Studies on the Copolymerization of 4-Aminostyrene With 4-Nitro- and 2,4-Dinitrostyrene

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Abstract

Poly(4-aminostyrene)-block-poly(4-nitrostyrene) (P4AS-b-P4NS) and poly(4-aminostyrene)-block-poly(2,4-dinitrostyrene) (P4AS-b-P2,4DNS) were successfully prepared. Conditions under which copolymerization of 4-aminostyrene (4-AS) with either 4-nitro- (4-NS) or 2,4-dinitrostyrene (2,4-DNS) proceed, have been investigated by adjusting the relative proportion of the two monomers and found to be 1:1 and 2:1 for 4-AS with both 4-NS and 2,4-DNS, respectively; and proceed as a block type. The diazonium salts of the produced copolymers have been coupled with different phenols and aromatic amines; the produced azo derivatives have good application potential as paints and monomer stabilizers. The copolymerization has been kinetically investigated by NMR spectroscopy and intrinsic viscosity measurements at different temperatures. Results indicate that the rate of reaction and structures of the produced copolymers are dependent upon the reaction temperature and the type of monomer. The rate constants of the copolymerizations which proceed via first order are: \( k = 3.01 \times 10^{-3} \text{s}^{-1} \) and \( 1.47 \times 10^{-3} \text{s}^{-1} \); \( t_{1/2} = 230.23 \text{s} \) and 471.43 s, whereas the activation energy parameters are: \( E_a = 59.31 \) and 67.43 kJ/mol; \( \Delta H^* \) are 56.79 and 64.9 kJ/mol and \( \Delta S^* \) are \(-102.55\) and \(-100.41 \text{ J mol}^{-1} \text{deg}^{-1} \) for the copolymerization of 4-AS with both 4-NS and 2,4-DNS, respectively.

Keywords: 4-Aminostyrene, copolymer; 2,4-Dinitrostyrene, 4-Nitrostyrene, azo-derivatives, rate constants, activation energy parameters

1. Introduction

Because of its unique physicochemical properties and some advantages with respect to synthesis, steadiness character, and environmental stability, poly(aminostyrene) (PAS) attracted considerable attention for its application in paints and stabilizers, as ionic conductive material, photo induced electron transfer materials, organic semiconductors, and fluorescent dyes. Several approaches including use of ring or \( N \)-substituted 4-aminostyrene for the synthesis of stable monomers and/or polymerizations to produce several types of polymers which are used for different purposes have been reported.

Our previous investigations reported that pure 4-aminostyrene salts (4-AS.HX) and their \( N \)-alkyl/benzyl derivatives are stable in \( D_2O \) at room temperature, they are spontaneously polymerized in the presence of 4-AS. The initiation step was caused by the nucleophilic attack of 4-aminostyrene molecule on the activated \( \beta \)-position of the double bond of the monomer salt to give a zwitterionic propagating species 1. On the other hand, the mechanism of propagation has been considered to occur by the nucleophilic addition of the zwitterionic propagating species 1 to a new monomer salt.

Copolymer of styrene and 4-nitrostyrene (SNS) may be prepared by direct nitration of polystyrene (PS) either...
in 3-nitrotoluene\textsuperscript{11} or in a mixture of nitrobenzene and 1,2-dichloroethane (3:1) with fuming nitric acid.\textsuperscript{14} Polymers and copolymers of 4-nitrostyrene may also be formed by free radical polymerization of the monomer.\textsuperscript{15–17} On the other hand, some researches showed that nitrostyrenes can be polymerized by anionic polymerization\textsuperscript{18,19} or charge transfer complex.\textsuperscript{20}

Concerning the polymerization of disubstituted nitrostyrenes, it was reported\textsuperscript{21} that 2,4-dinitrostyrene can be polymerized under the action of alcoholates of alkaline metals or primary and tertiary aliphatic amines. Moreover, Fernández et al.\textsuperscript{22} reported that styrene-2,4-dinitrostyrene copolymer (SDNS) was prepared by direct nitration of polystyrene (PS) in 1,2-dichloroethane with a 1:1 mixture of fuming nitric acid (96%) and sulfuric acid.

