SAN-*b*-P4VP Block Copolymer Synthesis by Chain Extension from RAFT-Functional Poly(4-vinylpyridine) in Solution and in Emulsion

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ABSTRACT: Reversible addition fragmentation chain transfer (RAFT)-mediated polymerization was successfully applied for the synthesis of poly(4-vinylpyridine) (P4VP) polymers of predetermined molar mass and of low polydispersity index. These RAFT end-functionalized polymers were then used as macro-RAFT agents and further chain extended with an azeotropic mixture of styrene (STY) and acrylonitrile (AN) (63 mol % STY). Initially, these chain extension experiments were carried out in solution. In that case, the formation of the P4VP-*b*-SAN block copolymers clearly demonstrated the large fraction of chain end functionality in these RAFT-functional P4VP polymers. Proof of the formation of low molar mass P4VP-*b*-SAN block copolymer was obtained by using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis. Gradient polymer elution chromatographic (GPEC) analysis confirmed successful formation of P4VP-*b*-SAN block copolymers. Block copolymer synthesis in emulsion was also investigated. The polymerization mediated by a RAFT-functional P4VP, macro-RAFT agent, was carried out as a semicontinuous process. The complete transformation of the P4VP starting block into P4VP-*b*-SAN block copolymer points to an efficient control of the polymerization in emulsion. This procedure leads to the formation of a colloidally stable latex. The results of GPEC analysis confirmed the successful block copolymer latex formation.

Introduction

Block copolymers are macromolecules consisting of two or more sequences or blocks, where the individual blocks have their own chemical composition. The application of block copolymers ranges from surfactants, dispersants, coatings and adhesives to microelectronics, membranes, and biomaterials.[1] We aim to use well-defined block copolymers as adhesion promoting linkers between a metal coating (copper) and an industrially relevant substrate, acrylonitrile−butadiene−styrene (ABS). Therefore, our block copolymer consists of a poly(styrene-*co*-acrylonitrile) (SAN) block and of a polar block. The SAN block interacts with the SAN continuous phase of the ABS substrate by entanglement formation,[2] while the polar block, i.e., poly(4-vinylpyridine) (P4VP) in the present case, contains 4VP polar moieties which are expected to enhance the interaction with the copper coating.[3,4] The most convenient way of preparing block copolymers is via a living radical polymerization (LRP)[1,5] technique. There are three main LRP techniques that have been used during the past decade, i.e., nitroxide-mediated polymerization (NMP),[6,7] atom transfer radical polymerization (ATRP),[8,9] and reversible addition fragmentation chain transfer (RAFT)-mediated polymerization.[10,11]

The RAFT process can be used for the polymerization of a wide range of monomer types.[12] RAFT-mediated polymerization has already been employed for the synthesis of homopolymers of 4VP.[13] These RAFT-functional polymers were also chain extended into block copolymers.[14] To the best of our knowledge, the chain extension of RAFT-functional P4VP polymer into P4VP-*b*-SAN block copolymer has not been reported. The first part of the present paper reports the chain extension of a RAFT-functional P4VP block with an azeotropic mixture of STY and AN in solution, in order to confirm the living character of the P4VP starting block and its ability to control the synthesis of P4VP-*b*-SAN block copolymer. After proving the successful synthesis of this block copolymer in solution via RAFT-mediated polymerization, the second part of this paper describes the synthesis of this block copolymer by RAFT-mediated chain extension of P4VP in emulsion.

Emulsion polymerization has received considerable industrial interest for the production of a wide range of synthetic latexes.[15] A latex is a colloidally stable dispersion of submicron polymer particles in water. Colloidal stability is usually provided by a surfactant. Unfortunately, the presence of surfactants may affect the properties of the end product. An emulsion polymerization in the absence of surfactant (referred to as surfactant-free emulsion polymerization) may result in better properties of the end product.

STY is a fairly hydrophobic monomer, and AN is a partially water-soluble monomer. Surfactant-free emulsion polymerization has been used to prepare SAN copolymer latex particles with CN groups at the surface.[16] Ammonium persulfate was used as the initiator, which introduces sulfate groups on the particle surface for additional electrostatic stabilization. The spherical particles had an average size of 446 nm. Tamai et al.[17] reported that the surfactant-free emulsion copolymerization of STY and hydrophilic monomers resulted in waterborne latexes. In this paper, we assumed that the water-soluble P4VP blocks will be oriented toward the aqueous phase. The SAN block will form the core of the particle. A colloidally stable latex is expected on the basis of this morphology. The morphology resembles that of traditional core−shell particles,

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Table 1. GC Temperature Gradient

temperature (°C)	40	110	230
time (min)	5	0	2
rate (°C / min)	10	25	

but in this case there is only a single type of block copolymer chain; in traditional core−shell particles, the core and the shell are composed of different types of polymer chains.

The use of P4VP homopolymer as an emulsifier for the polymerization of STY and of AN in acidic media has already been demonstrated in industry.[18] In the absence of emulsifier, little (if any) polymer was obtained. However, additions of about 2.0−5.0 wt % P4VP (relative to monomer) were required as emulsifier to obtain a well-processable and flowing polymer dispersion of a reasonable stability. In this specific case, the P4VP homopolymer acts as a conventional surfactant. RAFT-mediated polymerization in solution led to the formation of well-defined triblock copolymers, P4VP-*b*-PSTY-*b*-P4VP and PSTY-*b*-P4VP-*b*-PSTY.[19] The self-assembled aggregates of these triblock copolymers have also been reported by Yuan et al.[19] A reduction of the P4VP block length relative to the PSTY block led to the formation of rodlike aggregates. In this situation, the P4VP blocks form the aggregate corona and the PSTY blocks reside in the core. Stable aggregates were obtained due to the amphiphilic nature of the block copolymer.

