

Synthesis of poly(thioarylenes): nucleophilic displacement polymerization between dihaloarylenes and potassium thioacetate

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Abstract

The potential of potassium thioacetate as a new sulfur reagent in the nucleophilic displacement polymerization of aromatic haloaromatic compounds was investigated. Aromatic halogen compounds underwent nucleophilic substitution and formed the corresponding aryl sulfides in good yields. The reaction pathways were studied with the help of model compounds using ¹³C NMR spectroscopy. A three-step process with the formation of *S*-aryl thioacetate and thiolate as intermediates is put forward. The effective use of the reagent in polythioarylene synthesis was explored. Polythioetherketones, polythioethersulfones and poly(thio-1,4-phenylene) were prepared in good yields. Potassium thioacetate seems to be a milder sulfur nucleophile as compared to the conventional alkali sulfides which usually yield higher molar mass compounds. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(thioarylenes); Nucleophilic displacement; Potassium thioacetate

1. Introduction

Amongst engineering thermoplastic polymers, polythioarylenes occupy a prominent position and have found expanded applications in the electronic, automotive and aerospace industries due to their better retention of mechanical properties under harsh operating conditions [1,2]. Though several new synthetic methods have been developed recently [3–7], the commercial production of poly(thio-1,4-phenylene), (PPS), an important polymer in the class of polythioarylenes, is based on the polycondensation of dichloroaromatic compounds with sodium sulfide in *N*-methylpyrrolidinone (NMP) at high temperature [8]. From a study on model compounds, Fahey et al. [9] have concluded that the active reagent taking part in the PPS synthesis is a soluble product formed by the hydrolytic cleavage of NMP with hydrated sodium sulphide, noted “SMAB–NaSH”, where SMAB is the sodium salt of *N*-methyl-4-aminobutanoic acid. The exact structure of this compound remains unknown. It is remarkable that “SMAB–NaSH” also satisfy the same empirical formula as sodium *N*-methyl-4-aminothiobutanoate–NaOH. However, the presence of thiocarboxylates in reaction medium has never been investigated. Thioacetates or thiolacetic acid

are known to be efficient reagents for the nucleophilic substitution of acyclic and aliphatic halogens under basic conditions in NMP, yielding thio substituted products in good yields [10,11]. The reaction proceeds with the formation of a thioester, followed by subsequent hydrolysis yielding the thio product. We have adopted the same reaction methodology to replace aromatic halogens, to generate aryl sulfides. In the present article, we report the aromatic nucleophilic substitution of a model aryl halide with potassium thioacetate. We have further extended this methodology to synthesize polythioarylenes.

2. Experimental part

2.1. Chemicals

Potassium thioacetate was obtained from Fluka. 4-Chlorobenzophenone, 4,4'-dichloro benzophenone, 1,4-dichlorobenzene, 1,4-dibromobenzene and bis(4-chlorophenyl) sulfone were obtained from Aldrich. *N*-methylpyrrolidinone (NMP), dimethylsulfoxide (DMSO), *N*-cyclohexylpyrrolidinone (NCP) and methanol were obtained from Carlo Erba. Potassium hydroxide and acetic anhydride were from Prolabo. All chemicals were used as received.

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Table 1

Synthesis of poly(thio-1,4-phenylene-carbonyl-1,4-phenylene) at 200°C in NMP. Influence of the stoichiometric ratio of reactants on the yield, melting point (T_m) and inherent viscosity (η_{inh}) of resulting polymers

Polymer	Potassium thioacetate	4,4'-Dichloro benzophenone	KOH	Yield (%)	T_m^a (°C)	η_{inh}^b (dl/g)
P1	1.00	1.00	2.50	87	333	0.15
P2	1.00	1.00	1.50	92	327	0.13
P3	1.00	1.05	1.50	96	317	0.085
P4	1.00	0.95	1.50	96	331	0.15
P5	1.00	1.00	2.00	92	332	0.17
P6 ^c	1.00	1.00	2.00	98	325	0.12
P7 ^d	1.00	1.00	2.00	88	309	0.046

^a Determined by DSC at a scan rate of 20°C/min.

^b Determined using 0.1 g/dl solution in H₂SO₄ at 30°C.

^c K₂CO₃ was used instead of KOH.

^d Reaction carried out at 160°C.

