

REDOX CATALYTIC ACTIVITY AND STABILITY OF SULPHONATED POLYMERS CONTAINING QUINONE GROUPS

Václav BLAŽEK, Zdeněk PROKOP and Karel SETÍNEK

Institute of Chemical Process Fundamentals,

Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát

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In connection with the study of polymer redox catalysts, the properties of condensation products of hydroquinone with chloromethylated styrene-divinylbenzene copolymers have been examined in more detail. It was found that only part of the hydroquinone bonded is capable of electron exchange in aqueous medium and only this part is likely catalytically active for reaction in gaseous phase. The effect of reagents and temperature during preparation of polymers containing hydroquinone functional groups leads to destruction of macromolecules to form carbon clusters which have the same catalytic activity as functional hydroquinone groups. Only part of these clusters is, however, capable of electron exchange in aqueous medium. The higher the catalytic activity, the lower the thermal stability of the polymer.

In our previous work¹ we were concerned with the oxidation catalytic activity of macroporous styrene-divinylbenzene polymers containing quinone groups. We found that the catalytic activity of studied polymers for reactions in gaseous phase is rather small. It increases, however, if in addition to hydroquinone groups the polymer possesses also sulphonic acid groups. In both cases, the activity of polymers decreases in the course of the reaction, due to a slow reoxidation of the catalyst surface. Reoxidised surface exhibits again catalytic activity. If these operations are performed repeatedly, the catalytic activity of the polymer decreases slowly and irreversibly. It is therefore evident that in addition to reversible oxidation and reduction of the catalyst surface, there proceeds also an irreversible process that affects negatively the oxidation catalytic activity of the polymer. It was further found that there is no relationship between the redox capacity of the polymer determined by titration and its catalytic activity for reactions in gaseous phase. In the course of condensation of chloromethylated styrene-divinylbenzene copolymer with hydroquinone only part of chloromethyl groups reacts (as judged from the loss of chlorine) and titration exchange capacity of the polymer so obtained is lower than that based on the content of hydroquinone groups expected from the loss of chlorine.

All these facts indicate that the system investigated is not simple. This led us to perform a series of measurements aimed at explaining the above mentioned behaviour of these polymers.

EXPERIMENTAL

Polymers, the properties of which are summarised in Table I, are mostly identical with those described in our previous work¹. In both cases they were prepared from the same macroporous

styrene-divinylbenzene copolymer containing 25% of divinylbenzene. Also all the methods used to characterise polymers and to determine their catalytic activity were the same as those reported earlier¹.

Attempted condensation of dioxane with chloromethylated polymer was carried out such that dioxane was dried by distillation over sodium, the chloromethylated polymer (MK-Cl) was dried in a stream of dry nitrogen at 100°C. A total of 10 g of MK-Cl polymer was allowed to swell in 200 ml of dioxane for 16 h and then 100 ml of the swelling agent was removed by distillation through a column (azeotropic drying). After 0.7 g of melted $ZnCl_2$ had been added, the mixture was refluxed for 4 h. The product was extracted with methanol and dried.

Condensation of benzyl chloride with hydroquinone was performed analogously to the condensation of MK-Cl polymer with hydroquinone. The reaction mixture after condensation was analysed by liquid chromatography with the use of 250×4.1 mm column packed with Nucleosil C_{18} (5 μ m particle size), mobile phase being methanol-water (2:1), the column overpressure 17 MPa, the flow rate 1.2 ml/min and detection was realized by a flow UV analysator at wavelength 290 nm.

Thermal and oxidation stability of polymers was determined in the following way. A glass flask connected to Finnigan 3000 mass-spectrometer was charged with 1 g of the polymer. The polymer was evacuated at 100°C and then volatile components were removed until the pressure reached $1 \cdot 10^{-3}$ Pa. The temperature was raised to that desired and the known amount of oxygen was introduced. From this moment the composition of the gas phase above the polymer was analysed mass spectrometrically.

RESULTS AND DISCUSSION

When MK-Cl polymer is treated with hydroquinone, not all the chlorine present reacts and, furthermore, the titration redox capacity of the product is lower compared to that expected on assuming the substitution of all the chlorine atoms for hydroquinone groups. The first fact could be explained by the inaccessibility of chloromethyl groups located within the polymer particle in the condensation reaction medium. The second fact indicates, however, that either a part of condensed hydroquinone is not capable of reversible redox reaction or that a part of chloromethyl groups reacts with the solvent (dioxane). This last possibility was excluded experimentally. As it is seen from Table I, dioxane does not react with chloromethyl groups and also does not cause a more significant chlorine loss from the polymer. A slow decrease in the chlorine content due to dioxane action may be caused by water traces in the reaction medium.

