather, if the complex were to polymerize as a single unit, as has been proposed for the alternating copolymerization of MA and S or other combinations of electron-rich and -deficient monomers,[9] a higher degree of incorporation of MA would be preferred. Since this is unlikely based on the reluctance of MA to homopolymerize the most likely product would therefore be the alternating copolymer, as is usually encountered.

A depletion effect might provide an explanation. Because more MA than SD is incorporated into the complex the concentration of free MA is effectively lowered while, relatively, the concentration of free SD is increased. Assuming for a moment that the complex is less reactive in the polymerization this effect would lead to an effective feed ratio with higher amounts of SD than calculated, and therefore a more efficient incorporation of the SD.

Thus far such a depletion effect seems the most likely explanation. The fact that both VABoc, VAPiv and MOS show very similar reactivity ratios when fitted with the penultimate model indicates that, based on this series of monomers, neither sterics nor electron-density alone can explain the penultimate effect found in the RAFT copolymerization of electron-rich styrene derivatives and MA. Additionally, H-bonding cannot play a significant role (as could be proposed for monomer pairs that contain H-bond acceptors and donors) since no H-bond donors are present in either MOS or MA. Further studies are required to investigate this effect.

Altogether it seems clear that the electron-rich nature of the styrene monomers and an apolar (and likely nonaromatic) solvent are needed to achieve the penultimate effect described in this work. This work serves as a first step toward systems where a strict ABA-periodic copolymerization of styrene derivatives and MA might become accessible. Thus far only a small number of (free-radical) ABA-copolymerizations[14–17] are known to result in ABA-periodic copolymers. These copolymerizations, for example, rely on the copolymerization of maleimides with bulky monomers containing nonconjugated vinyl groups, often in solvents that coordinate to the carbonyl-group in the maleimide monomer.

CONCLUSIONS

In conclusion, we were able to show that the RAFT copolymerization of electron-rich styrene derivatives with maleic anhydride in 1,4-dioxane shows a relatively strong penultimate effect which results in the increased incorporation of the styrene derivatives as compared to the typical alternating copolymerization, that is, a certain tendency toward the formation of periodic (ABA) sequences is witnessed. Though the exact reason for this behavior has not yet been elucidated, the formation of 2:1 charge–transfer complexes of the monomers in apolar solvents seems to play a significant role. Further studies are currently under way to obtain a deeper understanding of these observations.

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