Hydrolysis of *N*,*N*-dimethyldithiocarbamide polystyrene end groups

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Dedicated to Professor Ing. A. Hrivík, CSc., in honour of his 60th birthday

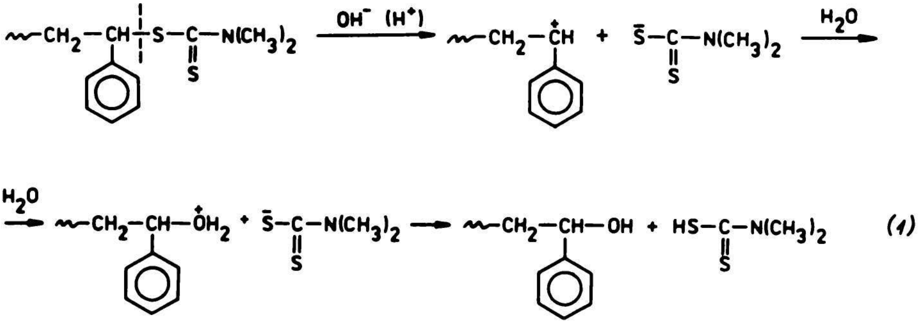
The *N*,*N*-dimethyldithiocarbamide (RS—) end groups of polystyrene are transformable to other functional groups by hydrolysis in acidic or alkaline media. The structure of the hydrolyzed end groups depends both on the kind of catalysis and type of the end carbon atom of the polystyrene chain, on which the functional group is bonded. The RS— group bonded to the secondary end carbon atom (—CH_2—) of polystyrene was chemically transformed into —SH group during alkaline hydrolysis, while as a result of acid hydrolysis, the formation of —S—C(S)—OH end groups was observed. The common feature of acid- and alkaline-catalyzed hydrolysis is quantitative splitting off of the RS— groups bonded to the tertiary end carbon atom of polystyrene.

Концевые *N*,*N*-диметилдитиокарбамидные (RS—) группы полистирола можно перевести в другие функциональные группы с помощью гидролиза в кислой или основной средах. Строение гидролизованных концевых групп зависит как от типа катализа, так и от типа концевого атома углерода полистирольной цепи, на который навязана функциональная группа. RS— группа, связанная со вторичным концевым углеродным атомом (—CH_2—) полистирола, была химически превращена в —SH группу в условиях основного гидролиза, в то время как в результате кислого гидролиза наблюдалось образование концевых групп —S—C(S)—OH. Общей чертой гидролиза с кислым или основным катализом является количественное отщепление RS— групп, связанных с третичным концевым углеродным атомом полистирола.

One possibility to prepare polymers with a changed structure of the end group is the subsequent chemical transformation [1—4] of the original end groups. In paper [4] the transformation of cyanogen end groups of polystyrene into amino group by hydrogenation and into carboxyl group by hydrolysis was discussed. Styrene oligomers with thiol and hydroxyl end groups were prepared by hydrolysis of the xanthate end groups.

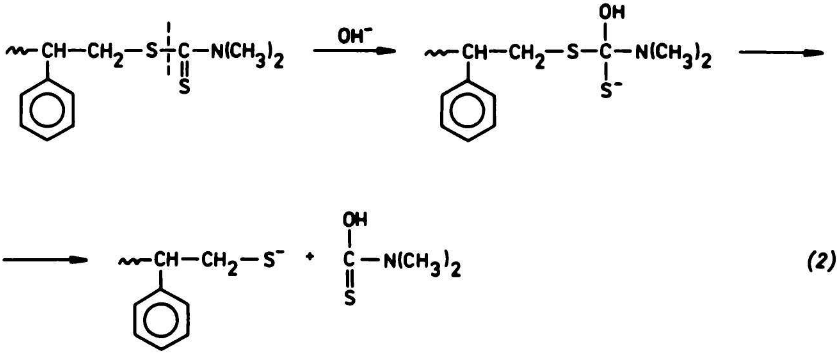
Styrene oligomers [5, 6] prepared by polymerization in the presence of tetramethylthiuram disulfide (TMTD) have on the macromolecule ends RS— groups, with the chemical structure of ester amides of dithiocarboxylic acids. These groups can be bonded to the secondary (—CH_2—) or tertiary (—ÇH) carbon end atom of the polystyrene chain. The reaction mechanism of the hydrolysis of RS— end groups can be derived from the low-molecular models of hydrolysis of carboxylic acid esters or acid amides. The reaction mechanism depends also on the kind of the bonding of end groups on polystyrene chain. Using the common knowledge of the mechanism of hydrolysis of esters and amides of carboxylic acids [7, 8] it is possible to assume three kinds of bond splitting:

