POLYMERIZATION OF N-SUBSTITUTED 4-AMINOSTYRENE.  
Part IV: THE POLYMERIZATION MECHANISM OF N-ALKYL AND N-BENZYL 4-AMINOSTYRENE SALTS.

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Abstract
The mechanism of the spontaneous polymerization of N-alkyl and N-benzyl 4-aminostyrene salts in different solvents has been investigated. Results indicate that initiation step is caused by nucleophilic attack of unalkylated 4-aminostyrene molecules on the double bond of styryl group leading to formation of a Zwitterion. However, the contribution of the halide ion (X) in the initiation step is insignificant.

Introduction
Spontaneous polymerization of 4-aminostyrene (4-AS) and N-substituted 4-aminostyrene salts (1) in aqueous and/or organic solvents to form the corresponding poly-4-aminostyrene and poly-(N-substituted 4-aminostyrene) salts have been previously reported.1-8 These reactions indicated that the reaction of 4-AS with hydrogen halides (HCl, HBr, and HI), alkyl and/or benzyl halides and phenacyl bromide led to the isolation of stable monomeric salts 1.

Barba et al. reported1,3 that the spontaneous polymerization of 4-AS salts occurred via zwitterionic mechanism. Our studies6-8 excluded free-radical or ionic mechanism and strongly supported the zwitterionic mechanism for such polymerization reactions. It is suggested that the spontaneous polymerization resulting from the addition of the counter ion (X⁻) or an unalkylated 4-AS molecule on the β-position of the double bond of (1a) to give a highly resonance stabilized zwitterion (2a). This is followed by the specific addition of 2 to the corresponding salt (1) to give poly-4-aminostyrene and poly-(N-substituted 4-aminostyrene) salts. At all time the highly resonance stabilized zwitterionic endgroup is being maintained.1,9 On the other hand, Salamone et al. reported9 that the mechanism of the spontaneous polymerization of 4-vinylpyridinium salts are taken place.
by the attack of unquaternized 4-vinylpyridine on the β-position of the double bond of a 4-vinylpyridinium ion to give a zwitterionic propagating species (3).

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{Nu} \text{--CH--CH} \\
X^- & \quad \text{+NH}_2\text{R} & \quad X^- & \quad \text{+NH}_2\text{R}
\end{align*}
\]

1

2

\(a\) Nu = X\(^-\) or 4-AS ; X = Cl, Br, or I; R = H, alkyl or benzyl

\(b\) Nu = 4-AS ; X = Br; R = phenacyl

The reaction of 4-AS with excess of ethyl chloride, benzyl chloride and some substituted benzyl chlorides at molar ratio 1:3 in dry ether or anhydrous tetrahydrofuran (THF), led to the isolation of stable monomeric salts 4a-f as illustrated in Scheme 1. Consequently, in aqueous and/or organic solvents the monomer salts are being spontaneously polymerized.

Besides, previous investigations revealed that no effect of the substituents in benzyl moiety on the polymerization rate was observed.\(^8\)

In addition, a \(^1\)H NMR study of the polymerization of monomer salts showed that although 4a-f were stable in D\(_2\)O and DMF-\(d_7\), polymerization could be initiated by the addition of aniline or unalkylated 4-AS. From these results, in accord with Salamone,\(^9\) it is suggested that the initiation step was caused by the attack of unalkylated 4-AS molecule on the activated double bond of 4 to give a zwitterionic endgroup like in 5.
The present work is concerned with further investigation of the mechanism of spontaneous polymerization of some N-substituted 4-aminostyrene salts (4) and the
elucidation of the structure of the resulting polymers. The synthesis and stabilities of several monomeric salts are also described.

Results and Discussion

The initiation of the spontaneous polymerization of N-substituted 4-aminostyrene salts (4) is believed to involve nucleophilic addition of 4-AS molecule on the β-position of the double bond. Initiation by this process is supported by the addition of some selected nucleophiles such as cyanide, sulfide, sulfite, thiourea and primary, secondary, or tertiary amines to 2-and 4-vinylpyridine under acidic conditions. Barba et al. has suggested that the spontaneous polymerization of 4-aminostyrene hydrohalides was initiated by the nucleophilic attack of the halide ion or 4-AS on the activated double bond. It was also reported that 4-AS favourably reacted with benzyl chloride at different molar ratios in DMF-$d_7$ to give poly-(N-monosubstituted or N,N-disubstituted 4-aminostyrene) salt. The rate of polymerization increased slightly when doubling the molar ratio of benzyl chloride, hence suggesting a cationic nature of mechanism.

