Synthesis and quaternization of nitroxide-terminated poly(4-vinylpyridine-co-acrylonitrile) macroinitiators and related diblock copolymers

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Abstract: Nitroxide-terminated 4VP–AN copolymers have been synthesized at 125 °C using an alkoxyamine (MAMA-SG1) as a unimolecular initiator. Their compositions were compared with those published for the conventional radical 4VP–AN copolymerization. To verify the initiation potential of the copolymers containing nitroxyl end groups, they were employed in chain extension with styrene (S). Both the prepared statistic copolymer macroinitiators and related diblock copolymers, poly(4VP-co-AN) and poly(4VP-co-AN)-block-poly(S), respectively, were quaternized with methyl iodide in N,N-dimethylformamide or methanol at ambient temperature. The size-exclusion chromatography and NMR were used for the characterization of the polymers; the completeness of the quaternization was checked by the IR spectrometry.

Introduction

Due to new approaches developed in the field of radical polymerization over the last decades, the polymer synthesis shows remarkable achievements. Polymers of well-defined structure and properties can be obtained using the advanced synthetic techniques, such as nitroxide-mediated radical polymerization (NMRP) [1-14]. A quasiliving polymerization takes place at elevated temperatures (usually above 100 °C) in mixtures containing monomer, a thermal initiator [(dibenzoyl peroxide, 2,2’-azobis(isobutyronitrile)] and a nitroxide stable radical. Instead of the conjunction of thermal initiator with nitroxide, an alkoxyamine-based unimolecular initiator carrying both a latent initiating group and nitroxide in the 1:1 mole ratio can be used [10, 15]. Some monomers and monomer pairs (styrene, styrene–maleimide or styrene–N-substituted maleimide derivative) polymerize in the quasiliving manner even without any added initiator, only in the presence of nitroxide [5, 16, 17]. The mediating role of the nitroxide consists in reversible termination of growing polymer chains under formation of thermally unstable N-alkoxyamine bonds. Dissociation of the bonds regenerates the polymer radicals; the latter add monomer units before being trapped again with the nitroxide. The obtained nitroxide-terminated polymers are virtually macroinitiators. They can be employed in chain extension reactions for the synthesis of block copolymers.

The NMRP was originally focused on styrene and its derivatives; however, it expanded also toward functional monomers. Of them, isomeric vinylpyridines are of great interest.
The nitrogen atom of the pyridine ring offers a number of modifying reactions, such as quaternization, reaction with acids and complexation of metals. Vinylpyridine polymers and their ionic derivatives rank among promising materials such as polyelectrolytes, polymeric reagents, membranes and in electrical applications [18]. So far, the NMRP studies of vinylpyridine monomers have been devoted mainly to their homopolymerization and copolymerization with styrene [11, 17, 19, 20]. Yet the incorporation of other monomer units in polymer chains could modulate the

Scheme 1. N-alkoxyamine-based unimolecular initiator (MAMA-SG1), the synthesized 4-vinylpyridine copolymers (A, B) and their quaternized derivatives (QA, QB).
properties of resulting products. For example, acrylonitrile (AN) units improve thermal stability, film-forming properties and, in addition, their pendant nitrile groups can be modified [21, 22].

Considering better accessibility of nitrogen in 4-vinylpyridine (4VP) than in 2- or 3-vinylpyridine to chemical reactions, this work was aimed at the preparation of 4VP–AN copolymers (A) using an alkoxyamine unimolecular initiator with the diethoxyphosphoryl group (MAMA-SG1). By chain extension with styrene (S), poly(4VP-co-AN)-block-poly(S) diblock copolymers (B) were synthesized. The prepared 4-vinylpyridine copolymers were converted to cationic derivatives (QA, QB) by quaternization with methyl iodide (Scheme 1) under mild conditions.