1. sulfur—polymer chain (reaction mechanism (*1*)) (Scheme 1);


(*1*)

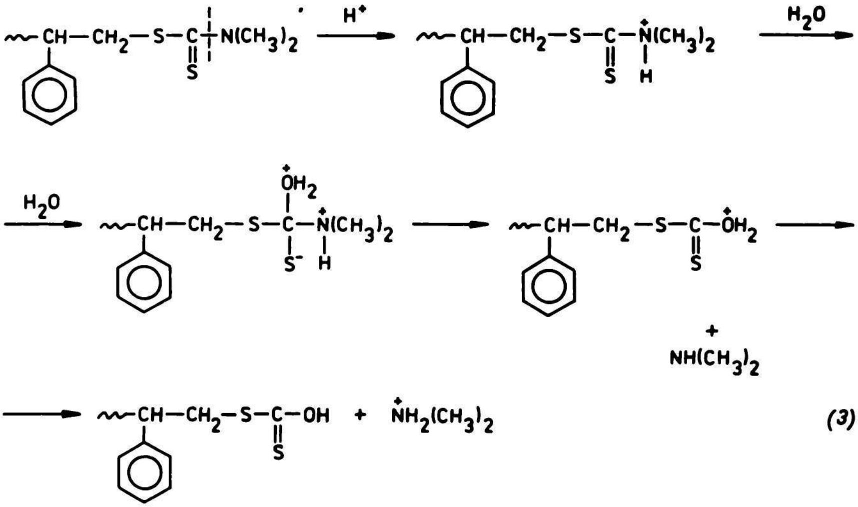
Scheme 1

2. thiocarbonyl—sulfur (reaction mechanism (*2*)) (Scheme 2);


(*2*)

Scheme 2

3. thiocarbonyl—nitrogen (reaction mechanism (*3*)) (Scheme 3).



(3)

Scheme 3

According to the literature [8] the bond sulfur—polymer chain can split only in the case, if the RS— group is bonded to the tertiary end carbon atom —$\overset{|}{\underset{|}{C}}$H of the polystyrene chain, on which a carbon ion is easily formed.

Experimental

The model polystyrene sample with the RS— end groups was prepared by block polymerization of styrene at 60 °C and at a concentration ϱ (TMTD in styrene) = 75 g dm^{-3}. The experimental procedure of the preparation is described in paper [5] or [6]. The average relative number molecular mass of the model polystyrene sample was $\bar{M}_{r,n} = 4460$ and the sulfur content $w(S) = 2.45$ %.

The polystyrene samples with RS— end groups were hydrolyzed in a homogeneous alkaline medium in a stainless steel autoclave, in nitrogen or air atmosphere at various temperatures (130—170 °C) in dependence on the time of hydrolysis. Into the 50 cm^3 autoclave 0.3 g of polystyrene, 28 cm^3 of benzene, and 12 cm^3 of 0.1 M-methanolic NaOH solution were added. After the hydrolysis acetic acid in equivalent amount to the used NaOH was added and the sample was heated under reflux for 30 min. Then the polystyrene sample was precipitated by pouring it into 250 cm^3 of CH_3OH. Finally the sample was purified by twofold precipitation from a 20 cm^3 benzene solution into 250 cm^3 CH_3OH solution.