In order to investigate the proposed initiation mechanism of Barba and Salamone, the addition of various nucleophiles to 4 were investigated by $^1$H NMR spectroscopy.

$^1$H NMR spectrum of a 10% solution of pure monomeric salts in D$_2$O and DMF-$d_7$ showed that no polymerization had taken place after 3 days at room temperature; however 10-15% polymerization had occurred in DMF-$d_7$ within 5 days. Furthermore, when 1 equivalent of NaBr, NaI or Na$_2$SO$_4$ was added to 10% solution of 4a or 4b in D$_2$O or DMF-$d_7$ no polymerization was observed after 3 days. On the other hand, when 1 equivalent of NaCN was added to the DMF-$d_7$ solution of 4a or 4b no vinyl protons were detected after 6 h at room temperature. When 0.5 equivalent of NaCN was added 60% polymerization had occurred within 18 h.

The fact that no addition could be observed with either bromide or iodide ion militates against the initiation mechanism suggested by Barba et al. In particular, it has been noted that nucleophilic reactivity in addition reactions corresponds closely with basicity, with weak bases such as bromide and iodide being unreactive.

It was shown for the polymerization of several vinyl monomers that the initiation ability of anions increases with their basicity. As a result of this investigation and previous studies it appears that the reactivity of nucleophiles towards N-substituted
4-aminostyrene salts corresponds to their basicity. Since bromide and iodide are much weaker bases than 4-AS, the spontaneous polymerization of \(N\)-substituted 4-aminostyrene salts can be caused by the attack of unalkylated 4-AS. Consequently, it could be expected that a monomeric salt, once formed and removed from excess 4-aminostyrene, would be stable in solution. In order to investigate this possibility we have prepared 4-(dibenzylamino)styrene hydrochloride (\(4b\)) and have studied its stability in solution. \(^1\)H NMR studies indicate that this salt is stable in D\(_2\)O or DMF-\(d_7\) solution for 3 days.

Since the attack of the chloride on the \(N\)-substituted 4-aminostyrene ions is a reaction between oppositely charged species to give a neutral (or zwitterionic species), the rate of the reaction might be expected to increase greatly in non polar solvents. On the other hand, the rate of addition of 4-AS to \(N\)-substituted 4-aminostyrene salts should be relatively unaffected by the polarity of the solvent. Although the rate of addition of chloride ion has been shown to be negligible in a polar solvent, chloride addition could become significant in nonpolar solvents. The relative rates of these additions were easily determined in dichloromethane. When 0.01 mol of 4-AS was added at room temperature to a solution of 0.01 mol of \(4b\) in 30 ml of dichloromethane, 1.33 g of \(6b\) was obtained after 3 h. However, when no 4-AS was added, only 0.05 g had formed after 10 hr. This difference in reactivity indicates that unalkylated 4-AS attack is much faster than chloride attack in both polar and nonpolar solvents.

The proposed initiation mechanism is supported by the addition of different mole\% of aniline and/or unalkylated 4-AS to 10% solution of 4-(benzylamino)styrene hydrochloride (4-BAS-HCl) in D\(_2\)O at 45 °C. The \(^1\)H NMR spectra taken after the addition 0.02 mole\% of unalkylated 4-AS revealed that 24% polymerization had occurred after 0.5 h, 50% after 1 h, 70% after 1.5 h and 84% after 2 h, while with aniline 17% polymerization had occurred after 0.5 h, 41% after 1 h, 59% after 1.5 h and 73% after 2 h (Table 1).

However, 4-BAS-HCl in DMF-\(d_7\) without aniline or 4-AS showed no observable polymerization after 72 h and less than 15% after 5 days. These results strongly support the proposed mechanism for the initiation step.

The mechanism of propagation has been considered to occur by the nucleophilic addition of 5 to a \(N\)-substituted 4-aminostyrene salt. Thus generating a continuous
zwitterionic endgroup, while the termination step is believed to occur on the protonated amino group –NH\(^+\) – or on the solvent molecule (Scheme 1). It is interesting to note that DP of 25-30 was determined by NMR endgroup analysis.

