

Debromination of di- and tetrabrominated compounds by crosslinked poly{1-[*p*-(mercaptomethyl)phenyl]ethylene}

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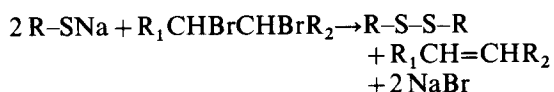
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Poly{1-[*p*-(mercaptomethyl)phenyl]ethylene} with a low content of divinylbenzene units as the crosslinking component was prepared from chloromethylated poly(styrene-co-divinylbenzene), and the activity of the thiolate form in the debromination reactions of 1,2-dibromocyclohexane was investigated with respect to the analytical content of the -SH groups. The extent of transformation of the -SH groups into the thiolate form, and the degree of crosslinking of the polymeric carrier were investigated. An almost complete conversion of 1,2-dibromocyclohexane and high yields of cyclohexene were obtained by using polymeric thiols with the initial DVB contents of 1 or 2%; the degree of functionalization of the carrier 100% or 30-60%; and the reaction times of polymeric thiols with sodium methoxide in methanol (1-2 h). The debromination reaction required 5 h for completion. Under optimum conditions, debromination of 1,2,5,6-tetrabromocyclooctane, α,β -dibromoethylbenzene, $\alpha,\beta,3,4$ -tetrabromoethylcyclohexane, diethyl 2,3-dibromosuccinate and stilbene dibromide gave olefins in yields of 60-100%

(Keywords: polymeric reagent; chloromethylated polystyrene; re-functionalization; polymeric thiol preparation; poly{1-[*p*-(mercaptomethyl)phenyl]ethylene}; debromination)

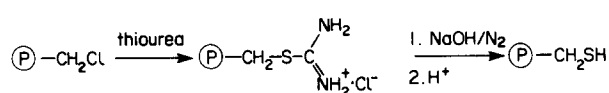
INTRODUCTION

The addition and elimination of Br₂ are often used in the protection reactions of double bonds. With respect to further functional groups present in the molecule, elimination reactions are carried out using metals such as Fe²⁺ (ref. 1), Cr²⁺ (refs. 2, 3), V^{III} (ref. 4) ions, and nucleophilic agents, such as halide ions^{5,6}, thiosulphates⁷, thiolates^{8,9}, thiourea¹⁰, selenides¹¹, tellurides^{12,13}, and derivatives of trivalent phosphorus^{14,15} as the dehalogenation agents. In reactions with nucleophiles, elimination of halogens is often accompanied by substitution reactions and the elimination of the hydrogen halide. The debromination of vicinal dibromo derivatives with thiolates proceeds according to the scheme



From the practical viewpoint, low-molecular weight thiols are difficult to manipulate and they are usually contaminated by their reaction products, e.g. olefins. Reagents with immobilized -SH groups on a crosslinked polymeric carrier should be free from these disadvantages. Crosslinked poly{1-[*p*-(mercaptomethyl)phenyl]ethylene} was synthesized for the first time for the purpose of selective ion exchange¹⁶. Its suitability for use as an intermediate in the preparation of special polymers has been shown several times^{17,18}. The use of its thiolate form in some debromination reactions has been reported quite recently¹⁹. Although, in principle, a direct

substitution of the chlorine atom with the -SH group can be used in the preparation of crosslinked polythiol from chloromethylated poly(styrene-co-divinylbenzene), this reaction may be complicated by consecutive reactions, characterized by the formation of sulphides and sulphonium structures. However, the transformation of the chloromethyl group into the mercaptomethyl group by way of the respective isothiuronium salt and its subsequent hydrolysis in an inert atmosphere appears to be unambiguous and without complication¹⁹⁻²². But a detailed study concerning the preparation of crosslinked polythiol is still lacking.



(P) = statistical poly(styrene-co-divinylbenzene)

The aim of this study is to investigate the thiolation modification of a chloromethylated copolymer of styrene and divinylbenzene (DVB as the crosslinking component) according to the scheme given above. A detailed description of the debromination reactions of 1,2-dibromocyclohexane and other brominated compounds by polymeric thiolates is also given.

