# Thermal stability of sulphonated styrene—divinylbenzene resins

**N. Bothe, F. Döscher, J. Klein and H. Widdecke**
*Institut für Chemische Technologie der Technischen Universität Braunschweig, D 3300 Braunschweig, Federal Republic of Germany*

*(Received 13 October 1978; revised 26 January 1979)*

Sulphonated styrene–divinylbenzene copolymers of different structures were heated in vacuum, a nitrogen stream, water, sulphuric acid and benzene. The stability behaviour was studied by differential thermal analysis at temperatures up to 600°C and by isothermal measurements at temperatures between 150°C and 240°C. In aqueous media decomposition of the resins is determined by hydrolysis of the sulphonic acid groups alone; in vacuum, nitrogen stream and benzene, reactions in the polymer backbone under the influence of sulphuric acid and additional crosslinking due to the formation of sulphones have also to be taken into account.

## INTRODUCTION

In recent years much attention has been given to the synthesis of functional polymers as polymeric reagents and catalysts. In most cases the reactivity and selectivity of the functional groups bound to the polymeric matrix, frequently a styrene–divinylbenzene copolymer, are studied in detail whereas little is known about the thermal and chemical stability which can often limit industrial application.

It was our objective to study the stability behaviour in more detail on a well-defined form of a polymeric reagent like an ion-exchange resin. Ion exchangers are often used at high temperatures under industrial conditions, e.g. in the deionization of industrial waters, the purification of radioactive solutions and many catalysed reactions of organic compounds.

The experiments were carried out in order to obtain quantitative results on the decomposition behaviour of ion-exchange resins, thus giving basis for the synthesis of new resins of increased thermal stability. In this work commercial sulphonated styrene–divinylbenzene copolymers have been used, and since macroporous resins are becoming increasingly important for many industrial applications, these were used in most experiments.

Some previous studies involving the thermal stability of polymeric sulphonic acids, mainly KU–gel type–resins, should be mentioned[1–6]. Unfortunately these resins are very little characterized.

## EXPERIMENTAL

The physical properties of the resins which were examined in this work are listed in *Table 1*. In most cases the macroporous resin Amberlyst 15 was used. Synthesis, pore structure and applications of Amberlyst 15 are described in the literature[7–9].

The experiments in the liquid phase were carried out with a glass flask in steel autoclaves, the experiments in vacuum in an evacuable glass apparatus at a pressure of 5 mbar. For d.t.a.–t.g.a. studies a Dupont Thermoanalyser 990 with d.s.c. cell and Thermobalance 951 was used.

Before starting a decomposition experiment, the resin was washed free from acid, extracted with methanol and benzene successively, and dried at 80°C in vacuum (0.1 mbar) for 12 h. Decomposition in water, 10 N sulphuric acid, and benzene was carried out with 1 g samples in 15 ml of liquid at 190 and 200°C. D.t.a. and t.g.a. measurements were carried out in a nitrogen stream with a flow rate of 50 ml/min and a heating rate of 10°/min. The exchange capacity (milliequivalents sulphonic acid groups/g initial resin) was determined by contacting samples with a 4% aqueous solution of $Na_2SO_4$ until

*Table 1* Polymeric solids used in this work

| | Lewatit | | | | |
|---|---|---|---|---|---|
| | SC 108 | SPC 108 | SPC 112 | SPC 118 | Amberlyst 15 |
| Producer | | Bayer | | | Rohm & Haas |
| Matrix | | styrene-divinylbenzene copolymer | | | |
| Structure | gel type | | macroporous | | |
| DVB-content | 8% | 8% | 12% | 18% | 20% |
| Porosity (%) | – | 23 | 8–14.5 | 46 | 32 |
| Inner surface ($m^2$/g) | – | 18 | 0.1–19.6 | 40 | 45–55 |
| Mean pore radius (A) | – | 480 | max. 235 | 620 | 288 |
| Functional group | | | $-SO_3H$ | | |
| Capacity (meq $-SO_3H$/g) | 4.5 | 5.1 | 4.2 | 4.7 | 4.8 |