Table 1. Data of The Polymerization of 4-(benzylamino)styrene. HCl in D\(_2\)O at 45 °C in presence of different concentrations of 4-AS.

<table>
<thead>
<tr>
<th>Conc. (M%)</th>
<th>Time (min)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>140</th>
<th>150</th>
<th>160</th>
</tr>
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<tbody>
<tr>
<td>0.02*</td>
<td>4.0</td>
<td>11.0</td>
<td>17.0</td>
<td>24.5</td>
<td>33.0</td>
<td>40.5</td>
<td>48.0</td>
<td>53.0</td>
<td>59.0</td>
<td>64.5</td>
<td>69.0</td>
<td>73.0</td>
<td>76.5</td>
<td>79.5</td>
<td>82.5</td>
<td>84.0</td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>9.0</td>
<td>16.5</td>
<td>24.0</td>
<td>32.5</td>
<td>42.0</td>
<td>50.0</td>
<td>58.0</td>
<td>63.5</td>
<td>70.0</td>
<td>75.0</td>
<td>79.0</td>
<td>84.0</td>
<td>87.0</td>
<td>90.0</td>
<td>92.0</td>
<td>93.0</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>15.0</td>
<td>27.0</td>
<td>38.5</td>
<td>49.5</td>
<td>60.0</td>
<td>69.0</td>
<td>75.0</td>
<td>81.0</td>
<td>85.0</td>
<td>88.5</td>
<td>93.0</td>
<td>96.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>0.08</td>
<td>30.0</td>
<td>51.0</td>
<td>65.5</td>
<td>75.0</td>
<td>82.5</td>
<td>88.0</td>
<td>94.0</td>
<td>97.0</td>
<td></td>
<td></td>
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</tbody>
</table>

* in presence of aniline.

The structures of monomer salts (4a-f) were based on both IR and \(^1\)H NMR spectral data, showing sharp stretching absorption vibration at \(\nu = 1640-1625 \text{ cm}^{-1}\) due to C=C group beside a band at 1020-990 cm\(^{-1}\) due to =CH group and a band at 935-915 cm\(^{-1}\) due to =CH\(_2\) group confirming the presence of vinyl group. \(^1\)H NMR (D\(_2\)O) spectra of these monomer salts reveal the presence of three signals at \(\delta: 4.30-5.49, 5.74-5.93\) and 6.73-6.92 ppm due to vinyl protons. These data show that no significant effect for substituents on the signals of vinyl protons.

However, IR and \(^1\)H NMR spectral data of produced polymers, showing no absorption bands in the stated regions with appearance of new strong bending absorption vibration band at \(\nu = 1450-1440 \text{ cm}^{-1}\) due to CH\(_2\) group and a sharp band at 1490-1480 cm\(^{-1}\) due to CH group. \(^1\)H NMR (DMF-\(\text{d}_7\)) spectrum of which reveals that the presence of a broad band at \(\delta: 1.00-1.39 \text{ ppm}\) due to the backbone CH\(_2\) and CH. These results indicate that without any doubt monomer salts are transformed into polymers.

Conclusions

The present work reports preparation, isolation and characterization of new monomers derived from 4-aminostyrene (4-AS) and ethyl chloride, benzyl chloride and some substituted benzyl chlorides. These monomers are being spontaneously polymerized in aqueous and/or organic solvents via zwitterion mechanism. \(^1\)H NMR study of these monomers showed that the polymerization can be initiated by the
nucleophilic attack of 4-aminostyrene molecule on the β-position of the double bond for the monomer salt. The monomers and polymers prepared are characterized by elemental analysis, infrared spectroscopy and proton magnetic resonance.

**Experimental**

Melting points reported are uncorrected, $^1$H NMR spectra recorded in D$_2$O and DMF-$_d_7$ solution with TMS as an internal standard (δ, ppm) on a Varian EM 390 90 MHz spectrometer and infrared spectra (KBr) were obtained on Perkin-Elmer 293 FT spectrophotometer (ν, cm$^{-1}$). Elemental analyses were performed on a Perkin-Elmer CHN-2400 analyzer.

