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Polymerization of 4-(substituted amino)styrene: Part III – spontaneous polymerization of 4-(benzylamino)styrene salts

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Summary

Spontaneous polymerization of 4-aminostyrene-benzyl chloride and/or benzyl bromide systems has been investigated. The results indicate that 4-aminostyrene on reacting with benzyl halides and/or some of its substituents yields corresponding 4-(benzylamino)styrene salts, which are found to polymerize spontaneously in aqueous solution as well as in organic solvents, leading to the formation of poly[4-(benzylamino)styrene] salts. The rates of these reactions clearly indicate that the courses of such reactions are governed by the polarity of the solvent, type of the halide ion and temperature, but no significant role of substituents at the benzyl moiety could be observed.

KEY WORDS
4-(benzylamino)styrene salts
poly[4-(benzylamino)styrene] salts
spontaneous polymerization
rate of polymerization

KLJUČNE RIJEČI
4-(benzilamino) stirenske soli
poli[4-(benzilamino)stiren] soli
spontana polimerizacija
brzina polimerizacije

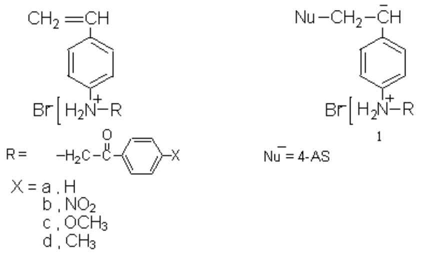
Polimerizacija 4-(supstituiranih amino)stirena: III. dio – spontana polimerizacija 4-(benzilamino) stirenskih soli

Sažetak

Ispitana je spontana polimerizacija 4-aminostiren-benzil klorida i / ili benzil bromida. Rezultati ukazuju da 4-aminostiren reakcijom s benzil halidima i / ili nekim od supstituenata tvori odgovarajuće 4-(benzilamino) stirenske soli koje spontano polimeriziraju u vodenoj otopini kao i u organskim otapalima. Polimerizacijom nastaju poli[4-(benzilamino)stiren] soli. Brzine reakcija ukazuju da je tok reakcije određen polarnošću otapala, vrstom halidnog iona i temperaturom, pri čemu nije primijećen bitan utjecaj supstituenata na benzilnom dijelu molekule.

Introduction

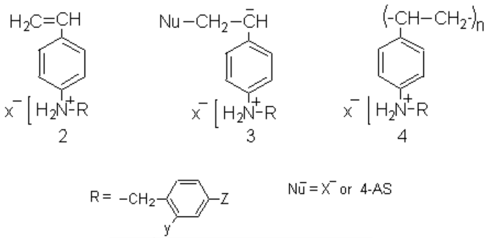
Spontaneous polymerization of 4-aminostyrene salts in aqueous solution or organic solvents to form the corresponding poly[4-(benzylamino)styrene] salts has been of considerable interest.[1-7] Previous investigation of these reactions indicated that stable 4-aminostyrene salts are easily obtained.[1,2] Barba et al. excluded free radical and ionic mechanisms as pathways for the polymerization of 4-aminostyrene salts.[1] Also, the author has reported similar finding for the spontaneous polymerization of 4-(alkylamino)styrene salts[6] and 4-(*p*-substituted-phenacylamino)styrene salts.[7] It was proposed then that spontaneous polymerization of (4-substituted-phenacylamino)styrene salts resulted from the nucleophilic addition of unalkylated 4-aminostyrene molecule to the-position of the double bond of 4-(*p*-substituted-phenacylamino)styrene salts to yield a highly resonance stabilized Zwitter-ion(1).[7] Propagation to form the poly [4-(*p*-substituted-phenacylamino)styrene] salts was considered to occur by the specific addition of I to an alkylated 4-aminostyrene molecule; maintaining a resonance stabilized zwitterionic endgroup.[8-11]



In the continuation of this work, we report the spontaneous polymerization of 4-(substituted-benzylamino)styrene salts in different solvents, in order to draw a line of comparison between the present and previous studies.

Experimental Part

The present work describes a comparative account of the spontaneous polymerization of 4-(substituted-benzylamino)styrene salts in different solvents based on the available viscosity data[12] at temperatures ranging from 30 C to 50 C. Thus, 4-aminostyrene (4-AS) reacts with benzyl halides and some of its substituents at the molar



	X	Y	Z
a	Cl	H	H
b	Br	H	H
c	Cl	H	OCH_3
d	Cl	OCH_3	H
e	Cl	H	NO_2
f	Cl	NO_2	H

ratio of 1:1 in dry ether or tetrahydrofuran (THF) leading to the formation of stable monomeric salts 2a-f. As the reaction progressed, spontaneous polymerization to give 4 occurred.

