

Synthesis and basic characterization of a macromolecular dibromoamine: *N,N*-dibromo-poly(styrene-*co*-divinylbenzene)sulfonamide

Romuald Bogoczek* and Elżbieta Kociolek-Balawejder

Institute of Chemical and Food Industry Technology, Academy of Economics, ul. Komandorska 118/120, 53-345 Wrocław, Poland
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A macromolecular-pendent-group *N,N*-dibromosulfonamide ($[P]-SO_2NBr_2$) having a macroporous styrene-divinylbenzene matrix structure has been obtained by three methods: by the action of (a) bromine in aqueous medium and (b) aqueous metal hypobromites in acidic medium, on the appropriate macromolecular-pendent-group sulfonamide, and by (c) the action of an aqueous metal bromide on the appropriate macromolecular *N,N*-dichlorosulfonamide. In the best case the product was obtained with nearly 100% functional yield and it contained $2.4 \text{ mmol g}^{-1} -SO_2NBr_2$ groups, i.e. ca. 0.38 g g^{-1} of active bromine. The stability of the resin was investigated in the range 20–100°C in the dry state as well as in aqueous media. Thermoanalysis (thermogravimetric, differential thermogravimetric and differential thermal analysis curves) was carried out up to 1000°C and its course was interpreted. The resin has brominating, oxidative and microbiocidal properties. It reacts in a reversible way: after loss of the active bromine, it can be reactivated again.

(Keywords: functionalized derivative; styrene-divinylbenzene; polymeric dibrominated sulfonamide; copolymeric brominating and oxidating agent; microbiocidal agent; reactive polymer)

INTRODUCTION

In a previous communication¹ we have described a new class of reactive macromolecular materials, i.e. reactive polymers or polymer-supported reagents, that are styrene-divinylbenzene copolymers and contain pendent *N*-monohalogeno and *N,N*-dihalogeno functional groups, where the halogen is Cl, Br or I. In separate papers we have reported on copolymers with *N*-monochlorosulfonamide groups², *N*-monobromosulfonamide groups³ and *N*-monoiodosulfonamide groups⁴, as well as with *N,N*-dichlorosulfonamide groups⁵. Although polymers and copolymers have been chemically modified to incorporate active halogens^{6,7}, only a few papers have dealt with polymeric sulfonamide halogen derivatives. Among them are the excellent works of Emerson^{8–10}, which are the closest to this paper. A recent paper concerning the preparation of monohalogenosulfonamides should also be mentioned¹¹.

This paper describes the successful results of sulfonamide dibromination as well as the product's properties and applications.

EXPERIMENTAL

Chemicals

A macromolecular sulfonamide (SA) comprising a macroporous styrene-divinylbenzene (80:20) copolymer (poly(*St-co-DVB*)) with $3.9 \text{ mmol g}^{-1} -SO_2NH_2$ and

$0.3 \text{ mmol g}^{-1} -SO_3H$ functional groups, obtained from a chlorosulfonyl copolymer¹² and ammonia, and a macroporous poly(*St-co-DVB*) SO_2NCl_2 resin with $2.75 \text{ mmol g}^{-1} -SO_2NCl_2$ and $0.25 \text{ mmol g}^{-1} -SO_3H$ functional groups were used.

Bromine was a practical-grade reagent.

Sodium, potassium and calcium hypobromite (1 M aq.) were obtained by reacting bromine with equivalent sodium, potassium or calcium hydroxide solution or suspension. An equimolar mixture of MOBr and MBr was the result, and this was used for reaction.

Sodium, potassium and calcium bromides were practical-grade reagents.

Synthesis of *N,N*-dibromo-poly(*St-co-DVB*)sulfonamide

Method A. The poly(*St-co-DVB*) SO_2NH_2 resin (5 g) was placed in water (100 cm³) and stirred while bromine was dropped in (1.50 cm³), causing a temperature increase from –5 to 20°C. After an initial period where the bromine was completely consumed by the resin, it finally remained in the solution as an excess as shown by the colour and oxidative reaction of the supernatant solution. Then the resin was filtered, water-washed and air-dried in the dark (8.1 g). Finally, the resin itself was analysed.