Results and discussion

Nitroxide-terminated 4VP-AN copolymers

According to the literature [23], conventional radical copolymerization of 4VP and AN proceeds with an azeotrope; the azeotropic composition corresponds to 60 mol % of 4VP, the published monomer reactivity ratios are 0.41 for 4VP (r_{4VP}) and 0.11 for AN (r_{AN}). Using these values, the dependence of the copolymer composition (F_{4VP}) on the feed composition (f_{4VP}) is plotted in Figure 1 (dashed curve).

![Copolymerization diagram for 4VP–AN](image)

**Fig. 1.** Copolymerization diagram for 4VP–AN. f_{4VP} and F_{4VP} are mole fractions of 4VP in the feed and in the copolymer, respectively. Black circles correspond to the experimentally determined F_{4VP} – f_{4VP} relationship for the nitroxide-mediated 4VP–AN copolymerization initiated with an alkoxyamine MAMA-SG1; the dashed curve was constructed using the published monomer reactivity ratios, r_{4VP} = 0.41 and r_{AN} = 0.11, for the conventional 4VP–AN copolymerization [23].

The same F_{4VP} – f_{4VP} relationship such as in the conventional process was observed also for the nitroxide-mediated copolymerization of these comonomers initiated with an alkoxyamine MAMA-SG1 (black circles). The MAMA-SG1 proved to be an efficient initiator in the controlled polymerization of monomers containing functional
The obtained SG1-terminated 4VP-AN copolymers exhibited a low polydispersity (Tab. 1), typical of a quasiliving mechanism.

**Tab. 1.** Bulk copolymerization of 4VP and AN initiated with MAMA-SG1 at 125 °C. 

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$f_{4VP}$</th>
<th>Conversion (wt %)</th>
<th>$F_{4VP}$</th>
<th>$M_n$ ($\times 10^4$)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>0.20</td>
<td>24.5</td>
<td>0.42</td>
<td>4.73</td>
<td>1.06</td>
</tr>
<tr>
<td>A4</td>
<td>0.40</td>
<td>22.7</td>
<td>0.53</td>
<td>5.46</td>
<td>1.11</td>
</tr>
<tr>
<td>A5</td>
<td>0.50</td>
<td>21.7</td>
<td>0.52</td>
<td>5.52</td>
<td>1.25</td>
</tr>
<tr>
<td>A6</td>
<td>0.60</td>
<td>28.3</td>
<td>0.60</td>
<td>6.04</td>
<td>1.14</td>
</tr>
<tr>
<td>A9</td>
<td>0.90</td>
<td>17.8</td>
<td>0.82</td>
<td>3.68</td>
<td>1.10</td>
</tr>
<tr>
<td>A91 c</td>
<td>0.90</td>
<td>16.2</td>
<td>0.80</td>
<td>8.52</td>
<td>1.34</td>
</tr>
</tbody>
</table>

$M_w/M_n$ b

| Poly(4VP) | 1         | 24.9              | 1         | 2.08                | 1.66      |

$f_{4VP}$ and $F_{4VP}$ are mole fractions of 4VP in the feed and in the copolymer, respectively.

a $5 \times 10^{-2}$ mol of the comonomers, $0.75 \times 10^{-4}$ mol of MAMA-SG1, 40 min.

b Determined by SEC.

c $0.5 \times 10^{-4}$ mol of MAMA-SG1, 1 h.

**Scheme 2.** Deactivation of nitroxide-terminated 4-vinylpyridine–acrylonitrile copolymer chains.

A comparison of the molecular weight and polydispersity values, which were determined for A9 ($M_n = 3.68 \times 10^4$, $M_w/M_n = 1.10$) and A91 ($M_n = 8.52 \times 10^4$, $M_w/M_n = 1.34$) having almost the same composition ($F_{4VP} = 0.80-0.82$), demonstrated a broader polydispersity at the higher molecular weight. This can be due to easier
irreversible deactivation of long copolymer chains containing terminal nitroxyl groups (Scheme 2) [11, 17].