The samples were hydrolyzed in a homogeneous acidic medium in glass ampoules in nitrogen atmosphere at various temperatures (120—150 °C) depending on the hydrolysis duration. Into the ampoules 0.5 g of polystyrene, 42 cm^3 of dichlorobenzene, and 18 cm^3 of 0.125 M-HCl solution in benzyl alcohol were added. After hydrolysis the polystyrene samples were precipitated in CH_3OH and purified by twofold precipitation as it was done in the case of the alkaline hydrolysis.

The hydrolyzed samples were characterized by UV spectra measuring the absorbance in dependence on the wavelength by means of the device Specord UV VIS. For measuring of polystyrene samples in cyclohexane the concentration $\varrho = 3\ \mathrm{g\ dm^{-3}}$ was used.

The sulfur content in the samples was determined by the modified Schöniger method.

The average relative number molecular mass $\bar{M}_{r,n}$ was determined by vapour pressure osmometry by means of the Knauer device.

Results and discussion

The RS— groups bonded to the polystyrene chain can be transformed by hydrolysis to other functional groups in consequence of splitting the single chemical bonds present in their structure. From the viewpoint of their structure, as mentioned in the general part, it is possible in the case of RS— groups to consider three possibilities.

The main purpose of the experimental work was to prove, which of the reaction mechanisms at the given reaction conditions of alkaline or acid hydrolysis is of use.

The hydrolyzed polystyrene samples were characterized by the average relative number molecular mass, total sulfur content and UV spectra as well.

A model polystyrene sample with a higher sulfur content (see Experimental) was synthesized to make possible the study of the kinetics of the alkaline or acid hydrolysis.

It has been shown that UV spectroscopy is a fast and convenient method to study the kinetics of the hydrolysis of RS— groups bonded to the polystyrene chain. The UV spectra with prolongation of the reaction time of hydrolysis illustrate the changes of the absorption bands with the successive chemical transformation of the bonded RS— end groups. By mutual comparison of the UV spectra of the original polystyrene sample with the spectra of the hydrolyzed polystyrene samples a marked decrease of the absorption bands in the whole region from 250 nm to 350 nm can be seen. The most significant decrease of the absorption bands is observed at wavelengths from 269 nm to 281 nm.

The absorption band with the peak at 281 nm is the most suitable for the study of the hydrolysis course of the RS— groups. It has been shown that the decrease of the absorbance values at 281 nm is proportional to the concentration decrease of the $-\overset{|}{C}=S$ groups and hence also to the concentration of the hydrolyzed RS— groups. After the total hydrolysis of the RS— groups in alkaline medium the value of the absorbance reaches at $\lambda = 281$ nm the value of the absorbance of a polystyrene sample with unbonded groups. The —CH_2—S— groups, present after the hydrolysis, in which the sulfur atom is bonded by a single bond do not influence the value of absorbance at the 281 nm wavelength.

Alkaline hydrolysis

The dependences of the absorbances measured at 281 nm wavelength on the reaction time of the alkaline hydrolysis are in Fig. 1. These dependences very well characterize the kinetics of the chemical transformation of the RS— end groups during their hydrolysis. It is evident that with increasing hydrolysis temperature the decrease of the absorbance is accelerated and the reaction time, which is necessary to reach the minimum of the absorbance. is shortened.