Method B. The poly(*St-co-DVB*) SO_2NH_2 resin (2 g) was placed in a 0.1–1.0 M aqueous hypobromite solution (400–40 cm³). The course of the reaction was followed by iodometric microtitration of the solution. When the reaction stopped, glacial acetic acid was added to the

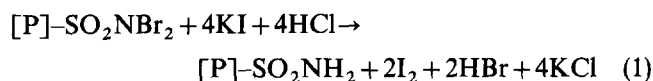
*To whom correspondence should be addressed

solution (5 cm³), after which a second bromination reaction followed, again controlled by titration. At both reaction steps a temperature increase from -5 to 20°C was observed. Then the resin was filtered, water-washed and air-dried in the dark; the resin was then analysed.

Method C. The poly(*St-co-DVB*)SO₂NCl₂ resin (1 g) was placed in 0.1–1.0 M aq. bromide solution (200–20 cm³) and was mixed at room temperature. The course of reaction was followed by bromide and chloride determination in the liquid phase by titration. When the reaction was finished, the resin was filtered, water-washed and air-dried in the dark.

The determination of active and overall bromine in the resins

The total bromine and chlorine content in the resin was determined as bromide and chloride after the resin was mineralized with Eschka mixture at 800°C, using AgX ion-selective electrodes. The active bromine and chlorine were determined by titration of the iodine generated in the following reaction:



where [P] stands for the crosslinked poly(*St-co-DVB*) matrix. A resin sample (0.3–0.5 g) was placed in 3 M HCl (50 cm³) and potassium iodide (4 g). After 24 h the liberated iodine was titrated by means of 0.1 N sodium thiosulfate solution.

I.r. spectra

The infra-red spectra of dibromosulfonamide or other related resins on KBr pellets were taken with a Perkin-Elmer 621 spectrophotometer.

Stability of the resins

Stability of the resin in its dry state was determined by storing a certain amount of the resin either in a closed orange vessel, in an open glass dish in the dark, or in a hot-box at 100°C. Stability in the wet state was examined by storing a certain amount of the resin in aqueous media in the range 20–100°C. Samples (1 g) were placed in water or in 1 M NaBr, 1 M NaOH or 1 M H₂SO₄ (50 cm³). The active bromine was determined after the set times shown in Table 2 had passed.

Thermoanalytical studies

The thermoanalytical curves were determined by the use of a Derivatograph OD-102 produced by MOM Budapest, Hungary. A sample (0.2 g) of the resin was heated at a heating rate of 10 K min⁻¹ in air (reference standard Al₂O₃).

Brominating properties of the resins

A resin sample (1 g) was placed in 0.1 M aqueous phenol solution (50 cm³) and stirred. After 24 h the products present in solution as well as the resin itself were qualitatively and quantitatively estimated. Gravimetry, titrimetry and paper and thin-layer chromatography were used.

Iodination by means of the resins

A resin sample (1 g) was placed in an aqueous solution,

which comprised 0.1 M phenol and 0.4 M potassium iodide solution (50 cm³). Qualitative and quantitative assays followed as described above.

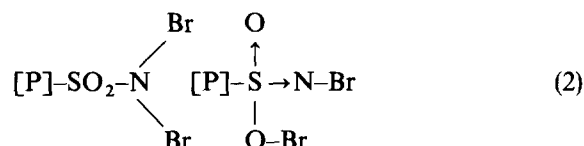
Oxidative properties of the resins

A resin sample (1 g) was placed in an aqueous solution (50 cm³) of 0.1 N FeCl₂ or Na₂SO₃, or in ascorbic acid, glucose or other species like cyanides or rhodanides. Time-dependent determinations of the solution composition were made.

RESULTS AND DISCUSSION

Synthesis of resins

The macroporous chemically active styrene-divinylbenzene (80:20) copolymer or 'polymer reagent' described in this paper consists of the following functional groups:



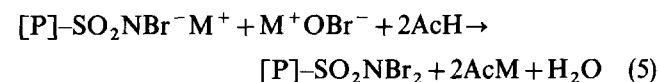
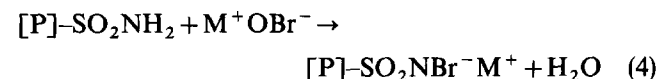
The nitrogen and bromine atoms are covalently bound within the group. The bromine atoms are of oxidation number +1. We believe that the bromosulfonamide groups in this macromolecular compound appear in the two given tautomeric forms. A discussion of this question will be given in a separate paper.