2.2. Model reactions between 4-chlorobenzophenone and potassium thioacetate

2.2.1. Stoichiometric reaction

4-Chlorobenzophenone (0.867 g, 4 mmol), 0.228 g (2 mmol) potassium thioacetate, 0.23 g (4 mmol) KOH and 10 ml NMP were placed in a 25 ml cylindrical glass pressure reactor. The reactor was closed under argon atmosphere and immersed in a oil bath at 180°C. The reaction was continued for 2 h under magnetic stirring. After cooling, the reaction mixture was poured in water, the precipitated 4,4'-thiodibenzophenone was filtered, washed with water, recrystallized from ethanol and dried at 50°C under vacuum. Yield: 86%; m.p.: 168°C (lit. [12]: 168.8°C).

¹³C NMR (62.9 MHz, CDCl₃, Ref. TMS): δ (ppm) 195.5, 140.2, 137.1, 136.2, 132.4, 130.8, 130.2, 129.7, 128.2.

To study the kinetics of the reaction, the same procedure was followed using various reaction times. The reaction medium samples were diluted with the same volume of NMP and the ¹³C NMR spectra recorded using external d₆-DMSO for deuterium lock.

2.2.2. Reaction with potassium thioacetate excess

4-Chlorobenzophenone (0.433 g, 2 mmol), 1.14 g (10 mmol) potassium thioacetate, 0.23 g (4 mmol) KOH and 15 ml NMP were reacted as above for 15 min. After cooling, the reaction mixture was poured into water. The medium was filtered, and the filtrate acidified to pH = 3 with diluted HCl. The precipitate of 4-mercaptobenzophenone was filtered, washed with water, recrystallized from ethanol/water and dried at 50°C under vacuum. Yield: 27%; m.p.: 79°C (lit [12]: 79.6°C).

¹³C NMR (62.9 MHz, CDCl₃, Ref. TMS): δ (ppm) 127.8, 128.1, 129.7, 130.7, 132.2, 134.2, 137.4, 138.0, 195.5.

2.3. S-(4-benzoylphenyl) thioacetate

4-Mercaptobenzophenone (0.5 g) prepared following Ref. [12] and 5 ml acetic anhydride were refluxed for 5 min. After cooling, the solution was poured into 100 ml

water. The medium was extracted with 20 ml chloroform, the extract washed three times with water and dried over MgSO₄. After evaporation of chloroform, a colorless oil was obtained. Yield: 90%.

Elemental analysis, calculated for C₁₅H₁₂O₂S (256.3): C 70.29, H 4.72, S 12.51. Found: C 70.35, H 4.65, S 12.24.

¹³C NMR (62.9 MHz, NMP, external d₆-DMSO, Ref. TMS): δ (ppm) 194.4, 191.5, 137.2, 136.4, 133.5, 132.7, 132.3, 129.6, 129.1, 128.1, 29.5 (overlapping with NMP).

2.4. Poly(thio-1,4-phenylene-carbonyl-1,4-phenylene) (PTEK)

4,4'-Dichlorobenzophenone (0.908 g, 3.616 mmol), 0.413 g (3.616 mmol) potassium thioacetate, 0.406 g (7.232 mmol) KOH and 9 ml NMP were taken in a 25 ml cylindrical glass pressure reactor. The reactor was closed under nitrogen atmosphere and immersed in a molten salt bath at 200°C for 4 h, under magnetic stirring. After cooling the polymer was precipitated by pouring the reaction mixture into methanol. The polymer was filtered out, washed with methanol and hot acetone and dried at 100°C under vacuum. Characterization: see Table 1.

Elemental analysis, calculated for (C₁₃H₈OS)_n (212.3n): C 73.56 H 3.80 S 15.10. Found: C 72.13 H 3.80 S 14.78 Cl 1.15.

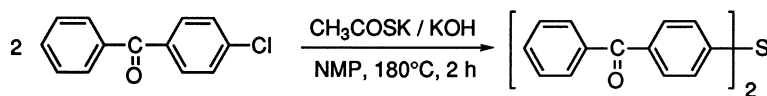
IR (KBr pellet) strong absorptions at: 1654, 1588, 1397, 1310, 1283, 1100, 927, 752 cm⁻¹.

2.5. Poly(thio-1,4-phenylene-sulfonyl-1,4-phenylene) (PTES)

The same procedure as above was adopted, using bis (4-chlorophenyl)sulfone as aromatic chloro monomer.