Because of their polarity caused by the strongly electron-withdrawing nature of the nitro group, nitrostyrenes have attracted attention for copolymerization with 4-aminostyrene. Since poly(4-aminostyrene) (PAS) is a reactive polymer with its amino group being responsible for a number of potential applications,\textsuperscript{1–5,9,10,23} it is worthwhile to synthesize poly(4-aminostyrene)-block-poly(4-nitrostyrene) (P4AS-b-P4NS) and poly(4-aminostyrene)-block-poly(2,4-dinitrostyrene) (P4AS-b-P2,4DNS). Herein, we report the controlled synthesis of these copolymers by spontaneous polymerization in aqueous solution. The polymerization rates and structures of the produced copolymers were kinetically investigated by NMR spectroscopy and intrinsic viscosity measurements at different temperatures. Activation energy parameters were also calculated. The produced copolymers have been treated as diazonium salts and coupled with different phenols and aromatic amines.

2. Results and Discussion

Poly(4-aminostyrene) hydrochloride (P4AS.HCl) is a reactive polymer with zwitterionic character that could be copolymerized with $\beta$-carbon of the vinyl group in either 4-nitrostyrene (4-NS) or 2,4-dinitrostyrene (2,4-DNS) to yield P4AS-block-poly(4NS) (P4AS-b-P4NS) and P4AS-block-poly(2,4-DNS) (P4AS-b-P2,4DNS). This finding is similar to that reported by Yang and Gaoni,\textsuperscript{20} concerning the copolymerization of 2,4,6-trinitrostyrene (TNS) with 4-vinylpyridine upon mixing at room temperature.

The copolymers were obtained after the addition of the 4-NS or 2,4-DNS to the 4-aminostyrene salt in bidistilled water. The relative proportion of the two monomers in the copolymers could be varied by adjusting the molar ratio of the two monomers in the polymerization mixture. The elemental analyses data revealed that a 1:1 mixture of the monomers reacted to give a 1:1 (4AS-b-4NS) (N: 10.57%) and 2:1 (4AS-b-2,4DNS) (N: 12.90%) copolymer whereas a 1:2 mixture gave a 1:1 (4AS-b-2,4DNS) (N: 13.54%) copolymer.

The intrinsic viscosity $[\eta]$ of the solutions of copolymer samples prepared in bidistilled water was measured at 30 °C and 45 °C using Ostwald viscometer. By using the following intrinsic viscosity-molecular weight relationship,\textsuperscript{1} the average molecular weight ($M_n$) of copolymer samples was determined from these intrinsic viscosities.

$$[\eta] = 7.7 \times 10^{-5} M_n^{0.7}$$

The intrinsic viscosity of copolymer samples was found to be in the range from 0.0315–0.0503 dl·g$^{-1}$ which gives molecular weight as 3300–10500.

Fig. 1 shows the effect of the temperature on the intrinsic viscosity $[\eta]$ of 4-AS with 4-NS and 2,4-DNS mixtures. The curves point to increasing trend of the intrinsic viscosity of the polymerizable monomers with increase of the temperature. The data in Fig. 1 indicate that the copolymerization rate obtained for the 4-NS is always higher than that for 2,4-DNS at the same monomer feed ratio. The dependance of the intrinsic viscosity on the temperature could be deduced from the slopes of the curves depicted in Fig. 1.

A more quantitative method to investigate the effect of reactants nature as well as the temperature on the rate of copolymerization process can be judged by the kinetic studies. Therefore, copolymerizations were monitored by following the kinetic appearance of the copolymer via intrinsic viscosity $[\eta]$ measurements of 4-AS with either 4-NS or 2,4-DNS in aqueous solutions at different temperatures as shown in Fig. 1. Under such experimental conditions the current polymerization reactions behave as first order, the rate constants ($K_r$) were calculated from the plot of $\ln(\eta_\infty - \eta_t)$ vs. time ($t$ in seconds) as shown in Fig. 2, where: $\eta_\infty$ refers to the final viscosity and $\eta_t$ refers to the
viscosity at a given time \( t \). The rate and activation parameters data of the current copolymers are given in Table 1.

These data indicate that the rate of copolymerization at 303 K for 4-AS with 4-NS is \( k = 3.01 \times 10^{-3} \text{ s}^{-1} \), \( \frac{t_{1/2}}{k} = 230.23 \text{ s} \) and is faster than that with 2,4-DNS (1.47 \( \times 10^{-3} \text{ s}^{-1} \), 471.43 s). These findings are supported by the activation energy values (\( E_a = 59.31 \) and 67.43 kJ/mol for 4AS-b-4NS and 4AS-b-2,4DNS, respectively). These values indicate that the polymerization is much hindered by a high activation free energy (\( E_a \)) in the case of 2,4-DNS compared to 4-NS. This behavior might be attributed to the presence of two strong electron withdrawing groups and the steric hindrance of the ortho nitro group. This is in a good agreement with the fact that 2,4,6-trinitrostyrene acts as an inhibitor of styrene polymerization.