The macromolecular reagent described was obtained by the following reactions:

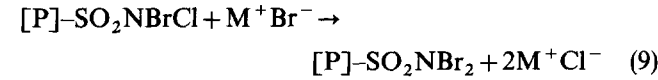
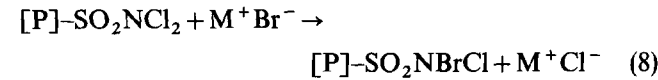
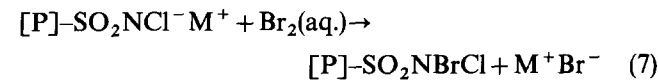
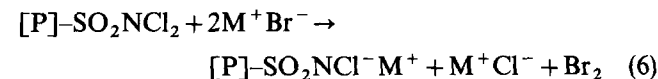
First method



Second method



Third method



Here M⁺ stands for sodium, potassium or equivalent of calcium cations. Reactions (3), (4) and (5) are analogous to reactions known from low-molecular-weight compounds: *p*-toluenesulfonamide under the influence of bromine or sodium hypobromite in acidic medium yields *N,N*-dibromo-*p*-toluenesulfonamide, the so called 'dibromoamine T'.

The first method is best carried out at 5°C using a 50% excess of bromine, dispersing the SA resin in such

Table 1 Macromolecular dibromoamine preparation

Macromolecular raw material	Brominating agent (mol ratio)	[Br] (mol dm ⁻³)	Reaction		Composition of final product		
			Temp. (°C)	Time (h)	Overall bromine (g g ⁻¹)	SO ₂ NBr ₂ (mmol g ⁻¹) ^a	
[P]-SO ₂ NH ₂ (SA)	Br ₂	(residual)					
		1:2.2	0.1	-5	2.5	0.30	1.90
		1:2.2	0.5	-5	2.0	0.35	2.10
		1:2.2	1.0	-5	1.5	0.37	2.20
		1:3.0	0.1	0	1.0	0.40	2.20
		1:3.0	0.1	5	0.8	0.42	2.40
	1:3.0	0.1	20	0.5	0.48	2.30	
[P]-SO ₂ NH ₂ (SA)	MOBr + MBr ^b + AcOH	(initial)					
		1:2.2	0.1	-5	2.0	0.34	2.05
		1:2.2	0.5	0	1.8	0.36	2.10
		1:2.2	1.0	10	1.5	0.39	2.20
		1:3.0	0.1	15	1.1	0.41	2.30
		1:3.0	0.5	15	0.8	0.43	2.40
	1:3.0	0.5	20	0.5	0.48	2.35	
[P]-SO ₂ NCl ₂ (DCh)	MBr	(initial)					
		1:4.0	0.1	-5	6.0	0.29	1.90 ^c
		1:4.0	0.2	18	3.0	0.31	1.95 ^c
		1:4.0	0.5	10	1.2	0.33	2.00 ^c
		1:4.0	1.0	20	0.9	0.32	2.00 ^c
		1:6.0	1.0	18	1.0	0.32	2.00 ^c
		1:8.0	1.0	18	1.0	0.32	2.00 ^c
	1:12.0	1.0	18	1.0	0.34	2.10 ^c	

^a Max. value is SA-dependent, here 2.41 mmol SO₂NBr₂/g of dry resin

^b M means Na, K or Ca

^c In addition, some -SO₂NBrCl as well as -SO₂NBrNa groups are present in the product

an amount of water that the residual unreacted bromine forms at least a 0.1 M solution. The reaction comes to an end within 50 min. The product obtained, the macromolecular 'dibromoamine', contains 2.4 mmol g⁻¹ *N,N*-dibromosulfonamide groups (i.e. 4.8 mmol of [+1] bromine), and 0.42 g g⁻¹ of overall bromine (i.e. 5.26 mmol of [+1, 0, -1] bromine). This means that about 0.04 g bromine (i.e. 0.50 mmol) per gram of resin is not active (is not in the [+1] state); it is carbon-bound (Table 1).

The second method based on reactions (4) and (5) is best carried out at 15°C using a 50% excess of bromine, and its initial concentration should not be lower than 0.5 mol dm⁻³. The reaction is completed within 50 min. The copolymeric product contains 2.40 mmol -SO₂NBr₂ groups and 0.43 g (5.38 mmol) of overall bromine per gram. Circa 0.05 g Br (0.62 mmol) per gram of resin is carbon-bound.