**Reaction of 4-aminostyrene with ethyl chloride, benzyl chloride and some substituted benzyl chlorides: Preparation of 4a-f. General Procedure.**

A solution of ethyl chloride, benzyl chloride or its substituents (0.03 mol) in anhydrous tetrahydrofuran (THF) or dry ether was added dropwise with stirring at 0 °C to 4-aminostyrene (0.01 mol) in anhydrous THF or dry ether. After suitable time the crystals were filtered, washed with the proper solvent and with dry ether, and then dried in vacuo at 25 °C to give 4a-f.

**4-(Diethylamino)styrene hydrochloride (4a).** To a stirred solution of 4-aminostyrene (1.19 g, 0.01 mol) in dry ether (25 mL) at 0 °C was added dropwise within 20 min a solution of ethyl chloride (1.935 g, 0.03 mol) in dry ether (25 mL) and the reaction mixture was left to stand at 0-5 °C for 1 h. Afterwards, the crystals so obtained were filtered off, washed with the proper solvent and with dry ether, and then dried in vacuo at room temperature (25 °C) to give 4a (1.69 g, 80%), mp 159-160 °C. Anal. Calcd for C$_{12}$H$_{18}$ClN: C 68.09, H 8.51, N 6.62, Cl 16.78. Found: C 67.95, H 8.55, N 6.67, Cl 16.83. IR (KBr) ν 1630 (C=C), 990 (=CH), and 915 (=CH$_2$). $^1$H NMR (D$_2$O) δ 2.11 (t, 6H, J$_{7}$ Hz, 2×CH$_3$), 3.93 (q, 4H, J$_{7}$ Hz, 2×CH$_2$), 4.88 (brs, 1H, NH), vinyl protons at δ 5.30 (d, 1H, H-2), 5.74 (d, 1H, H-3) and 6.73 (dd, 1H, H-1) J$_{gem}$ 1 Hz, J$_{cis}$ 10 Hz and J$_{trans}$ 17 Hz, 8.10 and 8.70 (dd, 4H, ArH).

**4-(Dibenzylamino)styrene hydrochloride (4b).** A solution of benzyl chloride (3.795 g, 0.03 mol) in anhydrous THF (30 mL) was added dropwise with stirring at 0 °C over 20 min to 4-aminostyrene (1.19 g, 0.01 mol) in anhydrous THF (25 mL). Afterwards, the reaction mixture was left at 0-5 °C for additional 1 h, and the formed
crystals were collected by filtration, washed with anhydrous THF and with dry ether, and then dried in vacuo at 25 °C to give 4b (2.35 g, 70%), mp 204 °C. Anal. Calcd for C_{22}H_{22}ClN: C 78.69, H 6.56, N 4.17, Cl 10.58. Found: C 78.87, H 6.49, N 4.15, Cl 10.49. IR (KBr) ν 1630 (C=C), 1000 (=CH) and 910 (=CH₂). ¹H NMR (D₂O) δ 4.95 (brs, 1H, NH), 5.35 (s, 4H, 2 × CH₂ benzyl), vinyl protons at δ 5.44 (d, 1H, H-2), 5.87 (d, 1H, H-3) and 6.87 (dd, 1H, H-1) J_{gem} 1 Hz, J_{cis} 10 Hz and J_{trans} = 17 Hz, 7.25-8.50 (m, 12H, ArH).

4-[(Di-p-methoxybenzyl)amino]styrene hydrochloride (4c). To 4-aminostyrene (1.19 g, 0.01 mol) in anhydrous THF (25 mL) was added dropwise with stirring at 0 °C over a period of 30 min, a solution of p-methoxybenzyl chloride (4.695 g, 0.03 mol) in anhydrous THF (50 mL) and the reaction mixture was left at 0-5 °C for additional 1 h. The crystals given were collected by filtration washed with anhydrous THF and with dry ether, and then dried in vacuo at 25 °C to give 4c (2.0 g, 50%), mp 223-224 °C. Anal. Calcd for C_{24}H_{26}ClNO₂: C 72.82, H 6.57, N 3.54, Cl 8.98. Found: C 72.91, H 6.53, N 3.54, Cl 8.92. IR (KBr) ν 1640 (C=C), 990 (=CH) and 925 (=CH₂). ¹H NMR (D₂O) δ 3.95 (s, 6H, 2 × OCH₃), 4.93 (brs, 1H, NH), 5.27 (s, 4H, 2 × CH₂ benzyl), vinyl protons at δ 5.42 (d, 1H, H-2), 5.82 (d, 1H, H-3) and 6.85 (dd, 1H, H-1) J_{gem} 1 Hz, J_{cis} 10 Hz and J_{trans} 17 Hz, 6.52-8.45 (m, 12H, ArH).