The enthalpy changes of activation \( \Delta H^* \) are 56.79 and 64.9 kJ/mol for 4-AS with both 4-NS and 2,4-DNS, respectively. These values indicate that the hindrance of the polymerization caused by a high activation free enthalpy changes in the case of 2,4-DNS is higher than that of 4-NS. Furthermore, the entropies of activation \( \Delta S^* \) are found to have negative values resulting from sterical and orientational requirements, as a result of polymerization. \( \Delta S^* \) values were found to be -102.55 and -100.41 J mol\(^{-1}\) deg\(^{-1}\); nearly the same for 4-AS with 4-NS and 2,4-DNS, respectively. This indicates that the effect of the sterically demanding ortho nitro group in 2,4-DNS on the \( \Delta S^* \) value is much smaller than the losses of degrees of freedom in the transition state of polymerization.

Fig. 3 shows conversion degree of the copolymerization process versus the time determined by using \(^1\)H NMR (D\(_2\)O) group analysis. The consumption of vinyl protons of 4-aminostyrene has been detected after 240 min without any change in the vinyl protons of 4-NS and 2,4-DNS. The propagation of spontaneous copolymerization can occur by the nucleophilic addition of the zwitterionic propagating species 1 to the \( \beta \)-position of the double bond of 4-NS or 2,4-DNS. The data in Fig. 3 again point to a higher conversion rate in the case of 4-NS in comparison with that for 2,4-DNS. These data agree well with the intrinsic viscosity measurements.

The ability of 4-aminostyrene to spontaneously copolymerize with either 4-nitrostyrene or 2,4-dinitrostyrene may be attributed to the zwitterionic propagating species 1 and the strongly electron-withdrawing nature of the nitro group. Hence a charge transfer complex is created between the zwitterionic propagating species and 4-nitrostyrene or 2,4-dinitrostyrene. This explanation is in a good agreement with that found by Yang et al.\(^{20}\)

The structures of copolymers were characterized on the basis of elemental analyses, IR and \(^1\)H NMR spectral data. IR
data show a sharp band at 1490–1480 cm⁻¹ due to the CH group and a strong bending absorption vibration band at 1450–1440 cm⁻¹ due to the CH₂ group and a further double peak pattern for a primary amine at 3430 and 3540 cm⁻¹ which might be attributed to NH₂ group. Furthermore, 4AS-b-4NS copolymer exhibited a symmetric stretching vibration band at 1350 cm⁻¹ and an asymmetric stretching band at 1525 cm⁻¹ characteristic for the nitro group. Further band at 850 cm⁻¹ indicates two adjacent hydrogens in a substituted benzene, which establishes the presence of a nitro group at para position in 4AS-b-4NS copolymer. In addition to these bands, the IR spectrum of 4AS-b-2,4DNS exhibited absorption pattern in the 2000–1600 cm⁻¹ region which is characteristic of a 1,2,4-substituted benzene ring, showing that the nitro groups are ortho and para. ¹H NMR spectrum shows the presence of a broad band at δ 3.5–5.2 ppm due to NH₂ and a broad band at δ 1.0–1.5 ppm due to the backbone CH₂ and CH.

IR spectra of diazo derivatives show a new band at 1310–1350 cm⁻¹ which could be attributed to C₆H₅–N= and a band at 835 cm⁻¹ due to para-substituted benzene. The IR spectra of diazo derivatives derived from aromatic amines show additional absorption band at 1240–1250 cm⁻¹ due to –HN–N=N– group. The nitrogen content of azo derivatives was found to be 10.05–13.51% with phenols and 13.33–16.46% with aromatic amines.

Because of the unique properties of the amino group and its utility for the formation of diazo derivatives, copolymers produced have been treated as diazonium salts and coupled with different phenols and aromatic amines. The obtained azo derivatives have good application potential as good stabilizers (when phenols are applied) and strength paints (when aromatic amines are used). The stabilizer has been tested with different vinyl monomers; e.g. acrylonitrile, 4-aminostyrene, methylmethacrylate, vinyl chloride, vinyl acetate, styrene, etc. and showed a high stability of the monomers towards polymerization. Moreover, the paints have good heat resistance up to 75 °C for a long time. The degradation of these copolymers will be investigated in further studies.

The produced polymers chelated with different transition metals and nonmetals might be used in some industrial applications. This possibility is under active investigation and may open a new field in the purification of waste water and reduction of waste disposal in the environment. Preliminary successful application has been done and gives promising results.