Investigation of the influence of free-radical inhibitors (benzoquinone and cupric salts) or the addition of acrylonitrile showed no effect on the polymerization rate and IR spectra produces no signal at 2 240 cm^{-1} indicating the absence of a CN group, thus excluding both the free radical and the ionic mechanism.

Reaction of 4-aminostyrene with benzyl halide (chloride or bromide) and substituted benzyl chloride: preparation of 2a-f

To a cold solution of 4-aminostyrene (1 mole) in dry ether or tetrahydrofuran (THF) was added dropwise with stirring to a solution of benzyl halide or substituted benzyl chloride (1 mole) in dry ether or THF. The precipitates were filtered, washed with dry ether and dried in vacuum at room temperature to give 2a-f (Table 1).

The structures of the compounds prepared were confirmed by elemental analysis, infrared spectrometry and NMR spectroscopy. IR spectra (KBr) were recorded on a Perkin-Elmer 598 spectrometer and ^{1}H-NMR spectra were obtained on a Varian EM 390/90 MHz spectrometer in D_2O and DMF-d_7 with TMS as an internal standard (ppm).

Polymerization

All polymerization reactions were carried out in aqueous and organic solution (benzene and nitrobenzene) of different concentrations (1.0 3.0 M) at the desired temperature. Following the re-

TABLE 1. Physical and analytical data of the compounds prepared
TABLICA 1. Fizikalna svojstva i analitički podaci sintetiziranih spojeva

Compound	m.p. °C	Yield %	Molar mass	Found (Calculated), %					^{1}H-NMR* δ, ppm
				C	H	N	Cl	Br	
2a	176	85	$C_{15}H_{16}ClN$ (245.5)	73.92 (73.32)	6.41 (6.52)	5.60 (5.70)	14.75 (5.70)	—— ——	7.22-7.83 (m,9H, Ar-H); 5.36, 5.79 and 6.79 (d,d, q, 3H, vinyl protons); 4.86 (s, 2H, -NH_2); 5.22 (s, 2H, -CH_2 of benzyl moiety)
2b	170	82	$C_{15}H_{16}BrN$ (290)	61.87 (62.07)	57.71 (5.52)	5.22 (4.83)	—— ——	27.20 (27.59)	7.25-7.80 (m, 9H, Ar-H); 5.45, 5.88 and 6.86 (d,d, q, 3H, vinyl protons); 4.98 (s, 2H, -NH_2); 5.32 (s, 2H, -CH_2 of benzyl moiety)
2c	197-198	77	$C_{16}H_{18}ClNO$ (275.5)	70.05 (69.96)	6.22 (6.53)	5.30 (5.08)	—— ——	—— ——	6.78-7.78 (m, 8H, Ar-H) 5.33, 5.77 and 6.81 (d,d, q, 3H, vinyl protons); 4.90 (s, 2H, NH_2); 5.18 (s, 2H, -CH_2 of benzyl moiety); 3.80 (s, 3H, -OCH_3)
2d	183-184	80	$C_{16}H_{18}ClNO$ (275.5)	69.94 (69.96)	6.45 (6.53)	5.10 (5.08)	12.61 (12.88)	—— ——	7.00-7.80 (m, 8H, Ar-H); 5.35, 5.78 and 6.79 (d,d, q, 3H, vinyl protons); 4.88 (s, 2H, -NH_2); 5.22 (s, 2H, -CH_2 of benzyl moiety); 3.62 (s, 3H, -OCH_3)
2e	191-192	90	$C_{15}H_{15}ClN_2O_2$ (290.5)	61.92 (61.96)	5.28 (5.16)	9.83 (9.64)	12.70 (12.88)	—— ——	7.51-7.78 (m, 8H, Ar-H); 5.36, 5.78 and 6.78 (d,d, q, 3H, vinyl protons); 4.80 (s, 2H, -NH_2); 5.36 (s, 2H, -CH_2 of benzyl moiety)
2f	180-181	95	$C_{15}H_{15}ClN_2O_2$ (290.5)	62.10 (61.96)	5.05 (5.16)	9.70 (9.64)	11.96 (12.22)	—— ——	7.76-7.70 (m, 8H, Ar-H); 5.34, 5.79 and 6.80 (d,d, q, 3H, vinyl protons); 4.84 (s, 2H, -NH_2); 5.29 (s, 2H, -CH_2 of benzyl moiety)
4b	——	——	——	——	——	——	——	——	6.00-7.60 (m, 9H, Ar-H);1.08-1.35 (3H, br, Chain-CH_2 and -CH); 4.86-5.20 (1H, br, -NH); 4.25 (s, 2H, -CH_2 of benzyl moiety)

actions under the desired conditions, the produced polymer was neutralized with the dilute solution of sodium bicarbonate. The solid precipitate was filtered off, washed with water and then with ethyl alcohol or ether and dried in vacuum at room temperature to give 4_b.