The third method based on reactions (6), (7), (8) and (9), which are new reactions, not described earlier, is best carried out at room temperature, using 4 mol of a water-soluble bromide to 1 mmol of the polymeric dichlorosulfonamide, with an initial bromide concentration slightly above 0.5 mol dm⁻³. The product has 2.00 mmol of -SO₂NBr₂ per gram of resin and the overall bromine is 0.34 g per gram of resin. Nearly all of this is active. Moreover, 1 g of the resin contains ca. 0.45 mmol inactive, i.e. carbon-bound, chlorine. A certain amount of *N*-bromo-*N*-chlorosulfonamide groups as well as *N*-monohalogenosulfonamide groups has been assumed too in that product.

Reactions (6), (7), (8) and (9) are interface redox reactions. They depend upon the action of the bromide anion on the polymer-bound *N*-chlorosulfonamide group, where the [+1] chlorine atom enters into solution in the form of chloride anion and the bromide anion combines with the resin phase as a [+1] atom.

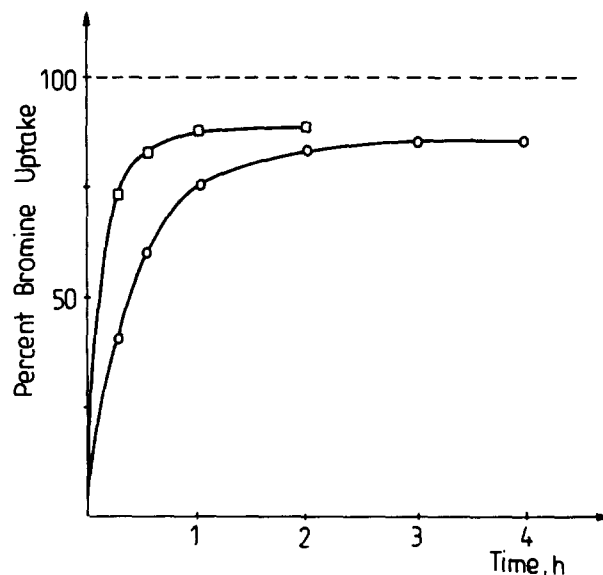


Figure 1 Reaction of the *N,N*-dichlorosulfonamide copolymer (1 g) with an excess of aqueous NaBr solution (100 cm³) at 20°C: (□) 1 M NaBr, (○) 0.1 M NaBr

The conversion of the *N,N*-dichloro group to the *N,N*-dibromo group at room temperature is rather fast, with reaction yields higher than 80% (Figure 1). It is concentration-dependent. It was interesting to find out the lowest concentration of bromide anions capable of achieving this transformation. So we mixed a stoichiometrically insufficient amount of bromide with the *N,N*-dichloro-poly(*St-co-DVB*)sulfonamide (1 g of resin, 50 cm³ of 0.05 M aqueous NaBr) accompanied by bromide-selective electrode measurements. After 4 h the bromide concentration dropped below 1 μmol l⁻¹.

In practice this resin behaves like an anion exchanger,

showing a very high selectivity towards the bromide anion. At the same time, the bromide ion is oxidized by two numbers — thus the resin proved to be a 'red-oxite' too¹³. As a matter of fact it has been stated that the resin product obtained especially by the action of an insufficient amount of bromide on the *N,N*-dichlorosulfonamide resin contained the following mixed functional groups: [P]–SO₂NBr₂ and [P]–SO₂NBrCl.

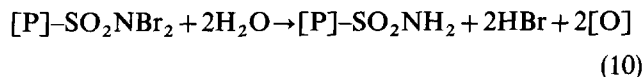
Physical form and chemical composition of the resins

The best resin products obtained are yellow-coloured pearls, 0.8–1.2 mm in diameter, having a distinct disinfecting odour. The fully brominated air-dried product used for further investigation contained 1.8% of water and 2.41 mmol g⁻¹ –SO₂NBr₂ groups, 0.42 g g⁻¹ overall bromine, 0.38 g g⁻¹ active bromine, 2.3 mmol nitrogen per gram, as well as about 0.3 mmol g⁻¹ –SO₃Na groups. This amount of sulfonic groups was already present in the raw material; it influenced the reaction rate advantageously by raising the hydrophilicity of the resin.

In order to identify the chemical structure of that resin, the i.r. spectra of the fully brominated copolymer and that of the monobrominated and non-brominated derivatives were compared (Figure 2). A full discussion of that problem will be published elsewhere.