The polymerization conditions and the requirements for the preparation of P4VP-*b*-SAN block copolymers in solution and in emulsion are discussed in the present paper.

Experimental Section

Materials. Styrene (STY, Aldrich, 99+%) was purified by filtration through a column filled with aluminum oxide (Al_2O_3, Aldrich, activated basic Brockmann I, standard grade, ca. 150 mesh). Acrylonitrile (AN, Aldrich, 99+%) was purified by filtration through a column filled with inhibitor remover (Aldrich). 4-Vinylpyridine (4VP, Aldrich, 99%) was distilled under reduced pressure (0.1 mbar) at 40 °C.[20] The solvents toluene (Hi-Dry, anhydrous solvent, Romil Ltd), butanone (Merck, 99%), and tetrahydrofuran (THF, Aldrich, AR) were used as received. 4,4′-Azobis(4-cyanovaleric acid) (ACVA, Fluka, >98%) was also used as received. *S*-Dodecyl-*S*′-(isobutyric acid) trithiocarbonate (DIBTTC) as the RAFT agent was prepared according to the literature.[21]

Analytical Procedures. *Gas Chromatography (GC).* A Hewlett-Packard (HP-5890) GC equipped with an AT-Wax capillary column (30 m × 0.53 mm × 10 μm) was used. Toluene was employed as the internal standard. The GC gradient which was used is given in Table 1.

Size Exclusion Chromatography (SEC). SEC was conducted at ambient temperature using a Waters GPC equipped with a Waters model 510 pump and a model 410 differential refractometer. Solutions (ca. 1 mg/mL) were filtered over a 13 mm × 0.2 μm PTFE filter, PP housing, Alltech. Tetrahydrofuran, THF (Biosolve, stabilized with BHT), with 5 wt % acetic acid[22] was used as the eluent at a flow rate of 1.0 mL/min. A set of two mixed bed columns (Mixed-C, Polymer Laboratories, 300 × 75 mm, 5 μm particle size, 40 °C) were used. Calibration was carried out using narrow molar mass distribution polystyrene (PSTY) standards ranging from 600 to 7×10^6 g/mol. The molar masses were calculated using the PSTY calibration curve. Data acquisition and processing were performed using Waters Millennium32 (v3.2 or 4.0) software.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS). MALDI-TOF-MS analysis was carried out on a Voyager DE-STR from Applied Biosystems. The matrix *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was synthesized according to literature procedures.[20] Potassium trifluoroacetate (KTFA, Aldrich, >99%) was added as the cationic ionization agent. The matrix was dissolved in THF at a concentration of 40 mg/mL. The KTFA salt was added to THF at typical concentrations of 1 mg/mL. Polymer was dissolved in THF at ∼1 mg/mL. In a typical MALDI-TOF-MS analysis the matrix, salt, and polymer solution were premixed in a ratio of 10:1:5. The premixed solutions were hand-spotted on the target and left to dry. Spectra were recorded in both the linear mode and reflector mode. Additionally, data obtained from the end-functional samples and the synthesized copolymers were analyzed using in-house-developed software.[23]

Table 2. Gradient Used for the Characterization of the P4VP-Based Polymers[a]

time (min)	water	MeOH	THF	time (min)
2	5	94	1	2
10	0	99	1	10
2	0	0	100	2

[a] The quantities given represent the volumetric ratio of eluents.

Gradient Polymer Elution Chromatography (GPEC). GPEC measurements were carried out on an Agilent 1100 HPLC system consisting of a quaternary pump, autosampler, column oven, and a UV-diode array detector (UV-DAD). An Alltech evaporative light scattering detector (ELSD), with nitrogen flow 1.6 L/min and temperature 60 °C, was placed after the DAD detector. The temperature of the cyano column (Zorbax SB-CN, 4.6 × 150 mm, 5 μm) was 40 °C. HPLC grade solvents were purchased from BioSolve. The flow of the eluent was 1.0 mL/min. The injection volume was 1 μL. For the data acquisition, version A10.01 of the Agilent Chemstation software was used.

The gradient of eluents employed for the characterization of the P4VP-based polymer was based on a mixture of water, methanol, and THF (Table 2). Note that the polymers P4VP and SAN, as well as the block copolymers, P4VP-*b*-SAN, are referred to as P4VP-based polymers.

The additional 1 vol % of THF which was added to the gradient mixture was required to guarantee the reproducibility of the obtained peak shape. The peak area, for two subsequent measurements, was constant. For these two systems, the column was reset for 14−20 min to the initial conditions at the end of the gradient time.

Dynamic Light Scattering (DLS). The particle size distribution of the aqueous dispersion was determined by dynamic light scattering using a Malvern 4700 light scattering apparatus with a 488 nm laser, a Malvern 7032 correlator, and a PCS7 stepper motor controller. The measurement temperature was 25 °C, and the scattering angle was 90°. The intensity-weighed mean-average diameter was measured three times to obtain an average value (d_n).

Synthetic Procedures. *Synthesis of RAFT-Functional P4VP.* DIBTTC (2.000 g, 5.48 mmol) and azo-initiator ACVA (0.324 g, 1.16 mmol) were transferred into a three-necked, round-bottom flask and dissolved in a mixture of toluene and ethanol (63:37 w/w, 8.8 g) followed by the addition of monomer 4VP (4.590 g, 4.37×10^{-2} mol). Subsequently, the reaction mixture was stirred and degassed with argon for 45 min until a completely homogeneous solution was obtained. The flask with the reaction mixture was immersed in an oil bath which was kept at 67 °C. The polymerization was carried out under an argon atmosphere. After 24 h the reaction was stopped by cooling to 20 °C and exposing it to air. The conversion of 4VP was >95%, as determined by GC, using toluene as internal standard. The final reaction mixture was diluted with toluene (1-fold volumetric excess with respect to the total polymer solution) and precipitated in *n*-pentane. The precipitated polymer was then dried for 2 days under vacuum at 40 °C. The M_n value of the final polymer P4VP-1 was 1.2×10^3 g/mol with a PDI = 1.06. Under similar conditions a second polymerization was carried out. This polymer (P4VP-2) had a $M_n = 0.8 \times 10^3$ g/mol and a PDI = 1.04.