In order to verify assumptions about the condensation of hydroquinone with chloromethylated styrene-divinylbenzene copolymer, we decided to perform the reaction in a way which would enable to follow on the basis of the polymer weight difference and the analysis of chlorine present in the polymer and of the hydroquinone present in the reaction mixture (see liquid chromatography in Experimental), how much hydroquinone reacted with the polymer and at the same time how much chlorine was lost. The results demonstrate that chlorine content decreases at a faster rate than the amount of hydroquinone and that titration redox capacity of the product is smaller than that expected on the basis of the hydroquinone reacted. The loss

TABLE I
Properties of Polymers Used

Polymer	Designation	Titration exchange capacity mequiv H ⁺ /g	Titration redox capacity mequiv H/g	Chlorine content %	Oxidation catalytic activity % acetone	EPR signal dB
Macroporous styrene-divinylbenzene copolymer (25% of divinylbenzene)	MK	0	0	0	0	0
Sulfonated MK	MS	3.76	0	0	1.5	14
Chloromethylated MK	MK-Cl	0	0	13.6	0	7
MK-Cl condensed with dioxan	MK-Diox	0	0	12.7	0	—
Sulfonated MK-Cl	MS-Cl	1.80	0.17	5.7	8	256
Sulfonated MK-Diox	MS-Diox	1.70	0.19	—	3	—
MK-Cl condensed with hydroquinone	MK-Hydr	0	0.45	8.1	0.6	44
Sulfonated MK-Hydr	MS-Hydr	1.46	0.67	—	14	666
MS-Cl condensed with hydroquinone	MS-Hydr	1.85	0.90	—	20	890

of chlorine could be explained also such that $ZnCl_2$ induces the condensation of the chloromethyl group with the neighbouring benzene ring to form the methylene bridge. This would lead to an increase in macromolecule crosslinking and might be responsible for the low conversion of condensation reaction with hydroquinone.

We have further carried out the reaction of benzyl chloride with hydroquinone under the same conditions as used in the case of chloromethylated polymer. The reaction mixture after condensation was analysed by liquid chromatography. It was found that the only product is 2-benzylhydroquinone, *i.e.* the monomeric analogue of the condensation product of hydroquinone with the chloromethylated polymer. Hydroquinonemonobenzyl ether was not formed. Its formation could have explained the reaction of hydroquinone to form a product which could not be able to undergo redox transformation.

Since during preparation and catalytic experiments the polymers were exposed to higher temperatures and to the action of gaseous oxygen in high concentrations, the thermal and oxidation stability of the polymers was also studied. This was followed by analysis of the composition of the gas phase above the polymer, using the procedure reported in Experimental. Time dependences of CO_2 and SO_2 molecular ion intensities are presented graphically in Figs 1 and 2. It was found that the most stable is the starting copolymer (MK) and the polymer which was only chloromethylated with the use of $AlCl_3$ (MK-Cl). The least stable were polymers which were subjected to two polymer-analogous reactions (chloromethylation and condensation with hydroquinone using $ZnCl_2$) followed by sulphonation (MS-Hydr) or those subjected to two consecutive condensations (ML-Hydr). As to their stability, the other polymers were between these extremes. This holds also for the cleavage of sulphonic acid groups from the polymer. Sulphonated copolymer (MS) was substantially more stable compared to those which in addition to sulphonation were subjected to one or two condensation reactions (MS-Cl and MS-Hydr). Fig. 2 shows also greater difference in stability on two temperature levels than does Fig. 1. This agrees with the fact that in the case of sulphonated styrene-divinylbenzene ion exchangers increasing temperature leads first to the cleavage of sulphonic acid groups and only after that to the destruction of hydrocarbon skeleton of the copolymer.

The overall extent of thermal and oxidation decomposition of polymer mass is, however, small. This was calculated on the basis of mass spectrometric analyses of the space above the polymer and from the concentration of decomposition products (CO_2 and SO_2). With the least stable polymer MS-Hydr, only 0.007% (by mass) was decomposed at 120°C after 90 min. The sulphonic acid groups are less stable under these conditions, since 0.12% of the original amount was lost by this treatment. It is therefore possible to consider studied polymers to be stable at temperatures up to 120°C and in experiments which do not last more than 2 h. As a result, in the interpretation of the results obtained, the thermal and oxidation decomposition can be neglected.