4-[(Di-o-methoxybenzyl)amino]styrene hydrochloride (4d). To a stirred solution of 4-aminostyrene (1.19 g, 0.01 mol) in anhydrous THF (25 mL) at 0 °C was added dropwise over 30 min, a solution of o-methoxybenzyl chloride (4.695 g, 0.03 mol) in anhydrous THF (50 mL). After 1 h at 0-5 °C the crystals so obtained were filtered off, washed with anhydrous THF and with dry ether, and then dried in vacuo at 25 °C to give 4d (2.38 g, 60%), mp 209-210 °C. Anal. Calcd for C_{24}H_{26}ClNO₂: C 72.82, H 6.57, N 3.54, Cl 8.98. Found: C 73.02, H 6.46, N 3.52, Cl 8.89. IR (KBr) ν 1630 (C=C), 1020 (=CH) and 915 (=CH₂). ¹H NMR (D₂O) δ 3.89 (s, 6H, 2 × OCH₃), 4.91 (brs, 1H, NH), 5.30 (s, 4H, 2 × CH₂ benzyl), vinyl protons at δ 5.40 (d, 1H, H-2), 5.85 (d, 1H, H-3) and 6.88 (dd, 1H, H-1) J_{gem} 1 Hz, J_{cis} 10 Hz and J_{trans} 17 Hz, 6.88-8.45 (m, 12H, ArH).

4-[(Di-p-nitrobenzyl)amino]styrene hydrochloride (4e). A solution of p-nitrobenzyl chloride (5.145 g, 0.03 mol) in anhydrous THF (50 mL) was added dropwise with stirring at 0 °C within 30 min to 4-aminostyrene (1.19 g, 0.01 mol) in anhydrous THF (25 mL). Afterwards, the reaction mixture was left at 0-5 °C for 1 h, then the crystals so formed during the course of reaction were filtered off, washed with anhydrous THF and with dry ether, and then dried in vacuo at 25 °C to give 4e (3.20 g, 75%), mp
218-219 °C. *Anal.* Calcd for C\(_{22}\)H\(_{20}\)ClN\(_3\)O\(_4\): C 62.04, H 4.70, N 9.87, Cl 8.34. Found: C 62.60, H 4.66, N 9.51, Cl 8.14. IR (KBr) \(\nu\) 1640 (C=C), 1000 (=CH) and 925 (=CH\(_2\)). \(^1\)H NMR (D\(_2\)O) \(\delta\) 4.98 (brs, 1H, NH), 5.50 (s, 4H, 2×CH\(_2\) benzyl), vinyl protons at \(\delta\) 5.49 (d, 1H, H-2), 5.93 (d, 1H, H-3) and 6.92 (dd, 1H, H-1) \(J_{gem}\) 1 Hz, \(J_{cis}\) 10 Hz and \(J_{trans}\) 17 Hz, 8.44 (m, 12H, ArH).

4-[(Di-o-nitrobenzyl)amino]styrene hydrochloride (4f). To a solution of 4-aminostyrene (1.19 g, 0.01 mol) in anhydrous THF (25 mL) at 0 °C was added dropwise with stirring over a period of 30 min, a solution of o-nitrobenzyl chloride (4.695 g, 0.03 mol) in anhydrous THF (50 mL). Then the reaction mixture was left at 0-5 °C for 1 h, and the crystals so separated were collected by filtration, washed with anhydrous THF and with dry ether, and then dried *in vacuo* at 25 °C to give 4f (2.77 g, 65%), mp 215 °C. *Anal.* Calcd for C\(_{22}\)H\(_{20}\)ClN\(_3\)O\(_4\): C 62.04, H 4.70, N 9.87, Cl 8.34. Found: C 62.60, H 4.66, N 9.51, Cl 8.14. IR (KBr) \(\nu\) 1625 (C=C), 995 (=CH) and 935 (=CH\(_2\)). \(^1\)H NMR (D\(_2\)O) \(\delta\) 4.95 (brs, 1H, NH), 5.48 (s, 4H, 2×CH\(_2\) benzyl), vinyl protons at \(\delta\) 5.47 (d, 1H, H-2), 5.90 (d, 1H, H-3) and 6.90 (dd, 1H, H-1) \(J_{gem}\) 1 Hz, \(J_{cis}\) 10 Hz and \(J_{trans}\) 17 Hz, 7.34-8.47 (m, 12H, ArH).