Synthesis of P4VP-b-SAN Block Copolymers via Solution Polymerization. P4VP-1 (0.304 g, 2.46×10^{-4} mol), as the macro-RAFT agent, ACVA (0.0187 g, 6.67×10^{-5} mol), and a solvent mixture of toluene and ethanol (1.15 g, 67:33 w/w) were mixed in a round-bottom flask. Then, the monomers, STY (8.00 g, 7.7×10^{-2} mol) and AN (2.42 g, 4.5×10^{-2} mol), were added. The

Table 3. Monomer Addition Profile

add. step	feed rate (mL/h)	time (h)	V_{add} (mL)
step 1	0	0	0.014[a]
step 2	0.60	3	1.8
step 3	1.20	5	4.2
step 4	4.64	6.7	12
step 5[b]	0	11	12

[a] An initial amount of monomers was added (as one drop), and then a controlled feed of monomers (steps 2−4) was started. The azeotropic monomer mixture of STY and AN (63 mol % of STY) was preformed and purged with argon prior to use. [b] After completion of the monomer mixture feed, the reaction was continued (indicated as step 5) to reach full conversion.

reaction mixture was deoxygenated, and subsequently the flask was immersed in an oil bath which was kept at 67 °C. Gravimetric analysis of a sample showed that the overall monomer conversion was 75.3% after 41 h. The reaction was stopped by cooling the reaction mixture to 20 °C and by exposing it to air. Subsequently, the reaction mixture was diluted with toluene (1-fold volumetric excess in comparison with the total polymer solution) and precipitated in an excess of cold *n*-pentane. After decantation and filtration, the polymer was finally dried for 3 days in a vacuum oven at 40 °C. The expected molar mass of the block copolymer was calculated on the basis of the ratio of converted monomer to macro-RAFT agent (using eq 1). The synthesized P4VP-*b*-SAN block copolymer for experiment **S2** had an experimentally observed molar mass value of 32.8 × 10^3 g/mol and a PDI of 1.16. The calculated molar mass value, $M_{n,calc}$, was 33.1 × 10^3 g/mol.

Synthesis of P4VP-b-SAN Block Copolymers via Emulsion Polymerization. P4VP-2 (0.167 g, 2.12 × 10^{-4} mol), HCl (0.3 g of 8 mol % aqueous HCl solution), and water (35 g) were charged to a three-necked jacketed glass reactor to carry out experiment **E1**. The reaction mixture was stirred at 300 rpm and purged with argon for 45 min until a completely homogeneous solution was obtained. An initial amount of 0.015 g of the azeotropic monomer mixture (where STY:AN = 63:37 mol/mol) was added to the reactor, and the reaction mixture was stirred for 15 min. After deoxygenating with argon, ACVA (0.053 g, 1.9 × 10^{-4} mol) dissolved in water (3 g) was added to the reactor. Then the polymerization was carried out at 80 °C and with a controlled feed of monomers (see Table 3) as a semicontinuous process. Samples were withdrawn during the process to determine conversion gravimetrically and to provide samples for subsequent SEC and GPEC analysis. Complete conversion was reached. The P4VP-*b*-SAN block copolymer product was a stable latex, with a particle size of 45 nm and with a monomodal particle size distribution. The experimentally observed molar mass value was 48.8 × 10^3 g/mol with a PDI of 4.

Results and Discussion

In this study, macro-RAFT agents, i.e., P4VP-TTC, were synthesized by trithiocarbonate (TTC)-mediated polymerization of 4VP. The obtained macro-RAFT agent (P4VP-TTC) was then chain extended with an azeotropic mixture of STY and AN (63 mol % of STY), in solution and in emulsion polymerization, resulting in P4VP-*b*-SAN block copolymers.

Synthesis and Characterization of RAFT-Functional P4VP (P4VP-TTC). The first successful RAFT-mediated polymerization of 4-vinylpyridine (4VP) has been reported by McCormic and co-workers,[24] by using cumyl dithiobenzoate (cumyl-DTB) as the RAFT agent. In our experimental work, a TTC with an isobutyric acid leaving group, i.e., *S*-dodecyl-*S′*-isobutyric acid trithiocarbonate (DIBTTC), was used as the RAFT agent for the polymerization of 4VP. The molar ratio between the RAFT agent and the initiator concentration was 4.75, as suggested by McCormic and co-workers.[24] The reaction temperature was 67 °C, which leads to a half-life time of the initiator of ∼10 h. For the performed experiments, complete conversion was obtained at the end of the polymerizations, i.e., after 24 h of reaction. RAFT-functional P4VP polymers, referred to as P4VP-1 and P4VP-2, were obtained.

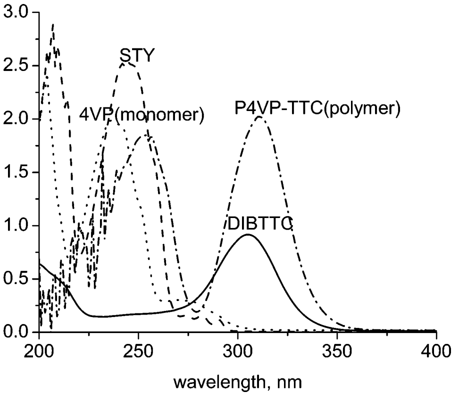

Figure 1. UV spectra of 4-vinylpyridine (4VP), styrene (STY), *S*-dodecyl-*S′*-(isobutyric acid) trithiocarbonate, and poly(4-vinylpyridine) trithiocarbonate (P4VP-TTC).