EXPERIMENTAL

Materials

Polymeric thiols were synthesized using copolymers of styrene and divinylbenzene of grain size 0.2-0.4 mm

(United Chemical and Metallurgical Works, Ustí nad Labem), extracted in advance with benzene using a Soxhlet apparatus for 24 h, and dried at 50°C (0.07 kPa, 48 h). Chloromethylated copolymers were prepared using a procedure described earlier²³. The bromo derivatives used in the debromination reactions were prepared by the addition of Br₂ to the respective unsaturated compounds (Fluka). Anhydrous methanol was prepared by the distillation of methanol from magnesium methoxide. 1,4-Dioxane was repurified by distillation over sodium, preceded by shaking with concentrated HCl and the with solid KOH. All other chemicals (Fluka) were used without previous purification.

Preparation of crosslinked polymeric thiols

A chloromethylated copolymer of styrene and divinylbenzene (3 g) was preswollen in 20 ml of 1,4-dioxane (or a given solvent) at 80°C for 1 h. Then, 2.50 g (32.8 mmol) of thiourea (dissolved while hot) in a dioxane-ethanol (4:1) mixture (or in a given solvent) was added, and the mixture was left to stand at 90°C for 24 h. The supernatant solution was removed by suction, the polymer washed three times in a flask with a dioxane-ethanol (4:1) mixture (or with a given solvent), and the polymeric isothiuronium salt was hydrolysed with 15 ml of 5 M NaOH at 90°C for 10 h in a nitrogen atmosphere. Then, the supernatant solution was removed by suction, and the polymeric thiol obtained by acidifying the mixture with 20 ml of 2 M HCl (10 h, at room temperature), washing with water, and methanol, and drying (50°C, 0.07 kPa, 24 h). Elemental analysis of polymeric thiols **1a-d** (see Table I), %S calculated/%S found: **1a** 21.33/20.86; **1b** 21.05/20.78; **1c** 15.15/14.97; **1d** 9.32/8.96.

In order to investigate the course of thiolation modification reactions of the chloromethylated copolymer of styrene and divinylbenzene, samples (50–100 mg) were taken at given time intervals. In the case of the formation of the polymeric isothiuronium salt, the samples were washed three times with the dioxane-ethanol (4:1) mixture (or with given solvent), then twice with ethanol, and dried (50°C, 0.07 kPa, 48 h). The samples taken in the hydrolysis of the isothiuronium salt were introduced into 10 ml of 2 M HCl and left to stand at room temperature for 24 h. After that, they were washed with water and ethanol, and dried (50°C, 0.07 kPa, 48 h). The extent of transformation of functional groups was determined from the average value of the result of elemental analysis of N and S.

Equilibration of polymeric thiols with sodium methoxide

To 0.200 g of polymeric thiol, 2.00 ml of 1 M CH₃ONa was added (prepared by dissolution of Na in CH₃OH) and the mixture was left to stand at 50°C in a nitrogen atmosphere for a given time. After that, 0.4–0.5 ml of the solution was taken as a sample and titrated with 0.10 M HCl using phenol-phthaleine as indicator.

Debromination reactions

A polymeric thiol (2 mmol of –SH groups) was heated under nitrogen with a given amount of methanolic 1 M CH₃ONa at 50°C for given time. Then, a bromo derivative in a methanolic solution of the given concentration was added, and the reaction mixture kept at 50°C for a known length of time. The concentration of the solution components was determined by the g.l.c. analysis

(Perkin Elmer model F30 apparatus, FID column 1.80 m, ϕ 2 mm, 3% GE-XE-60 Chromosorb W, N₂ as carrier gas, temperature programme 75°C–180°C) using decane as the internal standard.

Debrominations of diethyl meso 2,3-dibromosuccinate and meso-stilbene dibromide were carried out on a twofold scale and the respective products were isolated. The reaction solution was freed from the polymer by filtering the polymer with the respective reaction solvent. The solvent was removed by distillation. The residue was dissolved in CH₂Cl₂, filtered, and CH₂Cl₂ distilled off. Yields were: 0.31 g (1.8 mmol) of diethyl fumarate or *trans*-stilbene (m.p. 120°–122°C, ethanol).