Results and Discussion

There is no doubt now that these results confirm the Zwitterionic mechanism characteristic of such reactions,[5] in which the halide ion or an unalkylated 4-AS molecule initiates the reaction by its addition to the double bond of monomeric salt to yield a highly resonance stabilized Zwitterion (3a-f).

Furthermore, It has been found that the intrinsic viscosity of polymerizable monomer increases from the non-polar to the most polar solvent to keep the temperature constant.[13] Thus from the polymerization of 4-(benzylamino)styrene hydrochloride in aqueous solution, benzene or nitrobenzene (Fig. 1) at 40 °C, we conclude that the rate of polymerization increases by increasing the polarity of the solvents used. However, polymerization in nitrobenzene at a different temperature range (Fig. 2), shows that the reaction rate is temperature dependent.

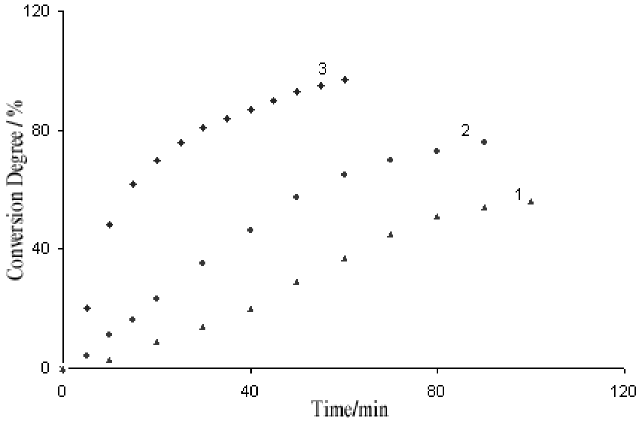


FIGURE 1. The dependence of the rate of polymerization for 4-(benzylamino)styrene hydrochloride on the nature of the solvent: 1) in benzene; 2) in nitrobenzene; 3) in H_2O; [M] = 2 moles; polymerization temperature 40 °C

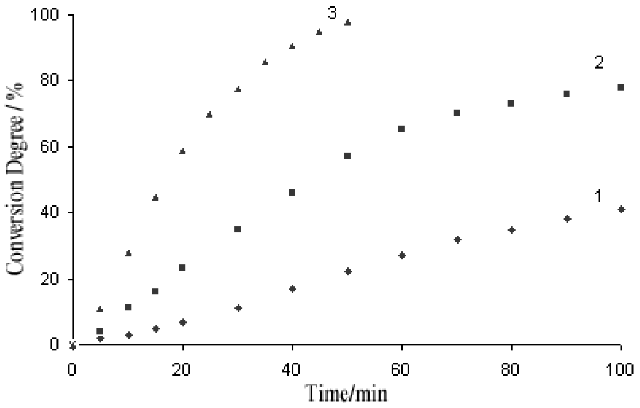


FIGURE 2. The dependence of the rate of polymerization for 4-(benzylamino)styrene hydrochloride on the temperature in nitrobenzene: [M] = 2 moles; 1) at 30 °C; 2) at 40 °C; 3) at 50 °C

However, the polymerization of 4-(benzylamino)styrene hydrochloride and/or hydrobromide in nitrobenzene at the temperature of 40 °C with monomer concentration [M] of 2 moles (Fig. 3), showed that the polymerization rate of hydrochloride monomer is higher than that of hydrobromide. This may be attributed to the higher electronegativity of the chlorine atom.