The molar masses of the obtained P4VP samples were experimentally determined by using both SEC and MALDI-TOF-MS. THF with 5 wt % acetic acid was used as the eluent for SEC analysis. It is important to mention that the P4VP polymers might show a strong adsorption on the stationary phase,[25] due to their high nitrogen contents. Furthermore, P4VP is poorly soluble in THF, which hampers its characterization by SEC. At the very least this will limit the molar mass range over which SEC can reliably be applied on P4VP. On the basis of preliminary work, it is estimated that significant deviations between the true molar mass (M_n) and experimentally determined M_n values might be obtained for P4VP with more than 20 units of 4VP. Note that in the present experiments the majority of the synthesized P4VP samples did not have more than 9 units of 4VP. For these samples SEC was successfully used to determine their molar mass values. MALDI-TOF-MS was used to confirm the M_n values obtained by SEC. Another reason to use MALDI-TOF-MS is the necessity to verify the presence of the RAFT end groups. UV spectra were recorded for additional proof of the presence of RAFT-functional chain ends.

The MALDI-TOF-MS analysis confirmed the complete end functionality of the P4VP polymer with the desired RAFT group. The presence of the RAFT moiety, i.e., the TTC group responsible for the living character of RAFT-functional polymer chains, was also confirmed by using UV (see Figure 1). The UV spectrum of a TTC group, i.e., DIBTTC, has a maximum absorption at a wavelength of 305 nm. The UV spectrum does not provide information about the fraction of functional chain ends. This information would require a thorough study in which molar extinction coefficients of the end groups need to be determined. Similarly, it is known that MALDI-TOF-MS is not a quantitative technique when it comes to relative amounts of polymer species present in a sample. Even the change of only a polymer end group can lead to significant changes in the relative intensity in the mass spectrum. Nevertheless, the results look promising, and chain extension experiments with STY and AN, described below, will provide additional information about the fraction of RAFT chain ends. The RAFT-functional P4VP polymers referred to as P4VP-1 and P4VP-2 were then used for the chain extension with an azeotropic mixture of STY and AN in solution and in emulsion, respectively.

Table 4. Block Copolymers Poly(4-vinylpyridine-*b*-(styrene-*co*-acrylonitrile)) (P4VP-*b*-SAN) with Different Lengths of the SAN Block[a]

sample code	[STY] (mol/L)	[AN] mol/L)	[CTA] (10^{-3} mol/L)	time (h)	conv (%)	$M_{n,calc}$ (10^3 g/mol)	$M_{n,SEC}$ (10^3 g/mol)	$M_{n,MALDI}$ (10^3 g/mol)	PDI_{SEC}
S1	5.22	3.07	120	2	59.7	4.7	5.7	4.5	1.23
				26	64.8	5.0	6.0	5.0	1.26
S2	5.90	3.61	19	41	75.3	33.1	32.8	n.a.	1.16
S3	6.20	3.58	6.8	48	62.4	77.8	77.8	n.a.	1.32

[a] The starting P4VP trithiocarbonate (P4VP-1) block was used as a macro-chain-transfer agent ($M_n = 1.2 \times 10^3$ g/mol).

Synthesis and Characterization of P4VP-*b*-SAN Block Copolymers by Solution Polymerization. In a first approach, a RAFT-functional P4VP starting block ($M_n = 1.2 \times 10^3$ g/mol), referred to as P4VP-1, was used as a macro-RAFT agent, for the experiments **S1**−**S3**. The results of the synthesized P4VP-*b*-SAN block copolymers are collected in Table 4.

The molar mass of the entire block copolymer is predicted by eq 1. In the specific case of RAFT-mediated block copolymerization, M_n values are calculated with the following equation:

$$M_{n,calc} = M_{n,macro-RAFT} + \frac{\sum[\text{mon}]_0}{[\text{macro-RAFT}]_0} \times FW_{mon} \times x \quad (1)$$

where $M_{n,macro-RAFT}$ represents the experimentally observed M_n value of the macro-RAFT agent, in this case the P4VP starting block, which is determined by SEC. FW_{mon} is the average molecular weight of the monomer mixture. The monomer conversion is represented by x. $\sum[\text{mon}]_0$ and $[\text{macro-RAFT}]_0$ are the initial concentrations of monomers and the macro-RAFT agent, respectively. Note that the concentration of initiator is low with respect to $[\text{macro-RAFT}]_0$. That is why the initiator-derived polymer chains produced during the RAFT-mediated polymerization are neglected and thus are not accounted for in eq 1.

The obtained block copolymer of the lowest molar mass, synthesized in experiment **S1**, had a short block of SAN attached to the even shorter P4VP starting block. On the one hand, the experimentally observed M_n value measured by SEC for the obtained block copolymer in experiment **S1** was higher than the M_n value calculated by eq 1 (see Table 4). However, good agreement was observed between calculated M_n value and the one determined by MALDI-TOF-MS. It is important to note that MALDI-TOF-MS is an absolute technique to determine molar masses, whereas SEC is a relative technique, and might be subject to artifacts induced by the polar nature of the P4VP block. In addition, MALDI-TOF-MS was used to determine the chemical composition of the obtained block copolymer (**S1**) as presented in Figure 2. The mass spectra of the analyzed polymer can be represented as a contour map[23] to give an indication of the chemical composition distribution.

Figure 2 shows the contour map of the block copolymer P4VP-*b*-SAN. P4VP-1 was used as a starting macro-RAFT agent and had already been analyzed by MALDI-TOF-MS. The contour map is constructed by deconvolution of the MALDI spectra and taking into account the mass spectrum of the starting block. The measurement confirms that the SAN chain is a statistical copolymer with negligible composition drift along the polymer backbone. The latter would have resulted in curvature of the axis of the contour map. The SAN chain contained approximately 10−50 STY units and 2−28 AN units. The highest intensity is at 32 STY and 17 AN units. On the basis of the MALDI-TOF-MS measurement, it was calculated that the block copolymer synthesized in experiment **S1** had the expected azeotropic composition of STY and AN (79:21 w/w or 65:35 mol/mol, respectively).