RESULTS AND DISCUSSION

Preparation of polymeric thiols

It has been shown previously^{17,18} that the –CH₂Cl groups of the chloromethylated copolymer of styrene and divinylbenzene can be transformed into the isothiuronium groupings even in highly crosslinked non-swelling polymers. However, the type of the solvent, the degree of crosslinking, and the degree of functionalization play a significant part in the course of formation of the isothiuronium salt (Figure 1). If the solvent is a good swelling agent for both the starting polymer and the product (e.g., DMF, 1,4-dioxane) a complete transformation of the –CH₂Cl groups into the isothiuronium groupings can be achieved with a wide range of values of the degree of functionalization of the starting chloromethylated copolymer (up to the theoretically attainable value). However, if swelling of the polymer is not guaranteed by the choice of the solvent (e.g. in ethanol), the reaction is much slower. An increase in the value of the degree of crosslinking slows down the pace of this course.

The dependence of the course of hydrolysis of polymeric isothiuronium salts on the formation of

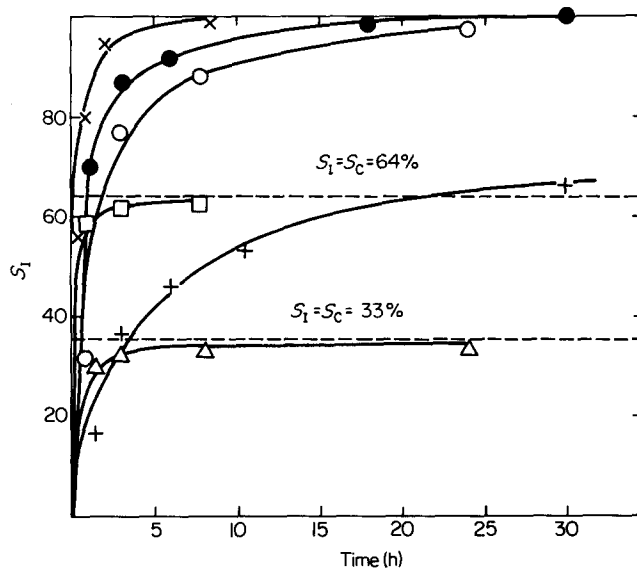


Figure 1 Refunctionalization reaction of chloromethylated copolymer of styrene and divinylbenzene (DVB) with thiourea at 90°C. S_C , S_1 ring-substitution with the chloromethyl or isothiuroniummethyl groups, respectively, % of theory. Starting $\text{—CH}_2\text{Cl}$ solvent: (x) 1% DVB, $S_C=100\%$, DMF; (●) 1% DVB, $S_C=100\%$, 1,4-dioxane; (○) 2% DVB, $S_C=100\%$, dioxane; (+) 2% DVB, $S_C=100\%$, ethanol; (□) 2% DVB, $S_C=64\%$, dioxane; (△) 2% DVB, $S_C=33\%$, dioxane

polymeric thiols is shown in Figure 2. An almost quantitative conversion can be achieved within a much shorter time than reported under the PTC conditions (benzene/NaOH/polymer-tetraheptylammonium chloride as catalyst, 48 h, boil)²¹. The profile of the reaction rate is practically independent of the degree of functionalization; perhaps, a polymer with a low degree of functionalization (where the hydrophobic character of the polymeric matrix is more expressive) requires more time to achieve satisfactory conversion.

By treating polymeric thiols with sodium methoxide in methanol, it is possible to perform ion exchange, thus transforming the polymer into the thiolate form. At the

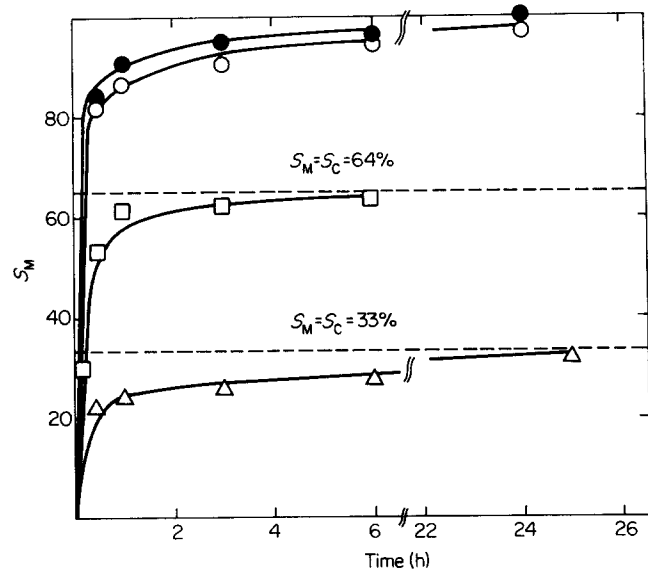
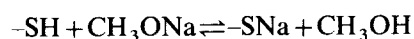