Stability and thermal behaviour

The resin stored under the dry state in a closed vessel at 20°C retained about 95% of its initial active bromine content after 40 days. After one year, this content dropped to about 40%. The resin stored with exposure to the air lost its activity at a faster rate (due to its contact with water vapour):



and after 40 days its active bromine content amounted to 75% of the initial value.

The resin stored at 100°C undergoes a rapid decomposition. After 1 h, 40% of its initial active bromine content is lost. After 24 h, the loss is 85%. The active

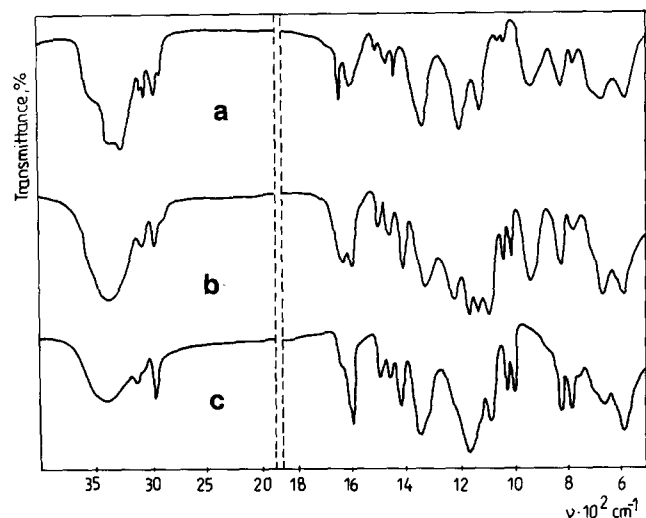


Figure 2 I.r. spectra (KBr) of (a) sulfonamide derivative, (b) *N*-monobromosulfonamide sodium salt and (c) *N,N*-dibromosulfonamide derivative of poly(styrene-co-divinylbenzene)

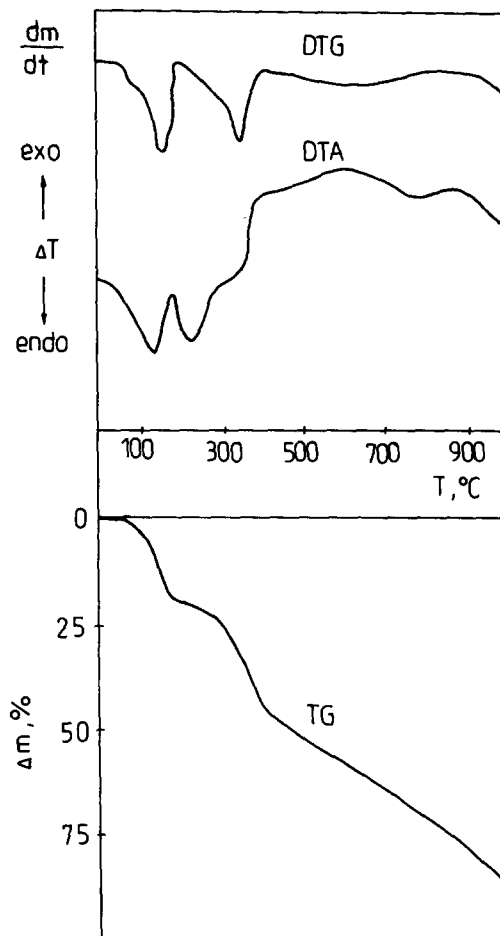
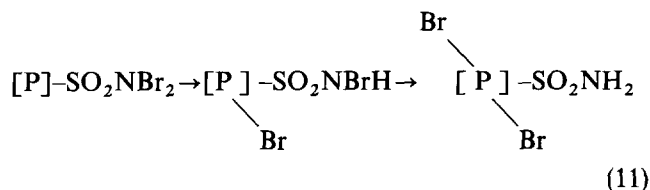


Figure 3 The thermograms of poly(*St-co-20%DVB*)SO₂NBr₂ (0.25 g in air): heating rate, 10°C min⁻¹; sensitivity, DTA 1/5, DTG 1/5

bromine loss is accompanied by a non-proportional mass decrement. Investigation has shown that part of the bromine undergoes an internal rearrangement reaction, thus becoming inactive:

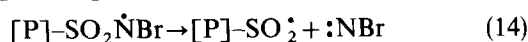
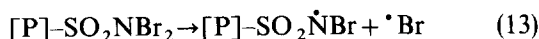
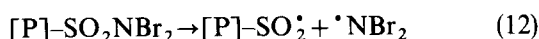


Some of these conclusions have been confirmed by the thermoanalytical curves (Figure 3), which are obtained at a comparatively fast heating rate. From these curves one can see that up to 165°C the resin loses free water as well as part of its bromine (23% weight loss) in an endothermic process. In the range 165–230°C residual bromine reacts actively with the matrix in an endothermic process without mass reduction. From 300°C up to 400°C a slight exothermic (SO₂N) functional group evolution process takes place, accompanied by an 18% mass decrement.

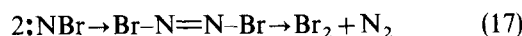
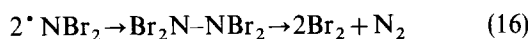
A comparison of the thermal behaviour of the resin with other macromolecular halogenoamines with the same matrix can be found in ref. 14.

On the basis of our own analytical data as well as published data concerning the pyrolysis of low-molecular-weight sulfonamides¹⁵, we can assume the participation of the following reactions in the temperature-

dependent decomposition process:



The bromine radicals can brominate the hydrocarbon matrix giving rise to HBr. The other radicals may combine and form stable compounds:

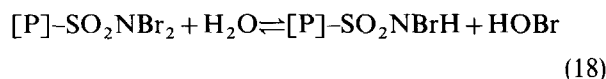


In the gaseous decomposition mixture HBr, Br₂, SO₂ and N₂ could indeed be detected.

Stability in the wet state

Investigations carried out in aqueous media showed that the resin is most stable in a neutral or slightly acidic medium (especially in the presence of bromides) and less stable in an alkaline medium. The results are listed in Table 2.

On reacting with water, the resin undergoes debromination:



In the acidic medium the hypobromite anion is unstable, and it transforms to bromide and/or bromine, which is partially absorbed by the resin again, but partially it may leave the medium, especially if the temperature is increased or if air is passed through. Bromide addition and sealing of the containers raise the stability of the brominated resins.

Chemical properties

The oxidative properties of the resin in aqueous medium are remarkable. After 24 h at room temperature there is complete absence of Fe²⁺ ions in the solution and an equivalent presence of Fe³⁺ and Br⁻. The resin still showed approximately 50% of its initial active bromine content.

Sodium sulfite and thiosulfate reacted even faster, forming sulfate ions. After 15 min all of the thiosulfate was oxidized, whereas for sulfite about 110 min were needed (Figure 4). When the reducing compound was used in excess, all active bromine was reduced to bromide, whereas the resin functional groups transformed to sulfonamide groups (-SO₂NH₂). Ascorbic acid gave similar results. D(+)-Glucose transformed to a mixture of D-gluconic acid and D-gluconolactone with about 80%

Table 2 Active bromine content in macromolecular *N,N*-dibromosulfonamide stored in various aqueous media. Initial active bromine content in resin is 0.38 g g⁻¹

Temperature (°C)	Time (h)	Retained active bromine (%)			
		Water	1 M NaBr	1 M NaOH	1 M H ₂ SO ₄
20	24	95	100	80	84
	20 × 24	88	98	65	70
60	3	86	97	52	61
100	3	27	68	14	18

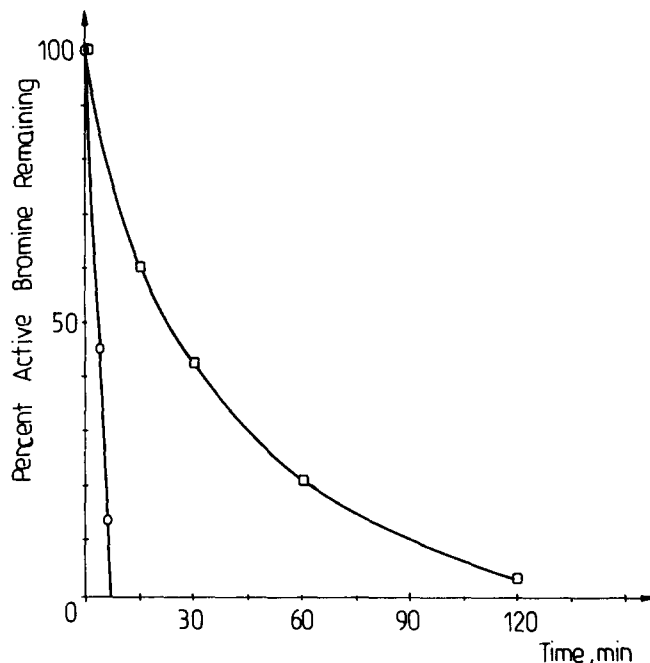
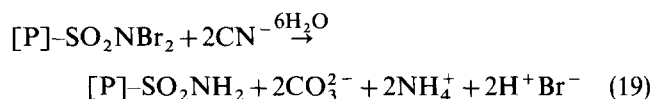