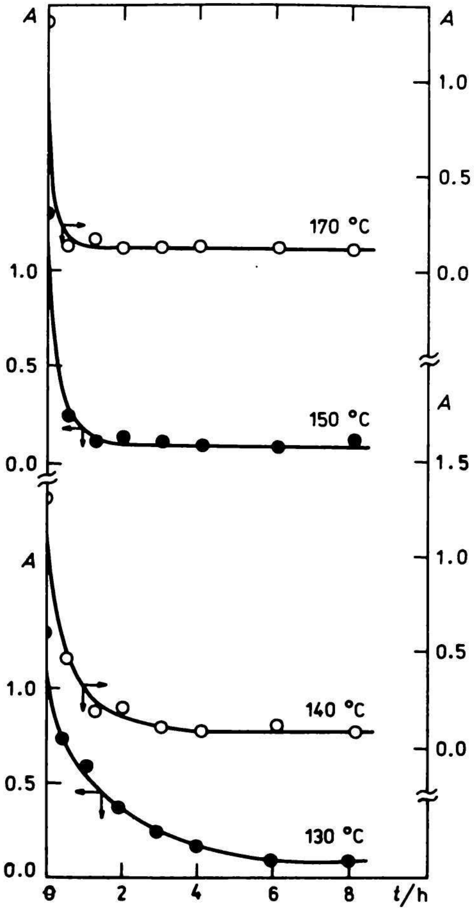


Fig. 1. Dependence of the absorbance at 281 nm wavelength of the model polystyrene sample hydrolyzed in alkaline medium in nitrogen atmosphere on the time of hydrolysis.

After reaching the minimum values of absorbance, *i.e.* after the total alkaline hydrolysis of the RS— end groups in nitrogen atmosphere, the sulfur content in the model polystyrene sample decreases from 2.45 % to 0.72 % and the average relative number molecular mass $\bar{M}_{r,n}$ from the original value of 4460 to 4300. With the prolongation of hydrolysis time, after reaching the equilibrium, the total sulfur content does not change any more. The average relative number molecular mass $\bar{M}_{r,n}$ of the polystyrene sample is changed by alkaline hydrolysis only in the range of the experimental error of determination of the molecular mass values. These facts indicate that after the total alkaline hydrolysis on one macromolecule of the polystyrene chain there will not remain more than one sulfur atom.

From the before mentioned it follows that during the alkaline hydrolysis of the RS— end groups also such a reaction mechanism must be of use, which leads to their quantitative splitting off. According to the facts mentioned in the general part such a mechanism can be used only in the case if the RS— groups are bonded to the tertiary end carbon atom $-\overset{|}{\underset{|}{C}}H$ of the polystyrene chain, where a carbon ion can be formed (see reaction mechanism (*1*)). Since the RS— groups are bonded to the polystyrene chain not only during the initiation, but also during the chain transfer

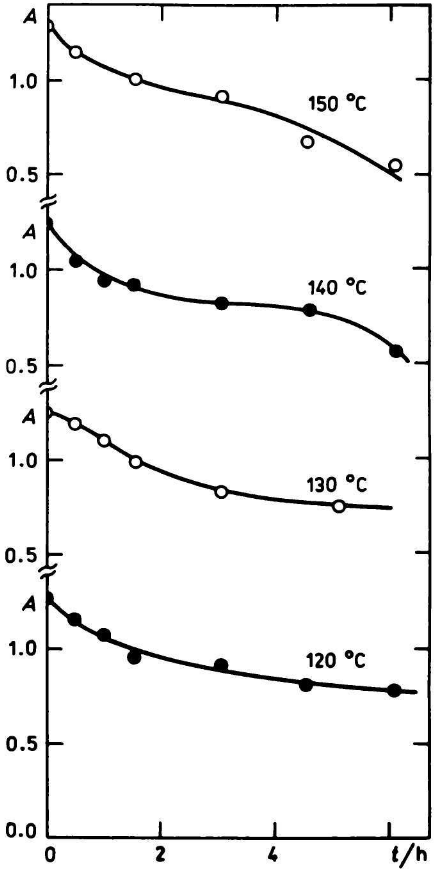


Fig. 2. Dependence of the absorbance at 281 nm wavelength of the model polystyrene sample hydrolyzed in acidic medium in nitrogen atmosphere on the time of hydrolysis.

reaction, there is always a part of these groups bonded to the tertiary end carbon atom of the polystyrene chain. The carbon ion can be stabilized by splitting off the hydrogen cation, whereby the double bond on the end of the polystyrene chain is formed, or by its hydration, which in excess of water occurs immediately (see reaction mechanism (*1*)).