Figure 2 Hydrolysis of polymeric isothiuronium salt with 5 M NaOH at 90°C. S_C , S_M ring-substitution with chloromethyl or mercaptomethyl groups, respectively, expressed as % of theoretical value. Original polymers: (●) 1% DVB, $S_C=100\%$; (○) 2% DVB, $S_C=100\%$; (□) 2% DVB, $S_C=64\%$; (△) 2% DVB, $S_C=33\%$

same time, vigorous swelling of the polymer takes place; the higher degree of functionalization and lower degree of cross-linking of the polymer, the more vigorous and more evident swelling occurs. Back titration of the unreacted base has revealed that the equilibrium



is shifted more in favour of the thiolate form in the polymer with a higher content of the $-\text{SH}$ groups. Equilibrium is a complex process and its kinetics are affected by the rate of swelling of the polymer, apart from the dependence on temperature and on the concentration of the solution of sodium methoxide. Thus, by treating polythiols **1a-d** with an equimolar amount of 1 M CH_3ONa in CH_3OH at 50°C, the equilibrium is reached with 1–2 h, yielding polymers with 67–78% of all $-\text{SH}$ groups in the thiolate form.

Debromination reactions

Table 1 presents data on the debromination process of *trans*-1,2-dibromocyclohexane with polymer thiols **1a-d**. Under the given reaction conditions (1 M CH_3ONa methanolic solution, 50°C, initial stoichiometric ratio of Br to the $-\text{SH}$ groups), debromination proceeds smoothly up to a high extent with the exclusive conversion of dibromo derivatives into cyclohexane. If $[-\text{SH}]_0/[\text{CH}_3\text{ONa}]_0$ is higher than unity, the debromination proceeds to an extent corresponding to the amount of the $-\text{SH}$ groups existing in the thiolate form. If because of the short time of treatment of the polymeric thiol with the methanolic solution of CH_3ONa only a small part of the starting amount of the $-\text{SH}$ groups has been transformed into the thiolate form (and consequently, even the polymer matrix has not been sufficiently swollen to facilitate a transport of the reactant added, or if $[-\text{SH}]_0/[\text{CH}_3\text{ONa}]_0 < 1$), debromination may be accompanied by dehydrobromination (formation of 1-bromo-1-cyclohexene). If the hydrophobic character of the polymer matrix is prevalent

Table 1 Reaction of 1,2-dibromocyclohexane (1 mmol in methanol, 2.0 mol l⁻¹) with polymeric thiolates at 50°C

(P)-CH ₂ SH ^a	$[-\text{SH}]_0^b$	t_e	Reaction	ξ^c	Yield of
starting	$[\text{CH}_3\text{ONa}]_0$	(h)	time (h)	(%)	cyclohexene ^d (%)
1a	0.5	2	5	100 ^e	86
	1.0	0.1	2	56 ^e	31
	1.0	0.1	5	98 ^e	70
	1.0	2	0.1	8	8
	1.0	2	0.3	44	43
	1.0	2	5	99	97
	2.0	2	1	40	39
	2.0	2	4	49	48
1b	1.0	2	0.1	11	11
	1.0	2	0.3	33	32
	1.0	2	5	82	80
1c	1.0	2	0.1	20	19
	1.0	2	0.3	45	45
	1.0	2	5	100	99
1d	1.0	2	0.3	53 ^e	50
	1.0	2	5	96 ^e	89

^a**1a**, 1% divinylbenzene (DVB), 100% of theoretical ring-substitution with the mercaptomethyl groups (S_M); **1b**, 2% DVB, $S_M = 100\%$; **1c**, 2% DVB, $S_M = 64\%$; **1d**, 2% DVB, $S_M = 33\%$

^bInitial molar ratio; before the reaction, polymeric thiols were treated with methanolic 1M CH_3ONa at 50°C for a given time (t_e)

^cConversion of 1,2-dibromocyclohexane

^dG.l.c. determination

^e1-Bromocyclohexene proved as the side product

(polythiol **1d**), and consequently the polymeric thiolate is less swollen, debromination proceeds to a small extent only.