A higher molar mass of the second SAN block, and therefore of the block copolymers P4VP-*b*-SAN, was targeted in the experiments **S2** and **S3**. The results are presented in Table 4. Figure 3 shows that the M_n value of the block copolymer increased linearly with the monomer conversion for experiments **S2** and **S3**, indicating that the polymerization had a living character. The good agreement between the M_n value predicted by eq 1 and the experimentally observed M_n value pointed to an efficient control of the radical polymerization using the starting P4VP-TTC block as macro-RAFT agent.

Figure 4 shows the evolution of the SEC traces for experiment **S2**. The SEC chromatogram (DRI traces) of the sample points to a monomodal molar mass distribution (see Figure 4a). Note that traces of the low molar mass polymer eluted between 17 and 19 mL. This indicates that there is always some remaining (nonfunctional) P4VP block present (see below). However, these traces correspond to a minimal amount of material and can be neglected in comparison with the amounts of the growing block copolymer. Some multimodality is observed in the low molar mass region of the starting P4VP macro-RAFT agent. It is very clear that the main peak of the P4VP distribution shifts to lower elution volume (higher molar mass) but that the two side peaks remain behind. It is therefore concluded that the P4VP macro-CTA contains a small fraction of low molar mass material that is clearly nonfunctional. It also needs to be pointed out that the SEC traces have been normalized with respect to polymer mass (macroinitiator plus converted monomer). In this fashion, a semiquantitative comparison of the evolution of the molar mass distribution is possible. In doing so, the difference in detector response for the two blocks caused by the difference in dn/dc is neglected. Despite this assumption, a reliable impression can be obtained of the extent of chain extension of the macroinitiator. This will be confirmed with additional measurements as described below.

Figure 4b represents the UV signals (at 305 nm) for the block copolymer P4VP-*b*-SAN (**S2**) and the P4VP starting block. The UV signal is normalized to constant area under the assumption that a negligible amount of UV chromophore (trithiocarbonate) is lost during the polymerization. It can clearly be seen that virtually the entire distribution shifts to lower elution volume, i.e., to higher molar mass. The DRI signal and the UV signal of the SEC chromatograms indicate that the growing block copolymer chains obtained in experiment **S2** were indeed functionalized with the TTC group. The P4VP starting block underwent subsequent addition of STY and AN units, resulting in a well-defined P4VP-*b*-SAN block copolymer. A relatively low PDI value was observed (1.16). The efficiency of the control of polymerization by using P4VP bearing a TTC group remained, even when a higher molar mass of the P4VP-*b*-SAN block copolymer was targeted. For example, in experiment **S3**, the targeted molar mass at complete monomer conversion was 124.0×10^3 g/mol. Note that at the end of the reaction, after 48 h, monomer conversion was 62% (see Table 4), and the experimentally observed and predicted M_n values were both 77.8×10^3 g/mol.

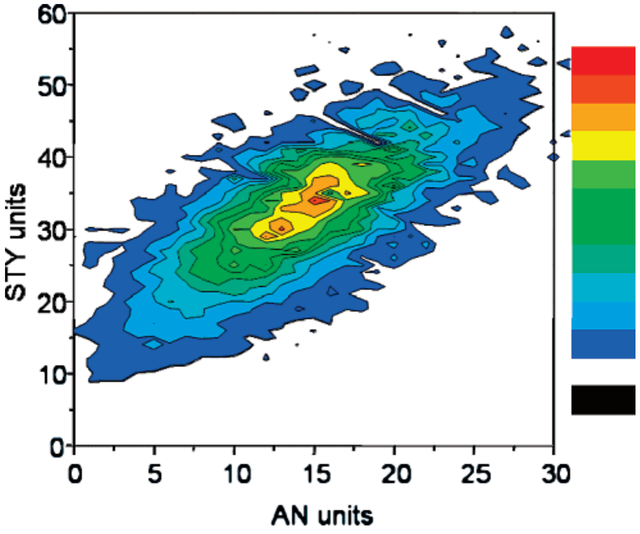

Figure 2. Contour map of the poly(4-vinylpyridine-*b*-(styrene-*co*-acrylonitrile)) (P4VP-*b*-SAN) block copolymer obtained in experiment **S1**. The RAFT-functional P4VP-1 starting block was used as a macro-RAFT agent. The contour map represents the number of styrene and of acrylonitrile units in the SAN as the second growing block within P4VP-*b*-SAN block copolymer.

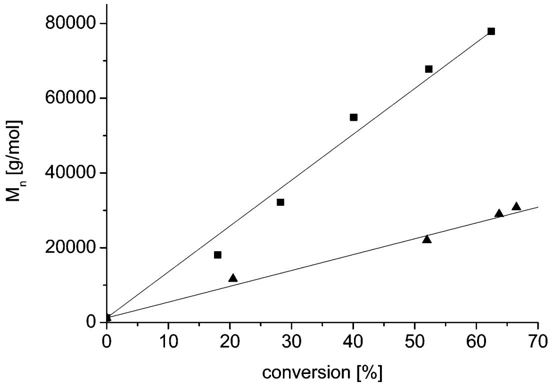

Figure 3. Number-average molar mass (M_n) of poly(4-vinylpyridine-*b*-(styrene-*co*-acrylonitrile)) (P4VP-*b*-SAN) as a function of conversion using the P4VP-1 starting block as a macrochain transfer agent. The lines represent the M_n values calculated with eq 1 ($M_{n,calc}$), whereas the symbols represent the experimental values ($M_{n,SEC}$) of the molar mass of the block copolymers during reactions (**S2**, ▲; **S3**, ■; see Table 4).