Elemental analysis, calculated for (C₁₂H₈O₂S₂)_n (248.3n): C 58.04, H 3.25, S 25.82. Found: C 57.78, H 3.35, S 25.42, Cl 0.45.

IR (KBr pellet) strong absorptions at: 1575, 1478, 1394, 1322, 1158, 1109, 1075, 1012, 705, 634, 630, 585 cm⁻¹.



Scheme 1.

2.6. Poly(thio-1,4-phenylene) (PPS)

Poly(thio-1,4-phenylene) was synthesized from 1,4-dibromo- or 1,4-dichlorobenzene. NMP was used for the reactions carried out at 200°C, whereas *N*-cyclohexyl pyrrolidinone (NCP) was used for higher temperatures. In a typical reaction, 0.735 g (5.00 mmol) 1,4-dichlorobenzene, 0.571 g (5.00 mmol) potassium thioacetate, 0.561 g (10.00 mmol) KOH and 12.5 ml NCP were taken in a 25 ml cylindrical glass pressure reactor. The reactor was closed under nitrogen atmosphere and immersed in a molten salt bath at 180°C under magnetic stirring. After 1 h reaction, the temperature of the bath was increased to 250°C and the reaction continued for further 5 h. After cooling, the polymer was precipitated by pouring the reaction mixture into cold methanol, filtered out, washed with methanol and hot acetone and dried under vacuum.

Elemental analysis, calculated for $(C_6H_4S)_n$ (108.2*n*): C 66.63, H 3.73, S 29.64. Found: C 66.05, H 3.65, S 29.05, Cl 1.50.

IR (KBr pellet) strong absorptions at: 1467, 1387, 1094, 1010, 815, 690, 555, 479 cm^{-1} .

2.7. Measurements

Infrared spectra were recorded in KBr discs using a Bruker IFS-45 instrument.

DSC measurements were carried out on a TA Instruments 9900 apparatus equipped with DSC910 module at a heating rate of 20°C/min under nitrogen. Melting points were taken at the maximum of the melting endotherm and glass transition temperatures at the mid-point of baseline shift. 1H and ^{13}C NMR analyses were carried out using a Bruker ARX 250 instrument. Tetramethylsilane (TMS) was used as the reference. The spectra of monomers and model compounds were recorded in $CDCl_3$ solutions. For the spectra of reaction mixtures, a capillary with d_6 -DMSO was placed in the NMR tube. For comparison purposes, the spectra of some model compounds were also recorded in NMP in these conditions. $^{13}C\{^1H\}$ decoupling, spin-echo, heteronuclear ^{13}C - 1H selective decoupling and homonuclear 1H - 1H selective decoupling experiments were carried out for the assignments of resonances. Inherent viscosities of PTEK and PTES samples were measured at 30°C from 0.1 g/dl solutions, respectively, in 95% H_2SO_4 and in NMP, using a Schott Geräte automatic viscosimeter with a Canon Ubbelohde Nr. 1c microviscosimeter. For PPS, 1-chloronaphthalene solutions (0.1 g/dl) at 190°C and a modified viscosimeter [15] were used. PPS molar mass was estimated using the relations given in Refs. [16,17].

3. Results and discussion

Model compound studies were carried out with 4-chlorobenzophenone and potassium thioacetate to investigate the feasibility of the reaction. The stoichiometric reaction between potassium thioacetate and 4-chlorobenzophenone in DMSO or NMP (1:2 molar ratio) in the presence of a base gave 4,4'-thiodibenzophenone in yields comparable to those reported for the stoichiometric reaction between lithium sulfide and 4-chlorobenzophenone [12] (Scheme 1).

Sulfide or hydrogenosulfide ions are well known nucleophiles and can readily react with aryl chlorides. To check whether potassium thioacetate can react with potassium hydroxide and yield potassium hydrogenosulfide and potassium acetate, a mixture of CH_3COSK and KOH in NMP was heated to 180°C for 2 h. The ^{13}C NMR spectrum of the final reaction mixture did not show any characteristic resonance related to potassium acetate. This indicates that the reaction path does not involve a simple formation of sulfide or hydrogenosulfide ions from potassium thioacetate in basic medium.