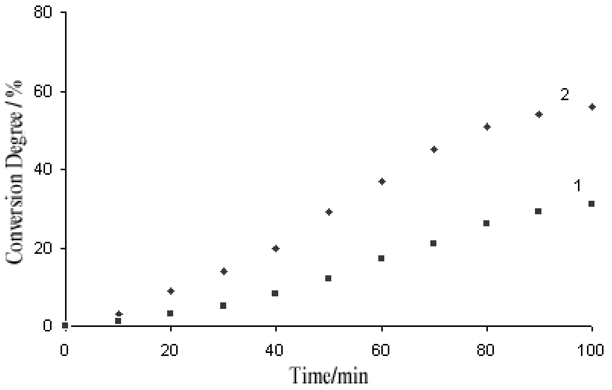
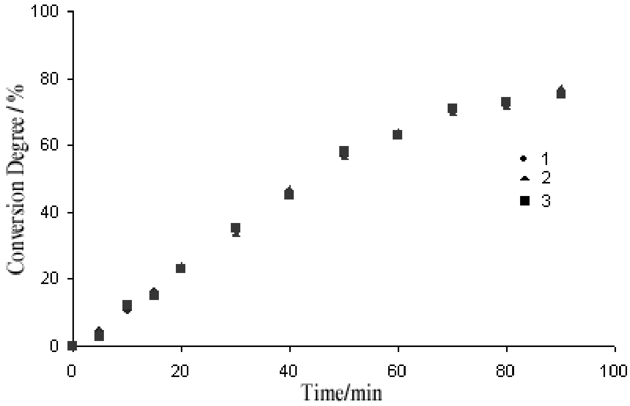
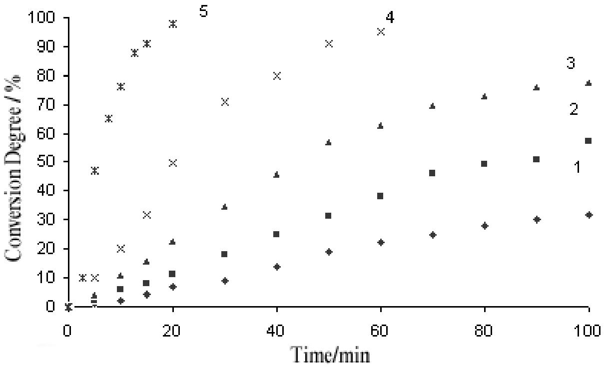


FIGURE 3. The dependence of the rate of polymerization for 4-(benzylamino)styrene hydrochloride on the nature of halogen atom in benzene: [M] = 2 moles. 1) hydrobromide monomer; 2) hydrochloride monomer; polymerization temperature 40 °C



On the other hand, investigation revealed that no variation in the rate of reaction was observed by the substituents on the benzyl moiety (Fig. 4).

FIGURE 4. Polymerization of 4-(benzylamino)styrene hydrochloride and some of its substituents in nitrobenzene: [M] = 2 moles;
1) 4-(benzylamino)styrene hydrochloride;
2) 4-(*p*-methoxybenzylamino)styrene hydrochloride;
3) 4-(*p*-nitrobenzylamino)styrene hydrochloride; polymerization temperature 40 °C



In the light of the above experimental facts, it is found that the concentration of the monomer is proportionally related to the rate of the reaction (Fig. 5).

FIGURE 5. The dependence of the rate of polymerization of 4-(benzylamino)styrene hydrochloride on the monomer concentration in nitrobenzene: 1) 1 mole; 2) 1.5 moles; 3) 2 moles; 4) 2.5 moles; 5) 3 moles; polymerization temperature 40 C

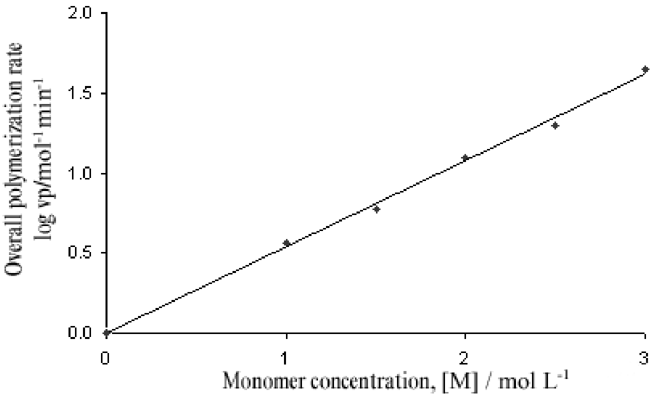


FIGURE 6. The dependence of the overall polymerization rate v_p in mol^{-1} min^{-1} of 4-(benzylamino)styrene salts on the monomer concentration [M] in mol L^{-1}. Polymerization temperature 40 C.

From studying the effect of monomer concentration on the rates of polymerization (as shown in Figure 6), it was confirmed that the overall rate of polymerization (v_p) correlated with monomer concentration, where the logarithm of the polymerization rates were plotted against the monomer concentration. All points lie on a single straight line, the slope of which is 0.51. This leads to a specific relationship between the overall polymerization rate (v_p) and the initial monomer concentration of $v_p[M]^{0.51}$.

Finally, the bove results showed that the rate of polymerization of 4-(benzylamino)styrene salts increases with an increase of the polarity of the solvent with the polymerization temperature depending on the nature of the halogen atom but with no significant effect of the substituents in benzyl moiety on the rate of polymerization.

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Acknowledgment / Zahvala

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