Subsequently, the block copolymers obtained in experiments **S1**−**S3** were analyzed by GPEC analysis. Note that the same P4VP starting block (referred to as P4VP-1) was used for the syntheses of these block copolymers, whereas the SAN block length was increased. The separation efficiency of SAN and P4VP polymers was studied by using a CN functionalized silica column and an applied eluent gradient from water to methanol to THF. Nonacidic water is a nonsolvent for both P4VP and SAN polymers, whereas methanol is a good solvent for P4VP and a nonsolvent for SAN. The ratio between water and methanol (5/94 v/v) was chosen in such a way that retention, and thus adsorption of P4VP on the stationary phase, was prevented. Note that at least 1 vol % of THF was always present in the eluent gradient. The P4VP homopolymer (P4VP-1) elutes after 2 min, at the moment when the volume of THF in the eluent just starts to increase. SAN copolymer elutes later (8.8 min) and requires a higher volume fraction of THF (methanol/THF $\approx$ 81/19 v/v).

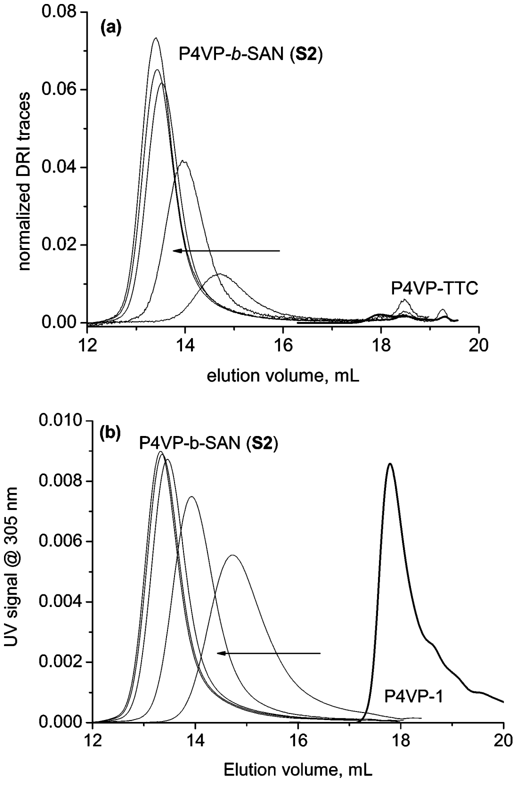

Figure 4. Size exclusion chromatograms: (a) the normalized differential refractive index (DRI) signals and (b) the UV signals at 305 nm, for poly(4-vinylpyridine-*b*-(styrene-*co*-acrylonitrile)) (P4VP-*b*-SAN) block copolymer (experiment **S2**) showing the evolution of molar masses with the increase of overall monomer conversion. Note that the arrows indicate increasing monomer conversion.

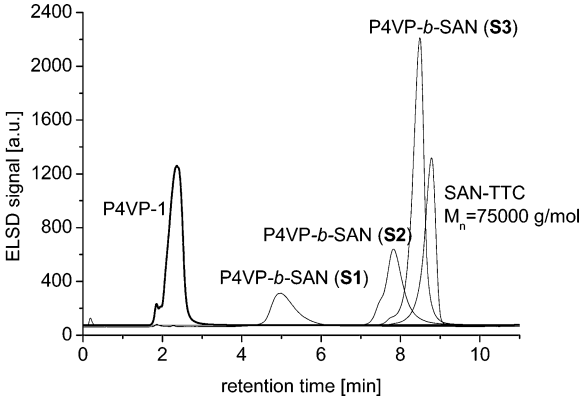

Figure 5. GPEC chromatograms of poly(4-vinylpyridine) (P4VP) and poly(styrene-*co*-acrylonitrile) (SAN) individual blocks and of poly(4-vinylpyridine-*b*-(styrene-*co*-acrylonitrile)) (P4VP-*b*-SAN) block copolymers **S1**−**S3**.

The difference of the solubility of polymers in the mobile phase (eluent) was sufficient to separate P4VP and SAN copolymers. The GPEC chromatogram in Figure 5 clearly shows well-resolved peaks for the separate P4VP and SAN blocks. Note that SAN copolymers of molar masses ranging from 15×10^3 to 120×10^3 g/mol always contained 20 wt % of AN, whereas sample SAN-TTC refers to a TTC end-functional SAN sample of $M_n = 74.6 \times 10^3$ g/mol. The P4VP-*b*-SAN block copolymers **S1**−**S3** elute between the separated blocks, i.e., P4VP and SAN blocks. It needs to be stressed that the elution behavior of polymers in GPEC is influenced by molar mass. The elution peak of the block copolymer of the higher molar mass, i.e., $M_n = 77.8 \times 10^3$ g/mol **(S3)**, is shifted toward the elution peak of SAN, compared to the elution peak of the low molar mass block copolymer **S1**. Note that the increase of the molar mass of the block copolymer is solely caused by an increase of the block length of the SAN block.

In summary, the obtained results from experiments **S1**−**S3** clearly demonstrate an efficient control of polymerization in solution media by using the P4VP starting block end-functionalized with a TTC group. The chain extension of P4VP-TTC with an azeotropic mixture of STY and AN resulted in complete transformation of the RAFT-functional chains into P4VP-*b*-SAN block copolymers.