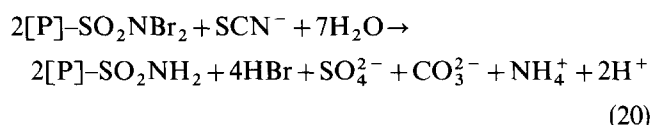
Figure 4 Debromination of macromolecular *N,N*-dibromosulfonamide (1 g) by means of 1 M aqueous solutions of (○) Na₂S₂O₃ and (□) Na₂SO₃ (50 cm³)

yield, within a few hours. Stoichiometric amounts of bromides as well as additional traces of hypobromite were detected in the post-reaction mixture.

Potassium cyanide was transformed into carbonate and ammonia within 1 h:

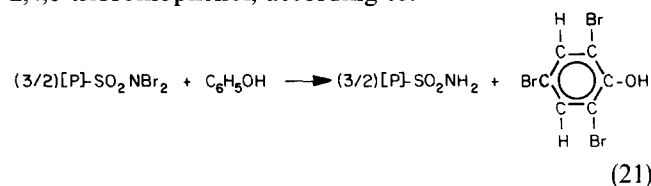


Alkaline medium promotes this reaction significantly. Rhodanide was oxidized within a few hours to give sulfate, carbonate and ammonia:



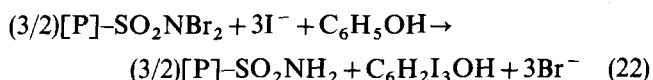
Also this reaction is carried out especially well in alkaline medium.

The resin showed active brominating properties. By contacting a sample of the resin with a dilute phenol solution, after a few minutes one can notice the beginning of the bromination reaction, as this is accompanied by a rise of turbidity and by a characteristic smell. After 2 h tribromophenol is precipitated and is partially absorbed by the debrominated resin itself. After 24 h about 95% active bromine was consumed. Of this, 12 wt% was in solution as bromide (as a consequence of the side reactions (18) and (10)) and 88% formed 2,4,6-tribromophenol, according to:



The iodinating test showed a similar result to the bromination reaction: triiodophenol was the only organic

product of the reaction. A part of this product was strongly absorbed by the sulfonamide resin. Approximately 95 wt% of the bromine formerly present in the resin was found in the solution, according to the reaction:



Disinfecting properties

The resin showed a very strong disinfecting activity. After contacting 500 cm³ of crude river-water with 1 g of the macromolecular dibromoamine, the amount of bacteria in 1 cm³ of that water dropped over a thousand times, i.e. (agar, 20°C, 72 h) from 42 800 to 26. Simultaneously the *E. coli* titre increased from less than 0.01 to about 300. Over 16 dm³ of the same river-water could be filtered through 10 g of the resin placed in a column (30 cm) until its disinfecting properties were exhausted.

CONCLUSIONS

The results of our experiments show that the macromolecular 'dibromoamine' can be obtained by three methods of preparation — each of them has its advantages. It would be relatively inexpensive to synthesize this resin on an industrial scale. Although no toxicity data are yet available for the new reactive copolymer, the structurally related low-molecular-weight compound as well as the macromolecular matrix have been shown to be safe in contact with either an animal or a human body.

The resin presented behaves like a [+1] bromine reservoir. Its stability in the dry state at room temperature

is limited to a few months. In aqueous media — especially alkaline — it is far less stable and hence more reactive. In the presence of bromides, its stability is good. In contact with liquids it is a very active brominating and oxidizing as well as disinfecting agent.

In summary, it would appear that *N,N*-dibromo-poly(styrene-*co*-divinylbenzene)sulfonamide has an excellent potential for use in science and in a variety of analytical, synthetic and disinfection applications.

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