Tab. 1 also presents some characteristics of a 4VP homopolymer. Its polydispersity, 1.66, was rather high. This value might be related to concomitant spontaneous thermal polymerization of 4VP, resulting in a decrease in molecular weight and, at the same time, in broadening its distribution in consequence of irreversible termination reactions. The unimolecular initiator MAMA-SG1, dissociating into an initiating C-radical and reversibly terminating nitroxyl radical in the 1:1 mole ratio, is evidently less convenient for the controlled synthesis of poly(4VP) than a two-component system of dibenzoyl peroxide/TEMPO containing a slight excess of the nitroxide TEMPO. Using the latter system, narrow-polydispersity homopolymers of 4VP ($M_w/M_n \sim 1.20$) have been prepared [19].

**Chain extension of nitroxide-terminated 4VP-AN copolymers with styrene**

The SG1-terminated 4VP-AN copolymers A2, A4, A6 and A9 were employed as macroinitiators in polymerization of styrene at 125 °C (Tab. 2).

**Tab. 2.** Chain extension of nitroxide-terminated 4VP–AN copolymer precursors with styrene at 125 °C. a

<table>
<thead>
<tr>
<th>Product</th>
<th>Precursor</th>
<th>$F_S$</th>
<th>$F_{AVP}$</th>
<th>$M_n$ ($\times 10^4$)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>A2</td>
<td>0.72</td>
<td>0.39</td>
<td>11.1</td>
<td>1.31</td>
</tr>
<tr>
<td>B4</td>
<td>A4</td>
<td>0.68</td>
<td>0.53</td>
<td>7.7</td>
<td>2.91</td>
</tr>
<tr>
<td>B6</td>
<td>A6</td>
<td>0.65</td>
<td>0.63</td>
<td>f</td>
<td>f</td>
</tr>
<tr>
<td>B9</td>
<td>A9</td>
<td>0.25</td>
<td>0.88</td>
<td>f</td>
<td>f</td>
</tr>
</tbody>
</table>

a 0.2 g of the precursor, 5 mL of S, 1 h.

b See Tab. 1.

c Mole fraction of styrene in the resulting polymer as determined by NMR.

d Mole fraction of 4VP in the incorporated 4VP-AN copolymer precursor as determined by NMR.

e Determined by SEC.

f A bimodal SEC curve.

Chain extension took place, in which polystyrene blocks (25 – 72 mol %) were attached to the 4VP-AN copolymer chains. The NMR measurement evidenced very close contents of 4VP in both the original and incorporated 4VP-AN copolymers (cf. $F_{AVP}$ values in Tab. 1 and Tab. 2). Considering a rather small amount of polystyrene blocks in B9 (25 mol %) in comparison with that in B2 (72 mol %), a favourable effect of AN units in the precursors on the styrene polymerization can be assumed; A2, the precursor of B2, contained about three times more AN than A9, the precursor of B9.

A unimodal SEC curve indicated that macroinitiator A2 provided poly(4VP-co-AN)-block-poly(S) diblock copolymer B2 exhibiting low polydispersity ($M_w/M_n = 1.31$). Copolymer B4, proceeding from A4 with a higher content of 4VP (53 mol %) than A2 (42 mol %), was a product with broad polydispersity ($M_w/M_n = 2.91$). Using the SG1-terminated 4VP-AN copolymers A6 and A9 (containing 60 and 82 mol % of 4VP units, respectively) as macroinitiators, polymer products B6 and B9 with bimodal eluograms were obtained. For illustration, the SEC curves of B2 and B9 are depicted in Fig. 2. The results in Table 2 and Fig. 2 suggest that along with chain extension irreversible deactivation side reactions occur to a large extent at high contents of 4VP-AN precursor chains with incorporated 4VP at their ends.
Fig. 2. SEC curves of copolymers B2 and B9 (Tab. 2) comprising poly(4-vinylpyridine-co-acrylonitrile) and polystyrene blocks.