The ^{13}C NMR spectra of 4-chlorobenzophenone/potassium thioacetate/KOH stoichiometric reaction mixture (2:1:2 molar ratio) were recorded at various reaction times. The spectra given in Fig. 1 show the gradual consumption of starting 4-chlorobenzophenone, and the formation of 4,4'-thiodibenzophenone, which is almost quantitative after 2 h of reaction. The resonances of CH_3COSK at 38 and 214 ppm also disappear and are replaced by resonances of potassium acetate at 22 and 177 ppm. When the reaction was carried out with a great excess of potassium thioacetate, the reaction proceeded to the formation of 4-mercaptobenzophenone potassium salt, identified by isolating 4-mercaptobenzophenone from reaction medium after acidification. A possible reaction scheme could, therefore, be written as: (1) nucleophilic aromatic substitution of chloride by thioacetate, (2) cleavage of the thiolester by potassium hydroxide to form the corresponding potassium thiolate, and (3) reaction of this nucleophile with 4-chloro benzophenone (Scheme 2).

The kinetics of the reaction corresponding to step 3 has already been studied [12]. At 180°C, the reaction is very fast. Starting from an equimolar amount of reactants, conversion should reach 95% after only 3 min reaction in the present experimental conditions. This is much more rapid than observed in the present case: It can be seen from Fig. 1 that conversion is only ca. 50% after 30 min reaction. It is, therefore, clear that step 3 is not the limiting step of the process. *S*-(4-benzoylphenyl) thioacetate was