Simultaneously with chemical reactions, a manifest and strong contraction (de-swelling) of the crosslinked reagent occurs, due to the additional crosslinking with dithio bridges. The most rigid structure of the polymeric reagent derived from polymer **1b** is probably because the total reaction time of 5 h is insufficient for complete conversion of 1,2-dibromohexane. In all cases, however, the reaction proceeds with a quantitative mass balance of compounds in the liquid phase, even if polymers extremely crosslinked with -S-S- groups are formed. After a complete debromination no absorption of the -SH groups at 2560 cm^{-1} can be observed in the i.r. spectra of the final polymers. All these observations lead to an idea that -S-S- bridges formed during the debromination reaction create a rigid but porous structure of polymer particles. This is also shown by the fact that heating of the polymeric disulphide with LaAlH_4 (THF) to 40°C again gave a polymer with -SH groups (absorption at 2560 cm^{-1} found).

The activity of polymeric thiolate **1a** in the debromination reactions of various di- and tetrabromo derivatives is illustrated by data in Table 2. In the majority of cases the debromination proceeds smoothly. Two cases call for comments. The formation of the activated double bond of methacrylonitrile is accompanied by a subsequent addition of nitrile to the polymeric thiolate; this was confirmed by a blank test. The debromination process of 1,2-dibromooctane is surprising. It has been shown earlier⁹ that the debromination of 1,2-dibromoalkanes by

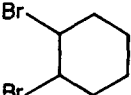
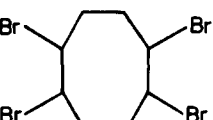
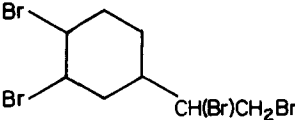
means of sodium butanthiolate can be accompanied by debromination. However, the extent of such side reactions decreases with increasing length of the hydrocarbon chain of 1,2-dibromoalkanes, and for 1,2-dibromooctane has not been observed⁹. The considerable extent of debromination of 1,2-dibromooctane recorded in this study can be related to the structure of the polymeric thiolate used (benzylic type of the crosslinked reagent).

The use of crosslinked polymeric thiolates in debromination reactions has the following advantages: (i) an easy and smooth preparation from a commercially available polymer of polymeric thiols with a high content of -SH groups, (ii) they can easily be handled (compared to low-molecular weight thiols), (iii) quantitative mass balance with yields of debrominated compounds ranging from good to excellent, (iv) easy and total separation of the reaction components, (v) possibility of reusing the polymer after reduction of the -S-S- groups.

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Table 2 Debromination of di- and tetrabrominated compounds with polymeric thiol **1a** in methanol at 50°C

Compound ^a	Concentration ^b (mol l ⁻¹)	Reaction ^c time (h)	Yield ^d (%)
	2.0	3.5	95
	0.1	5	100
$\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}_2\text{Br}$	0.4	2	100
$\text{C}_6\text{H}_{13}\text{CH}(\text{Br})\text{CH}_2\text{Br}$	2	5	60 ^e
	0.3	4	62
$\text{BrCH}_2\text{C}(\text{CH}_3)(\text{Br})\text{CN}$	1.0	0.5	50 ^f
$\text{EtOC}(\text{:O})\text{CH}(\text{Br})\text{CH}(\text{Br})\text{C}(\text{:O})\text{OEt}$	0.1	1 ^g	90 ^h
$\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}(\text{Br})\text{C}_6\text{H}_5$	0.13 ⁱ	1 ^g	92 ^h

^aInitial molar ratio $[\text{Br}]_0/[-\text{SH}]_0 = 1$; if not noted otherwise, 1 mmol was used

^bConcentration of a methanolic solution of the brominated compound

^cPolymeric thiol **1a** (characterization as shown in Table 1) was treated in advance with methanolic 1M- CH_3ONa ($[-\text{SH}]_0/[\text{CH}_3\text{ONa}]_0 = 1$) at 50°C for 1 h

^dYield of an unsaturated compound; g.l.c. determination

^e1-Bromo-1-octene and 2-bromo-1-octene proved as side products

^fConsecutive addition of methacrylonitrile to polymer takes place

^gReaction was carried out with 2 mmol of dibromo derivative at room temperature

^hYield of the isolated product

ⁱIn THF

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