Quaternization of 4VP polymers

The prepared 4VP homopolymer and copolymers can be readily transformed to ionic derivatives by quaternization. The disappearance of pyridine band at 1414 cm\(^{-1}\) in the IR spectrum was taken as evidence for quantitative alkylation of vinylpyridine units. According to a report of Eisenberg et al. [25], the IR technique, in contrast to elemental and iodine analyses, represents a sensitive and reliable method for evaluation of the extent of quaternization.

Usually, quaternization of vinylpyridine polymers was carried out by refluxing in a polar solvent, such as tetrahydrofuran or methanol, with excess alkylating agent [19, 25]. We have found, however, that the synthesized copolymers A and B as well as 4VP homopolymer react with a five-fold stoichiometric excess of CH\(_3\)I in DMF (~10\% solution) at ambient temperature in a markedly shorter time yielding a completely modified product (Tab. 3). Under these conditions, all the 4VP units in poly(4VP) (\(M_n = 2.08\times10^4\)) or in copolymer A5 (containing 52 mol % of 4VP, \(M_n = 5.52\times10^4\)) were converted to the quaternized form even in 30 min, despite the different composition and molecular weight of both the polymers.

Methanol also appears to be a good solvent for the quaternization though the reaction proceeds more slowly. Thus, the 30-min reaction time was insufficient for complete quaternization of poly(4VP) or A5 (Tab. 3). An experiment with A91
indicates that a reaction period of 24 h might suffice for the complete modification in methanol at room temperature using all the 4VP polymers under study. Figure 3 presents the IR spectra of copolymer A91 before and after quaternization in methanol.

Conclusions

Radical copolymerization of 4VP and AN at 125 °C initiated with an alkoxyamine MAMA-SG1 proceeded with an azeotrope (the azeotropic composition being 60 mol % of 4VP) and afforded nitroxide-terminated copolymers with a low polydispersity. Using the copolymers as macroinitiators in polymerization of styrene, diblock copolymers poly(4VP-co-AN)-block-poly(S) were synthesized. In this chain extension reaction the irreversible termination occurred and hence the obtained diblock copolymers were contaminated with inactive polymer chains. Their amount increased with increasing content of 4VP units in the macroinitiator.

The complete quaternization of the prepared vinylpyridine polymers with methyl iodide was reached in DMF or methanol at ambient temperature giving corresponding quaternary ammonium derivatives.

Experimental part

Materials

2-((tert-Butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino)oxy)-2-methyl propanoic acid (MAMA-SG1, Scheme 1) (m.p. 125 °C) was supplied by Atofina. 4-Vinylpyridine (4VP) (Fluka) (b.p. 58-61 °C/1.56 kPa), acrylonitrile (AN) (Fluka) (b.p. 78 °C/101.2 kPa) and styrene (S) (Kaučuk Group Co., Kralupy, Czech Republic) (b.p. 36 °C/1.56 kPa) were distilled prior to use. The solvents used were of analytical grade.

Synthesis

-Nitroxide-terminated 4VP-AN copolymer macroinitiators

The SG1-terminated 4VP-AN copolymers (A) of various composition (Tab. 1) were synthesized as follows: An alkoxyamine MAMA-SG1 (0.75×10^{-4} mol) was dissolved in the comonomers (5×10^{-2} mol total), the mixture was poured into a glass ampoule, bubbled with nitrogen and sealed. The polymerization was conducted at 125 °C for 40 min. After cooling, the ampoule was opened and its content precipitated with hexane. The obtained copolymer was reprecipitated from chloroform with hexane and dried in vacuum (6.6 Pa) at 60 °C.