Table 2. Characterization data of the polymers prepared.

<table>
<thead>
<tr>
<th>Polym.*</th>
<th>(DP)</th>
<th>Formula</th>
<th>Calcd. (Found) %</th>
<th>(^1)H NMR (in DMF-d(_7)) (\delta) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>30</td>
<td>(C(<em>{12})H(</em>{17})N)(_x)</td>
<td>82.29 9.71 8.00 (82.37 9.84 7.78)</td>
<td>1.03-1.33 (br, 3H, backbone CH(_2) and CH), 1.60 (t, 6H, 2×CH(_3)), 2.00 (q, 4H, 2×CH(_2)), 6.05-7.70 (m, 4H, ArH).</td>
</tr>
<tr>
<td>6b</td>
<td>27</td>
<td>(C(<em>{22})H(</em>{21})N)(_x)</td>
<td>88.29 7.02 4.68 (88.48 6.94 4.55)</td>
<td>1.05-1.36 (br, 3H, backbone CH(_2) and CH), 4.58 (brs, 4H, 2×CH(_2) benzyl). 6.11-7.76 (m, 14H, ArH).</td>
</tr>
<tr>
<td>6c</td>
<td>29</td>
<td>(C(<em>{24})H(</em>{25})N)(_x)</td>
<td>80.22 6.96 3.90 (80.12 7.11 3.87)</td>
<td>1.03-1.35 (br, 3H, backbone CH(_2) and CH), 3.80 (s, 6H, 2×OCH(_3)). 4.22 (brs, 4H, 2×CH(_2) benzyl). 6.00-7.70 (m, 12H, ArH).</td>
</tr>
<tr>
<td>6d</td>
<td>25</td>
<td>(C(<em>{24})H(</em>{25})N)(_x)</td>
<td>80.22 6.96 3.90 (80.42 6.78 3.56)</td>
<td>1.00-1.30 (br, 3H, backbone CH(_2) and CH), 3.73 (s, 6H, 2×OCH(_3)). 4.50 (brs, 4H, 2×CH(_2) benzyl). 6.07-7.71 (m, 12H, ArH).</td>
</tr>
<tr>
<td>6e</td>
<td>28</td>
<td>(C(<em>{22})H(</em>{19})N(_3)O(_4))(_x)</td>
<td>67.87 4.88 10.80 (68.16 5.19 10.58)</td>
<td>1.02-1.35 (br, 3H, backbone CH(_2) and CH), 4.65 (brs, 4H, 2×CH(_2) benzyl). 6.17-7.90 (m, 12H, ArH).</td>
</tr>
<tr>
<td>6f</td>
<td>27</td>
<td>(C(<em>{22})H(</em>{19})N(_3)O(_4))(_x)</td>
<td>67.87 4.88 10.80</td>
<td>1.03-1.39 (br, 3H, backbone CH(_2) and CH), 4.63 (brs, 4H, 2×CH(_2) benzyl). 6.13-7.85 (m, 12H, ArH).</td>
</tr>
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</table>

* after neutralization.

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Polymerization

The sample of 10% solution of the monomer salt in D$_2$O and different mole% of 4-AS or aniline (Table 1) were introduced in the NMR spectrometer and the course of polymerization was monitored at 45 °C. After disappearance of the vinyl protons, the produced polymer was neutralized with dilute sodium bicarbonate solution. The precipitate was filtered, washed with water and with ethanol, and then dried in vacuo at room temperature. The $^1$H NMR data of polymers prepared are given in Table 2.

Acknowledgments

The author gratefully acknowledges the support and encouragement of Professor R. M. Abdel-Rahman and Professor M. A. AlKhader during the course of this work.

References and Notes

# For Part III please see reference 8.

Povzetek

Proučevali smo mehanizem spontane polimerizacije soli N-alkil in N-benzil 4-aminostirena v različnih topilih. Rezultati kažejo, da je začetna stopnja nukleofilna reakcija nealkilirane molekule 4-aminostirena na dvojno vez stirena, kar vodi do nastanka zwitteriona. Prispevek halogenidnegaiona (X$^{-}$) je v začetni stopnji nepomemben.