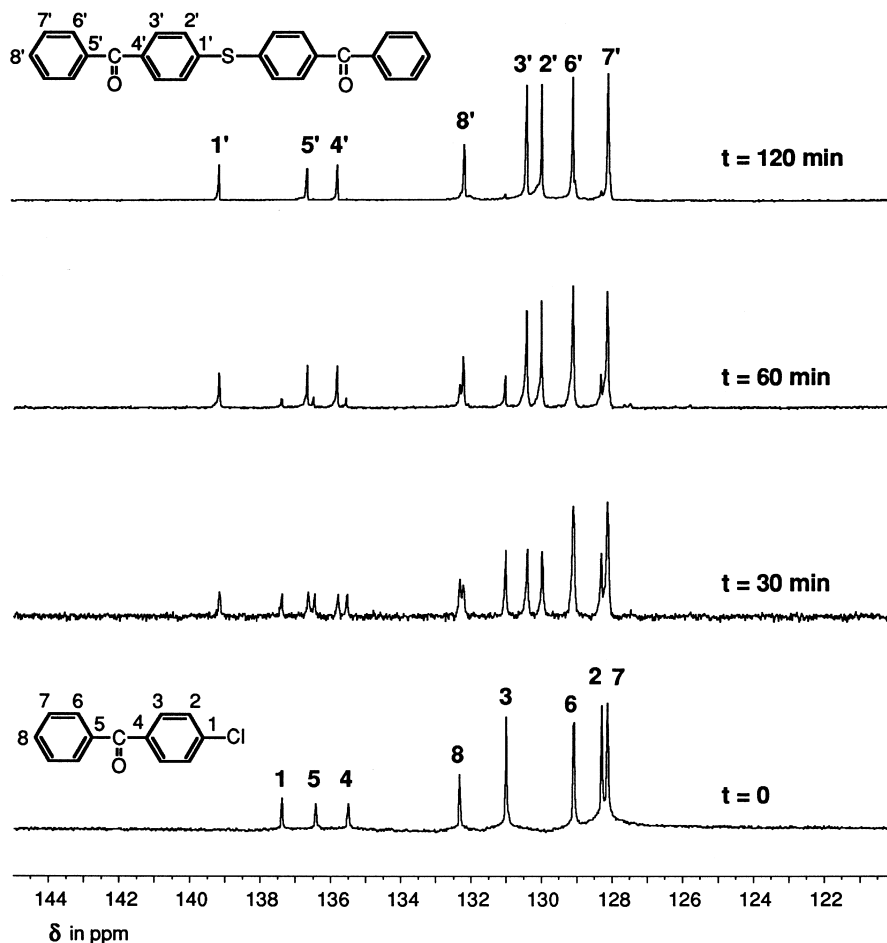


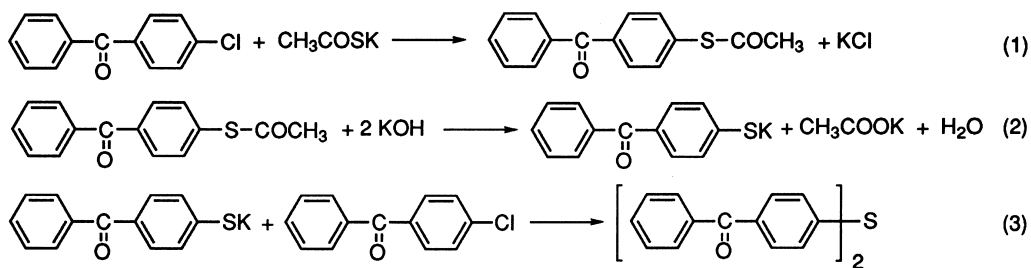
Fig. 1. Model reaction between 4-chlorobenzophenone and potassium thioacetate (2:1 molar ratio) in NMP at 180°C: ^{13}C NMR spectra (62.9 MHz, external $\text{d}_6\text{-DMSO}$, Ref. TMS) of reaction medium at various reaction times.

synthesized to study the reaction corresponding to step 2. After only 15 s heating in NMP/KOH at 180°C, the characteristic ^{13}C NMR peaks of the thioacetate were replaced by those of the corresponding thiolate, showing the very low stability of the ArS-CO bond in basic medium. It must be underlined that the ArS-CO bond cleavage in basic medium has also been reported by Petrillo et al. [13] during the cyclic voltammetry study of *S*-arylthioesters and by Ding et al. [14] during the synthesis of polythioarylenes using carbamate protected thiophenols. The limiting step of the process is, therefore, the nucleophilic substitution of

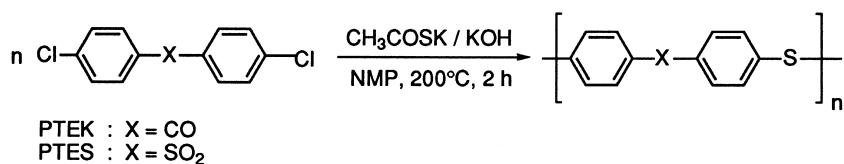
chlorine by thioacetate (reaction 1). As soon as they are formed, the intermediate thiolester and thiolate are consumed through reactions 2 and 3. This explains why their resonances cannot be detected in the spectra of Fig. 1.

3.1. Poly(thio-1,4-phenylene-carbonyl-1,4-phenylene) (PTEK)

When 4,4'-dichlorobenzophenone was reacted with potassium thioacetate in the reaction conditions described above (Scheme 3), polythioetherketones were obtained in



Scheme 2.



Scheme 3.

Table 2

Synthesis of poly(thio-1,4-phenylene-carbonyl-1,4-phenylene) (PTEK), poly(thio-1,4-phenylene-sulfonyl-1,4-phenylene) (PTES) and poly(thio-1,4-phenylene) (PPS) using potassium thioacetate as sulfur nucleophile. Yield, melting point (T_m), glass transition temperature (T_g) and inherent viscosity (η_{inh}) of final polymers.

Polymer	Yield (%)	T_m^a (°C)	T_g^a (°C)	η_{inh} (dl/g)
PTEK ^b	92	332	–	0.17 ^c
PTES ^b	97	–	211	0.15 ^d
PPS-1 ^e	53	253 ^f	76	0.09 ^g
PPS-2 ^h	56	262 ^f	81	0.11 ^g

^a Determined by DSC at a scan rate of 20°C/min.

^b Reaction carried out at 200°C in NMP.

yields comparable to those reported for the conventional synthesis [18]. T_m and inherent viscosities (Table 1) were lower than those reported for these conventional synthesis carried out at 200°C (335–345°C and 0.23–0.50 dl/g) [18,19], indicating somewhat lower molar masses. The infrared spectra of the polymers exhibited the characteristic peaks of aromatic polythioetherketones. The stoichiometric amount of base between 1.5 and 2.5 molar ratio do not have a critical influence on yields and viscosities. However, the reaction failed when it was carried out without any base. As expected for a polycondensation process, the best results were obtained using stoichiometric balance of reactants and base, while a slight excess of dichloro monomer yielded a polymer with lower viscosity value. A lower reaction temperature did not affect the yield of the polymer but affected considerably the molar mass as reflected by the decrease in T_m and and viscosity. This is understood as (i) premature precipitation of low molar mass polymers may occur at lower temperature and (ii) reaction kinetics is obviously slower. Since alkali carbonates have been used

to generate thiophenoxide ion from masked aryl thiols, [14] the reaction was also carried out in the presence of potassium carbonate. Inherent viscosity was in the same range as obtained in the presence of potassium hydroxide (Table 1).