Synthesis and Characterization of P4VP-*b*-SAN Block Copolymers by Emulsion Polymerization. In a second approach, P4VP-TTC was used as a macro-RAFT agent and as a precursor for polymeric surfactant in the RAFT-mediated emulsion polymerization. The P4VP starting block is soluble in acidic aqueous media.[26,27] This RAFT-functional polymer contains a large hydrophobic group, i.e., the dodecyl thio group ($S{-}C_{12}H_{25}$), and a hydrophilic group, i.e., the isobutyric acid group (C_3H_6COOH), attached to the P4VP polymer chain. P4VP-TTC acts as a macro-RAFT agent and remains soluble in water (at pH 4−5) until a sufficiently long SAN block has been incorporated. The growing block copolymer P4VP-*b*-SAN can form micelles in water. At this stage, the RAFT moiety, i.e., $S(S)C{-}S{-}C_{12}H_{25}$, is located in the interior of micelle, while subsequent polymerization with STY and AN results in particle formation. The polymerization was carried out as a semicontinuous process. The feed rate of STY and AN monomers was carefully adjusted, in accordance with the suggested model by Ferguson et al.,[28] with a predefined feed of STY and AN monomer. The presence of monomer droplets was avoided at the beginning of the reaction by using very low feed rates. Once the particles had been formed, the feed rate of the monomers was increased. As a consequence, the approximately monomer-saturated conditions in the particles led to relatively high rates of polymerization.

The samples taken during the polymerization were analyzed by SEC to determine molar mass values. The monomer conversion was measured gravimetrically. The DRI signal and the UV signal (at 305 nm) of the SEC chromatograms in Figure 6 indicate that most of the polymer chains present in the polymerization latex mixture of experiment **E1** were indeed functionalized with the TTC group. These chains underwent subsequent chain extension with STY and AN units. The obtained latex was colloidally stable, having average particle size of 45 nm and a monomodal particle size distribution as measured by DLS.

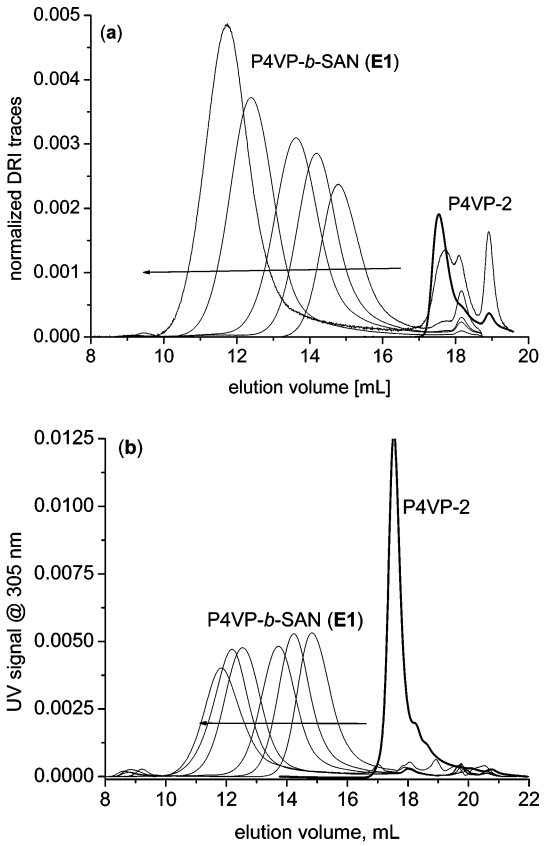

Figure 6. Size exclusion chromatograms (SEC): (a) the normalized differential refractive index (DRI) signals and (b) the UV signals at 305 nm, for poly(4-vinylpyridine-*b*-(styrene-*co*-acrylonitrile)) (P4VP-*b*-SAN) block copolymer in experiment **E1** showing the evolution of SEC traces with time. Note that the arrow indicates increasing monomer conversion.

Table 5. Molar Masses and Polydispersity Indexes (PDIs) of the Obtained Polymer as a Function of Reaction Time in the Semicontinuous Emulsion Polymerization of Styrene and Acrylonitrile Started with the Poly(4-vinylpyridine) Trithiocarbonate Macro-RAFT Agent (P4VP-2) in Experiment E1

sample code	*t* (h)	conv (%)	$M_{n,calc}$ (10^3 g/mol)	$M_{n,SEC}$ (10^3 g/mol)	PDI
E1.2	3	11	6.1	4.1	1.9
E1.3	4	18	9.7	7.6	2.0
E1.4	5	23	12.0	11.0	2.3
E1.5	6	51	26.0	26.7	2.5
E1.6	8	77	39.0	37.1	2.8
E1.7	11	100	49.6	48.8	4.0

Figure 6a illustrates an increase of molar mass during the reaction. Nevertheless, the SEC chromatograms show a slight tailing toward lower molar mass as well as high molar mass shoulders. There are several possible reasons why this could occur in a RAFT-mediated emulsion polymerization. First of all, we mention the generation of freshly formed short chains by initiator decomposition as well as the high efficiency of radical termination within the latex particles. An additional issue is the long feed time of monomer, which will reduce the propagation rate over an extended period. As the reaction goes to completion at the end of the monomer feed, the monomer concentration decreases, and therefore the probability of termination increases. So the probability for bimolecular termination during the whole course of the process will increase as compared with the situation of saturation swelling in a batch process. An increased probability for bimolecular termination is an important issue for the rather high PDI of the final product (i.e., PDI = 4; see Table 5). The UV traces of the P4VP starting block and of the growing polymer latex are presented in Figure 6b. The extensive presence of the UV signal (recorded at 305 nm) indicates that the TTC moiety, i.e., the RAFT moiety, is evenly distributed over the growing SAN block length. This observation clearly confirms that the slightly acidic conditions did not destroy the TTC group.[29] Therefore, the P4VP-TTC polymer was suitable for use as a macro-RAFT agent in emulsion polymerization. The fact that the tailing is also visible in the UV trace seems to indicate that bimolecular termination is not the predominant cause of the tailing. For some reason it seems to point at a situation where a large variation in local concentrations occurs. Most probably this is due to the compartmentalization that is characteristic for emulsion polymerization. The details of this phenomenon are currently under investigation in our lab.