-Poly(4VP-co-AN)-block-poly(S) diblock copolymers

0.2 g of 4VP-AN copolymer precursor (A) was dissolved in 2 mL of N,N-dimethylformamide and 5 mL of styrene was added. The polymerization was carried out at 125 °C in a sealed glass ampoule in nitrogen atmosphere. After one hour, the ampoule was opened and its content poured into a 50 mL flask. The solvent and unreacted styrene were evaporated under reduced pressure at 60 °C. The polymer product (B) was precipitated with hexane from a chloroform solution and dried in vacuum (6.6 Pa) at 60 °C. Tab. 2 summarizes the results of the chain extension reaction for some 4VP-AN copolymer precursors.
Tab. 3. Quaternization of 4VP-containing polymers with methyl iodide at room temperature. a

<table>
<thead>
<tr>
<th>4VP polymer b</th>
<th>Solvent</th>
<th>Reaction time (h)</th>
<th>Extent of quaternization (%) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>DMF</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>A5</td>
<td>DMF</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>0.5</td>
<td>&lt;100</td>
</tr>
<tr>
<td>A91</td>
<td>DMF</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>24</td>
<td>100</td>
</tr>
<tr>
<td>poly(4VP)</td>
<td>DMF</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>MeOH</td>
<td>0.5</td>
<td>&lt;100</td>
</tr>
<tr>
<td>B2</td>
<td>DMF</td>
<td>1</td>
<td>100</td>
</tr>
</tbody>
</table>

a 0.1 g of the 4VP polymer, 1 mL of solvent, five-fold excess of CH$_3$I relative to the content of 4VP.
b See Tab. 1 and Tab. 2.
c From the IR spectra.

Fig. 3. IR spectra of nitroxide-terminated 4-vinylpyridine–acrylonitrile copolymer A91 (Tab. 1) before (a) and after (b) 24-h quaternization with CH$_3$I in methanol (Tab. 3).

-Quaternization

A copolymer (A or B) containing pyridine groups (0.1 g) was placed in a 50 mL flask and dissolved in 1 mL of N,N-dimethylformamide (DMF) or methanol (MeOH) (Tab. 3). Then, five-fold molar excess of methyl iodide (relative to the 4VP unit content) was added. The quaternization was carried out at room temperature. After the time period given in Tab. 3, the unreacted methyl iodide and solvent were withdrawn under vacuum and the product (QA or QB, Scheme 1) was thoroughly washed with methanol or hexane. It was dried in vacuum (6.6 Pa) at 60 °C.
Characterization of the copolymers

The yields of copolymers were determined gravimetrically, their compositions by $^1$H NMR measurements. The molecular weights and their distributions (MWD) were evaluated by size-exclusion chromatography (SEC). The IR spectroscopy was used for the determination of the degree of quaternization.

-Size-exclusion chromatography

The SEC measurements for evaluation of number- and weight-average molecular weights ($M_n$ and $M_w$) were carried out on a Biospher GM 1000 column (8 x 500 mm, Labio, Czech Republic) filled with 10-μm sorbent particles. Distilled $N$,$N$-dimethylacetamide (Fluka) with addition of 0.5 % of LiBr served as a mobile phase. The data from refractive index detector were collected and treated using CSW 1.7 software (Data Apex, Czech Republic). For the determination of molecular weights, a universal calibration equation calculated from the data on polystyrene standards (Merck, Germany) was used.

-NMR

$^1$H NMR spectra of 10 % w/w copolymer solutions in deuterated chloroform were measured with a Bruker Avance DPX 300 spectrometer operating at 300.13 MHz. The integrated intensities were determined using the spectrometer integration software with an accuracy of ±1%. In all measurements the temperature was kept constant within ±0.2 K using a BVT 3000 temperature unit. Typical measurement conditions were as follows: 90° pulse width 8.3 μs, relaxation delay 10 s, spectral width 5995.204 Hz, acquisition time 2.73 s, 32 scans at temperature 330 K.

-IR spectroscopy

The FT-IR spectra were recorded on a Perkin – Elmer Paragon 1000PC FT-IR spectrometer using the reflective ATR (attenuated total reflection) technique Specac MKII Golden Gate Single Reflection ATR System with a diamond crystal with the angle of incidence 45°. All spectra were measured in the wavenumber range 4400 - 450 cm$^{-1}$ with resolution 4 cm$^{-1}$ and with 16 scans. Software Spectrum v2.00 was used for processing the spectra. The samples were directly placed on the diamond crystal and measured.

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