3.2. Poly(thio-1,4-phenylene-sulfonyl-1,4-phenylene) (PTES)

Aromatic polythioethersulfone (PTES) was obtained in 97% yield, when the reaction was carried out in NMP, with bis(4-chlorophenyl)sulfone as a monomer and potassium thioacetate as a sulfur source (Scheme 3, Table 2). The ¹³C NMR spectrum of the polymer (Fig. 2) corresponds to the expected one, and does not show any characteristic resonance relative to C–Cl (139 ppm) end-groups.

3.3. Poly(thio-1,4-phenylene) (PPS)

Similarly the reaction between 1,4-dichlorobenzene and potassium thioacetate was carried out in the same conditions to synthesize poly(thio-1,4-phenylene) (PPS). The reaction did not yield any polymer at 180 or 200°C. At higher temperature, 250°C in *N*-cyclohexopyrrolidinone, PPS was obtained (Table 2). The polymer showed a melting point, 253°C, lower than that of commercial PPS (T_m = 285°C). Using the more reactive 1,4-dibromobenzene as starting monomer, PPS was obtained with slightly higher T_m and viscosity. From the viscosity data, however, the estimated molar mass is only ca. 10 000.

4. Conclusion

Potassium thioacetate was successfully used for the nucleophilic substitution polymerization of aromatic dihalogen compounds. PPS, polythioetherketones or

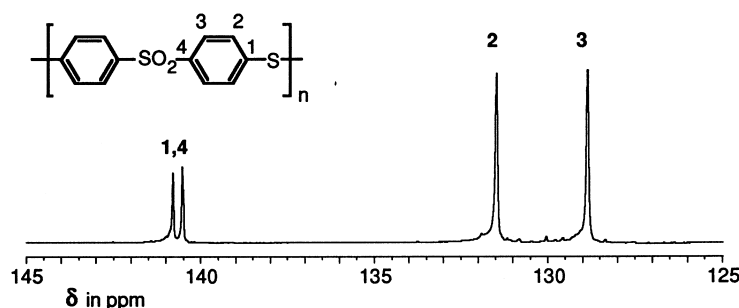
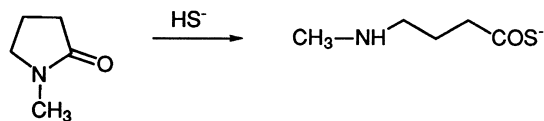


Fig. 2. ¹³C NMR spectrum (62.9 MHz, NMP, external d₆-DMSO, Ref. TMS) of poly(thio-1,4-phenylene-sulfonyl-1,4-phenylene) (PTES).



Scheme 4.

polythioethersulfones were synthesized in very good yields by reacting this nucleophile with 1,4-dichloro- or 1,4-dibromobenzene, 4,4'-dichlorobenzophenone and bis(4-chlorophenyl)sulfone. The reactivity of thioacetate seems, however, to be lower than that of the sodium sulfide/NMP reagent used in the conventional syntheses, since polymers of lower molar mass were obtained. The proposed reaction pathway (Scheme 2) involves the nucleophilic substitution of chloride by thioacetate, followed by the cleavage of the *S*-aryl thioester bond by KOH resulting in the formation of aryl thiolate. The limiting step of the process seems to be the nucleophilic substitution step.

The results presented here indicate that thiocarboxylic acid salts can be used as sulfur nucleophiles in the polythioetherification reactions of dihaloaryl monomers, such as chlorobenzophenones or chloroarylsulfones, or of their mixtures.

The results also give some indications on the reactions which may take place during the conventional PPS synthesis. During this synthesis, it is known that NMP is hydrolytically cleaved to sodium *N*-methylaminobutanoate by reaction with hydroxide ion [9]. NMP may react with hydrogensulfide ions as well, leading to the formation of sodium *N*-methylaminothiobutanoate (Scheme 4). This thiocarboxylate could be involved in the synthetic pathway through a reaction similar to the one studied here.

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