The M_n values calculated with eq 1 agree well with the experimentally observed molar mass values (see Table 5). The results in Figure 7 clearly demonstrate that the molar mass of the block copolymer increases linearly with monomer conversion, indicating that the polymerization exhibited living char-

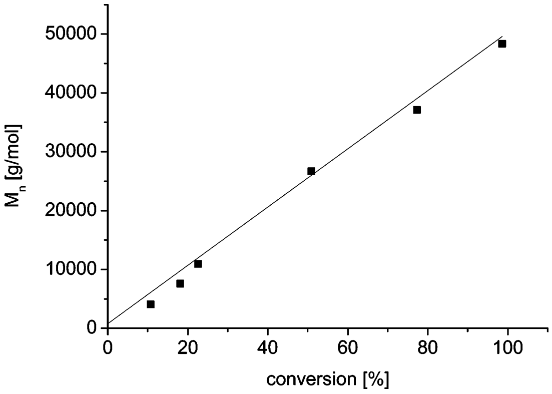

Figure 7. Number-average molar mass (M_n) as a function of conversion. The solid line represents molar mass values calculated with eq 1 ($M_{n,calc}$). Symbols (■) represent experimentally observed values of molar mass ($M_{n,SEC}$) for the obtained block copolymer latex in experiment **E1** (see Table 5).

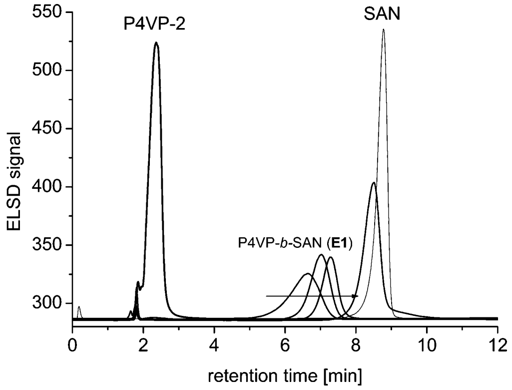

Figure 8. Gradient polymer elution chotmatography traces of the poly(4-vinylpyridine) and poly(styrene-*co*-acrylonitrile) (SAN) separate blocks and of the poly(4-vinylpyridine-*b*-(styrene-*co*-acrylonitrile)) (P4VP-*b*-SAN) block copolymer latex obtained in experiment **E1**. Note that the arrow indicates increase of the monomer conversion (after 11, 18, 23, and 51% of monomer conversion, respectively) and of the SAN block length. Note that the peaks after 77 and 100% of monomer conversion are overlapping with the one for 51% of monomer conversion.

acteristics in emulsion. These results are similar to those obtained in solution polymerization (see Figure 3).

Subsequently, GPEC analysis was used to confirm the block copolymer structure which was formed by the RAFT-mediated emulsion polymerization. Figure 8 clearly illustrates well-resolved peaks for the SAN and P4VP separate blocks and for the block copolymer latexes at different monomer conversions. The position of the entire block copolymer latex peak is shifted away from the P4VP peak, toward the peak of SAN. Note that the shift of the block copolymer latex peak toward the SAN peak is more pronounced for the higher monomer conversions. It is important to mention that the obtained latex was colloidally stable before, during and after the polymerization. After the polymerization, no coagulum was found in the reactor.

In summary, the P4VP-TTC starting block was transformed into a P4VP-*b*-SAN block copolymer latex, as illustrated by the results obtained in experiment **E1**. The P4VP-TTC starting block is expected to be located at the particle surface. Colloidal stability of the latex was already obtained in the presence of the P4VP-TTC starting block, which is a precursor for a polymeric surfactant. The growing latex particles were stabilized by the P4VP-*b*-SAN, a polymeric surfactant, which expectedly plays a dominant role in the nucleation of the latex particles. The block copolymer latex particles were increasing in size and in overall hydrophobicity by increasing the monomer conversion. It implies a basic difference in comparison to a conventional surfactant. The obtained results are comparable to those reported by Ferguson et al.[28]

The complete transformation of the P4VP starting block into the P4VP-*b*-SAN block copolymer points to an efficient control of the polymerization in solution and in emulsion. The results of GPEC analysis confirmed the successful block copolymer formation.

Conclusion

The P4VP starting block bearing trithiocarbonate end group (P4VP-TTC) was successfully chain extended with an azeotropic mixture of STY and AN in solution and emulsion polymerization. The obtained results demonstrated that RAFT-functional P4VP can be used as an effective macro-RAFT agent in solution to synthesize P4VP-*b*-SAN block copolymers of different molar masses and with monomodal molar mass distributions. In that case, the formation of P4VP-*b*-SAN block copolymers clearly demonstrated the large fraction of RAFT-functional chains in the P4VP polymer. P4VP can be used as polymeric reactive surfactants or as precursor for polymeric surfactant in emulsion polymerizations as demonstrated by the successful preparation of block copolymer latex products. The obtained P4VP-*b*-SAN block copolymer latex was colloidally stable. Controlled monomer feed resulted in a gradually growing block copolymer in emulsion. The experimentally obtained molar mass increased linearly with monomer conversion and was in agreement with the calculated value. This behavior confirms the living character of P4VP-TTC as well as the good control of the RAFT-mediated emulsion polymerization. The combined results of the GPEC and of the SEC analyses are an indication of a successful block copolymer latex formation. The SEC traces provide strong evidence that the great majority of the block copolymer latex was formed under the RAFT control. We can conclude that the P4VP-TTC starting block can successfully be used to synthesize block copolymers in aqueous dispersions. The P4VP-TTC macro-RAFT agent acts as a precursor for a polymeric reactive surfactant in order to stabilize the latex and to produce a block copolymer in emulsion.

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