3. Conclusions

The copolymers were successfully prepared through spontaneous copolymerization of 4-aminostyrene (4-AS) with 4-nitrostyrene (4-NS) and 2,4-dinitrostyrene (2,4-DNS) in aqueous solutions. The copolymers produced were characterized by elemental analysis, infrared spectroscopy and proton magnetic resonance.

The rate of growth of copolymerization was monitored by ¹H NMR and intrinsic viscosity measurements at different temperatures. The rate constants of the copolymerization which proceed via first order were found to increase during the increase of temperature. The activation energy parameters indicate that the rate of copolymerization for 4-AS with 4-NS is faster than with 2,4-DNS. The steric effect of the ortho nitro group in 2,4-DNS on the ∆S* values is much smaller than the losses of translational and rotational degrees of freedom in the transition state.

The variation of the proportion of the two monomers in the copolymer by adjusting the monomers feed ratio in the polymerization mixture was established. The produced copolymers have been treated as diazonium salts and were coupled with different phenols and aromatic amines; the produced diazo derivatives have good application potential as paints and monomer stabilizers.

4. Experimental

4.1. Materials and Methods

4-Aminostyrene was synthesized from 2-phenylethanol.¹ 4-Nitrostyrene and 2,4-dinitrostyrene were synthesized from 2-bromoethylbenzene as described elsewhere.¹⁹ 4-Aminostyrene was purified by double distillation under reduced pressure before use. 4-Nitrostyrene and 2,4-dinitrostyrene were purified by sublimation.¹⁹ Polymerization and other experiments were carried out in bidistilled water.

4.2. 4-Aminostyrene Hydrochloride (4-AS.HCl)

4-Aminostyrene hydrochloride (4-AS.HCl) was prepared from 4-aminostyrene as described elsewhere.¹ A current of dry hydrogen chloride gas was passed through a
solution of 4-aminostyrene (1.19 g, 0.01 mol) in dry ether
(20 mL), and the reaction mixture was left to stand at 0–5
°C for half an hour. Afterwards, the crystals obtained were
filtered off, washed with dry ether, and then dried in vacuo
at room temperature to give 1.5 g (98%), mp. 165 °C.

4. 3. Physical Measurements

Compounds prepared were characterized by elemental
analysis, infrared spectrometry, NMR spectroscopy and viscosity measured by Ostwald viscometer. 1H
NMR spectra were recorded in D2O with TMS as an internal
standard (δ, ppm) on a Varian EM 390 spectrometer at
90 MHz and infrared spectra (KBr) were obtained on a
Perkin-Elmer 293 FT spectrophotometer (ν, cm⁻¹). Elementa
analyses were performed on a Perkin-Elmer CHN-
2400 analyzer.

4. 4. Copolymerization

4. 4. 1. In Aqueous Solution

The viscosity of the copolymer solutions samples
which were prepared by mixing an aqueous solutions of
4-AS with either 4-NS (1:1) or 2,4-DNS (1:1 and 2:1),
was measured by Ostwald viscometer at 30 °C and 45 °C.
*Anal.* Calcd for 4AS–b–4NS (1:1) C₁₆H₁₆N₂O₂: C, 71.64;
H, 5.97; N, 10.45. Found: C, 71.28; H, 6.03; N, 10.57.
*Anal.* Calcd for 4AS–b–2,4DNS (2:1) C₁₆H₁₅N₃O₄:
C, 61.34; H, 4.79; N, 13.42. Found: C, 61.10; H, 4.86; N,
13.54.

4. 4. 2. 1H NMR Studies

The course of polymerization of a sample of 5% so-
lution mixture of the zwitterionic propagating species of
4-aminostyrene hydrochloride (4-AS.HCl) and purified 4-
nitrostyrene (4-NS) or 2,4-dinitrostyrene (2,4-DNS) (1:1)
in D₂O at 45 °C was monitored by NMR spectroscopy. Af-
ter disappearance of the vinyl protons, the produced poly-
mer was neutralized by dilute solution of sodium bicarbo-
nate. The precipitate was filtered off, washed with water and
with dry ether, and then dried in vacuo at room tempe-
rate.