The starting macroporous styrene-divinylbenzene copolymer (MK) is inactive in the gas phase oxidation of isopropanol by oxygen. Its colour is snow white. After its sulphonation, one obtains a light brown polymer (MK) which does not exhibit

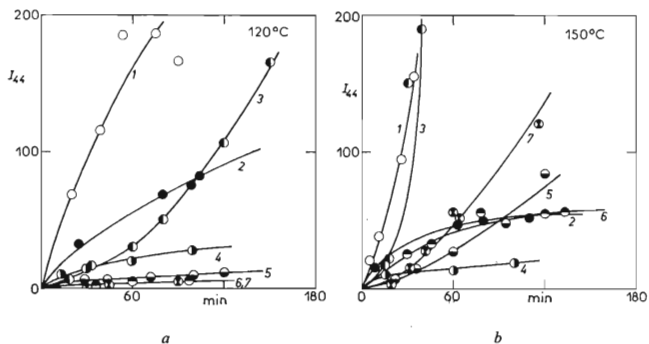


FIG. 1

Time Dependence of Amount of CO_2 Above the Polymer

a 120°C , *b* 150°C , I_{44} the height of signal of CO_2 molecular ion, 1 MS-Hydr, 2 MS-Cl, 3 MK-Hydr, 4 MS, 5 MK, 6 MK-Cl, 7 MK-Diox.

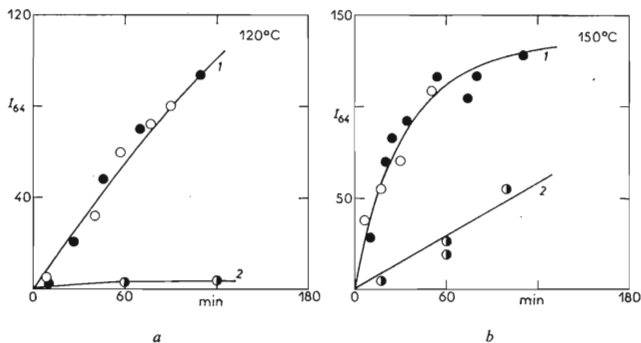


FIG. 2

Time Dependence of Amount of SO_2 Above the Polymer

a 120°C , *b* 150°C , I_{64} the height of signal of SO_2 molecular ion, 1 MS-Hydr, MS-Cl, 2 MS.

redox capacity but possesses a certain small catalytic activity. Condensation of polymer MK with chloromethyl methyl ether in the presence of AlCl_3 produces a chloromethylated polymer (MK-Cl), the brown colour of which is lighter than that of MS polymer. This one has no titration redox capacity and catalytic activity. If this polymer is subjected to sulphonation, a dark brown product (MS-Cl) is formed which shows titration redox capacity and catalytic activity. Condensation of MK-Cl polymer with hydroquinone under the action of ZnCl_2 results in a hydroquinonated polymer (MK-Hydr) which is brown-orange and shows both titration redox capacity and catalytic activity. Sulphonation of MK-Hydr polymer gives a product (MS-Hydr) containing both hydroquinone groups and sulphonic acid groups; the polymer is black-brown and exhibits a considerable redox capacity and catalytic activity. If condensation is performed with hydroquinone and sulphonated polymer MS-Cl, one obtains a similar product as MS-Hydr with analogous properties.

In the course of synthesis of sulphonated styrene-divinylbenzene copolymers containing quinone or hydroquinone groups, the reagents and temperature used lead to degradation of hydrocarbon chains of macromolecules. This manifests itself in a lowered thermal and oxidation stability. In the case of sulphonated polymers defects are formed which exhibit titrationally determinable redox capacity. The degradation of polymer leads also to the appearance of catalytic activity. In the sulphonation of polymer MK, the product does not show redox capacity, but is catalytically active. On the other hand, polymers MS-Cl and MS-Diox show similar properties, but their catalytic activity is different. It seems therefore likely that there exist catalytically active sites which are not capable of electron exchange in aqueous medium.

The extent of decomposition increases in dependence upon how many chemical operations were performed successively. With the increasing extent of decomposition, the colour of the polymer turns from white to black brown and at the same time the redox capacity and catalytic activity increase. Since we deal here with the formation of sites which are catalytically active for the reaction which proceeds *via* electron exchange, we measured the EPR signal for the series of polymers at room temperature using ERS 200 instrument (Acad. Sci. GDR). The values obtained are presented in Table I and are recalculated to standard conditions, so that they are comparable. It was found that the greater the catalytic activity, the stronger the EPR signal. The signal obtained in the magnetic field scale within 0–5000 Gauss had G value equaling to 2.003. Its position and character indicates that the signal belongs to free electrons located in carbon clusters².

In the preparation of polymers containing hydroquinone groups and in their sulphonation, due to the effect of chemical reagents and temperature there proceeds decomposition of macromolecules, *i.e.* the cleavage of carbon-carbon bonds and formation of decomposition products. In places where such destruction is taking place clusters of carbon atoms are formed which along with hydroquinone resp.

qionone functional groups possess also catalytic activity for oxidation of isopropanol by gaseous oxygen. A part of these clusters is also capable of electron exchange in aqueous medium. It is therefore impossible to prepare a sulphonated polymer, in which only functional hydroquinone or quinone groups would be solely responsible for redox properties and oxidation catalytic activity and the polymer skeleton would be inactive.

REFERENCES

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