The RS— groups bonded to the secondary end carbon atom —CH_2— of the polystyrene chain are in alkaline medium chemically transformed by a mechanism, which leads by splitting of the bond thiocarbonyl—sulfur to the formation of the —SH group (see reaction mechanism (*2*)).

The acknowledgement of the fact that the alkaline hydrolysis takes place according to mechanism (*2*), which leads to the formation of polystyrene oligomer with one —SH group bonded to the end of the polystyrene chain are also the results of alkaline hydrolysis obtained in the presence of oxygen. In samples hydrolyzed in this way there occurs an instant quantitative oxidation of the mercapto groups and a joining of the macromolecules through the disulfidic bonds [9], which was manifested by doubling the polystyrene macromolecules after hydrolysis (Table 1).

The mechanism of joining the polystyrene macromolecules by the oxidation of —SH groups is as follows [9]

$$2R\text{—}SH + 1/2O_2 \rightarrow R\text{—}S\text{—}S\text{—}R + H_2O \qquad (4)$$

Table 1

Characteristics of parallelly prepared polystyrene samples hydrolyzed for 6 h in alkaline medium at 150 °C in the presence of oxygen

Sample*	$\bar{M}_{r,n}$	$w(S)/\%$	$\bar{M}'_{r,n}$	$w'(S)/\%$	k
PS 70/40 *a*	5500	1.90	10 800	0.57	1.92
PS 70/40 *b*	5800	1.94	11 200	0.64	2.24
PS 70/40 *c*	5700	1.94	11 100	0.59	2.04
PS 70/40 *d*	5600	1.85	11 000	0.51	1.75
PS 70/40 *e*	6100	1.79	11 900	0.57	2.12

* The number of the polystyrene sample denotes the polymerization temperatures in °C/ϱ (TMTD in styrene) (in g dm^{-3}).

$\bar{M}'_{r,n}$ — the average relative number molecular mass of polystyrene samples after hydrolysis.
$w'(S)$ — sulfur content in polystyrene sample after hydrolysis.
k — the number of sulfur atoms for one polystyrene macromolecule after hydrolysis calculated from the relation

$$k = \frac{w'(S) \cdot \bar{M}'_{r,n}}{100 \times 32.066}$$

Similarly also *Otsu* [1] assumes that during the hydrolysis of polystyrene with —S—C(O)—C_6H_5 end groups there are formed polystyrenes with —SH groups, which are in the presence of O_2 oxidized, whereby the joining of the macromolecules through the disulfidic bonds takes place.

Acid hydrolysis

The same model polystyrene sample as for the study of the alkaline hydrolysis of polystyrene RS— end groups was used. The course and the degree of acid hydrolysis was again evaluated from the changes of the absorbance of UV spectra at 281 nm wavelength.

It is evident from Fig. 2 that the dependences of the absorbance on the reaction time are stabilized at higher levels of absorbances in comparison with dependences of polystyrene samples hydrolyzed in alkaline medium (Fig. 1).

Table 2

Characteristics of polystyrene samples hydrolyzed for 6 h in acidic medium at 130 °C in nitrogen atmosphere

Sample	$\bar{M}_{r,n}$	$w(S)/\%$	$\bar{M}'_{r,n}$	$w'(S)/\%$	k
PS 80/110	3080	3.54	2670	2.36	1.97
PS 70/90	3330	3.12	2980	2.18	2.03
PS 60/75	4110	2.45	3710	1.70	1.97
PS 60/50	5810	1.86	5400	1.19	2.00
PS 60/35	8810	1.29	8420	0.76	2.00
PS 60/20	12340	1.01	11720	0.58	2.10

The notes are stated in Table 1.