4. 5. Diazotization and Coupling
of Copolymers

4. 5. 1. With Phenols

To a cold solution (0 °C) of a selected copolymer
(0.0036 mmol) in concentrated hydrochloric acid (15 mL) a
cold solution (10% at 0 °C) of sodium nitrite in water (3 mL)
was added dropwise with a continuous stirring. The solution
mixture was left to stand at 0 °C for 30 min; the crystals so
obtained were filtered off, and then added 2 g of sodium ace-
tate in 10 mL water. The appropriate phenol (0.003 mmol)
dissolved in 3 mL of 10% sodium hydroxide was added
dropwise with energetic stirring to couple with the prepared
diazotized solution at 0 °C over a period of 30 min and ad-
ded 50 mL hot water, and then the reaction mixture was left
at 0 °C for additional 30 min. The crystals obtained were
collected by filtration, washed with cold water and with eth-
anal, and then dried in vacuo at 25 °C (98% yield).

4. 5. 2. With Amines

Similarly as above, to the diazotized solution prepa-
red, a cold solution (5%, 0 °C) of appropriate amine
(0.003 mmol) in water (1 mL) was added dropwise with
energetic stirring and then 4 mL of a saturated solution of
sodium acetate. Then the reaction mixture was left at 0 °C
for additional 30 min. The crystals obtained were collect-

Table 2. Characterization data for the azo derivatives of 4AS–b–4NS (1:1)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Coupling compound</th>
<th>Color</th>
<th>Anal.</th>
<th>Calcd. (Found) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂₃H₂₂N₄O₂</td>
<td>p–Toluidine</td>
<td>Orange</td>
<td>71.48</td>
<td>5.74 14.50</td>
</tr>
<tr>
<td>(386)</td>
<td></td>
<td></td>
<td>(71.36</td>
<td>5.59 14.65</td>
</tr>
<tr>
<td>C₂₃H₂₂N₄O₂</td>
<td>N–Methyl aniline</td>
<td>Yellowish–brown</td>
<td>71.48</td>
<td>5.74 14.50</td>
</tr>
<tr>
<td>(386)</td>
<td></td>
<td></td>
<td>(71.27</td>
<td>5.61 14.66</td>
</tr>
<tr>
<td>C₂₆H₂₃N₃O₂</td>
<td>α–Naphthylamine</td>
<td>Brown</td>
<td>73.93</td>
<td>5.21 13.27</td>
</tr>
<tr>
<td>(422)</td>
<td></td>
<td></td>
<td>(73.75</td>
<td>5.28 13.33</td>
</tr>
<tr>
<td>C₂₆H₂₃N₃O₂</td>
<td>β–Naphthylamine</td>
<td>Red</td>
<td>73.93</td>
<td>5.21 13.27</td>
</tr>
<tr>
<td>(422)</td>
<td></td>
<td></td>
<td>(73.54</td>
<td>5.35 13.46</td>
</tr>
<tr>
<td>C₂₁H₁₉N₃O₂</td>
<td>Phenol</td>
<td>Magenta red</td>
<td>70.78</td>
<td>5.09 11.26</td>
</tr>
<tr>
<td>(373)</td>
<td></td>
<td></td>
<td>(70.47</td>
<td>5.14 11.35</td>
</tr>
<tr>
<td>C₂₆H₂₁N₃O₂</td>
<td>α–Naphthol</td>
<td>Beige–yellow</td>
<td>73.76</td>
<td>4.96 9.93</td>
</tr>
<tr>
<td>(423)</td>
<td></td>
<td></td>
<td>(73.82</td>
<td>5.07 10.05</td>
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<tr>
<td>C₂₆H₂₁N₃O₂</td>
<td>β–Naphthol</td>
<td>Orange–red</td>
<td>73.76</td>
<td>4.96 9.93</td>
</tr>
<tr>
<td>(423)</td>
<td></td>
<td></td>
<td>(73.97</td>
<td>4.63 10.12</td>
</tr>
</tbody>
</table>
ted by filtration, washed with cold water and with ethanol, and then dried in vacuo at 25 °C (90% yield). The characterization data for the azo derivatives of 4AS-b-4NS (1:1) and 4AS-b-2,4DNS (1:1) are given in Tables 2 and 3.

5. Acknowledgments

The author would like to gratefully thank Prof. Ali Taha for his support and encouragement.

6. References

Povzetek

Z uporabo B3LYP metode (z baznimi seti 6-31G in 6-311G ter z vrsto različnih polarizacijskih in difuznih funkcij) smo teoretično raziskali pet izomerov citozina in njihove medsebojne pretvorbe. Pokazali smo, da je od vseh tautomerov citozina najbolj stabilen kanonski aminookso tautomer, vendar pa ima neplanarno geometrijo. Pokazali smo tudi, da so izračunane energije in energijske bariere v preučevanih sistem precej odvisne od tega, če v bazni set vključimo polarizacijske funkcije, medtem ko je občutljivost na vključitev difuznih funkcij manjša.