The course of the absorbance dependences on the time of the acid hydrolysis is changed with hydrolysis temperature. At 120 °C and 130 °C the decrease of the absorbance is stabilized at a relatively high value (Fig. 2), which is connected with the remaining of a great deal of the —$\overset{|}{\mathrm{C}}$=S groups bonded to the end of the polystyrene chain. As it can be seen from the dependences in Fig. 2 the reaction mechanism of acid hydrolysis is up to 130 °C unchanged. At higher temperatures, *i.e.* at 140 °C and 150 °C, after reaching equilibrium, such reactions begin to play their role, which cause the splitting off of the —$\overset{|}{\mathrm{C}}$=S groups.

During hydrolysis in acidic medium up to 130 °C the absorbance is stabilized after a 39.5 % decrease of its original value. In paper [5] it was shown that the average functionality of the RS— end groups is $\bar{f}_n = 1.66$, this value denoting the average number of RS— groups bonded to one macromolecule of the polystyrene chain. It was proved by the alkaline hydrolysis that on each secondary end carbon atom $-CH_2-$ of the polystyrene chain one RS— group is bonded. Then there must be on an average 39.8 % of RS— groups bonded to the tertiary end carbon atoms of the polystyrene chains. The calculated 39.8 % portion of the RS— groups bonded to the tertiary end carbon atom of the polystyrene chain is in good agreement with the observed decrease of the absorbance of polystyrene samples hydrolyzed in acidic medium up to 130 °C.

From the above mentioned it is evident that also in the acidic medium there will occur the total splitting-off of the RS— groups bonded to the tertiary end carbon atoms of the polystyrene chain. Thus during the acid hydrolysis as well as during the alkaline one the splitting of the bond sulfur—polystyrene chain will occur according to reaction mechanism (*1*).

From the dependences in Fig. 2 it is further evident that the acid hydrolysis of the RS— groups bonded to the secondary end carbon atoms of the polystyrene chains will take place in such a manner that after hydrolysis, the structure of the $-\overset{|}{C}{=}S$ groups will remain. The latter can remain only in accordance with mechanism (*3*), that means in the case of splitting the bond thiocarbonyl—nitrogen. The formation of the quaternary ammonium salt in acidic medium obviously supports the splitting of the thiocarbonyl—nitrogen bond in the RS— groups bonded to the secondary end carbon atoms of the polystyrene chains. The course of the acid hydrolysis according to mechanism (*3*) was also proved by the determination of nitrogen, which decreased in polystyrene samples hydrolyzed in acidic medium (Table 2) to equilibrium down to zero values.

The functional groups of the type —S—C(S)—OH formed during the acid hydrolysis of the RS— groups bonded to the secondary end carbon atoms of the polystyrene chains are at higher temperatures of the hydrolysis unstable and undergo a secondary chemical transformation according to the reaction mechanism (*3*). It is obvious that the splitting of the thiocarbonyl—sulfur bond according to the reaction mechanism (*2*) is beginning to take place. This is shown by a decrease of the absorbance values, which are measured at 281 nm wavelength (Fig. 2).

The mechanisms of the chemical transformations of the polystyrene RS— end groups were proved also by the experimental results of the acid hydrolysis of polystyrene samples which differed in the average molecular mass and sulfur content. The polystyrene samples were hydrolyzed, according to the procedure mentioned in Experimental, in a homogeneous acidic medium at 130 °C for 6 h. The experimental results are summarized in Table 2. These have proved the validity of the considered reaction mechanisms of the chemical transformations of the RS— end groups bonded to the polystyrene chains during the acid-catalyzed hydrolysis.

The preparation of polystyrene oligomers with bonded reactive sulfur functional end groups of the type —SH, or —S—C(S)—OH was patented [10].

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