0032–3861/79/070850–05$02.00

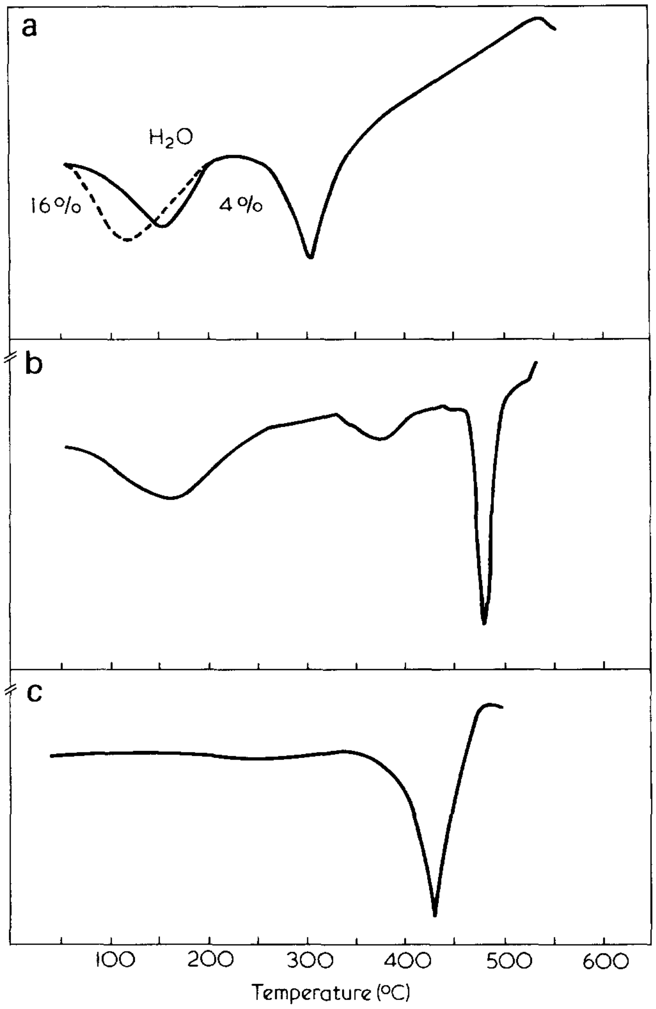

*Figure 1* Differential thermal analysis (a) Amberlyst 15, H-form, water content 4% (———) and 16% (– – –), (b) Amberlyst 15, Na-form, (c) Styrene/18% DVB-copolymer

the eluate is free of acid. The eluate was titrated with 0.1 N NaOH and Methyl Red as indicator.

## RESULTS AND DISCUSSION

### *Differential thermal analysis*

The differential thermal analysis (d.t.a.) gives an initial qualitative survey about those temperature ranges in which variations in the resin caused by thermal treatment can be observed. D.t.a. curves of Amberlyst 15 ($-SO_3H$ form), Amberlyst 15 ($-SO_3Na$ form) and an unsulphonated styrene–divinylbenzene copolymer are shown in the *Figure 1*. Three different effects, all representing an absorption of heat, have to be discussed:

(1) *Endothermic effect between 90°C and 180°C.* The first endothermic transformation is interpreted as the dehydration of the resin. The peak size increases with increasing moisture content while the peak maximum is shifted simultaneously to lower temperatures. This may indicate that small moisture traces are bound intensively to the resin.

(2) *Endothermic effect beyond 300°C.* The second transformation is caused by the desulphonation of the polymeric acid. Leikin[4] has observed a clear decrease of the sulphur content in this temperature range.

(3) *Endothermic effect beyond 400°C.* At temperatures beyond 400°C decomposition of the polymer matrix takes place since in the case of the styrene–divinylbenzene copolymer and Amberlyst 15 (Na form) a sharp endothermic peak can be observed. The unsulphonated polymer changes colour and becomes liquid while the sulphonated cation-exchanger retains its spherical form. The decomposition of the resin in the acid form obviously is somewhat more complex since there is no sharp peak at temperatures beyond 400°C. This is probably due to the formation of sulphones.

### *Isothermal decomposition in the gas phase*

The temperature, given by the peak maximum of the desulphonation peak in the differential thermal analysis, does not indicate thermal stability up to this temperature. Desulphonation can be observed at more than 150°C below this temperature. For practical applications therefore it is more suitable to examine the decomposition behaviour in isothermal measurements for long periods. In *Figure 2* the decomposition (weight loss) of Amberlyst 15 in a nitrogen stream at temperatures between 150° and 240°C is shown. A more detailed study was undertaken at 200°C (*Figure 3*) including the same substances already used for the d.t.a. measurements.

In accordance with d.t.a. the salt form of Amberlyst 15 exhibits a greater thermal stability than the acid form (*Figures 3a* and *3b*). Therefore one can conclude that at 200°C a real thermal splitting of the C–S bond does not occur. Furthermore the strong weight loss of the polymeric acid is not caused by a thermal decomposition of the matrix, which means a splitting of C–C bonds, because the styrene–divinylbenzene copolymer looses only little in weight at 200°C (*Figure 3c*).

The splitting-off of $SO_3$ as the reason for the decreasing exchange capacity can be excluded by stoichiometric calculation because this gives a greater loss in weight from the capacity curve than was measured in our experiments (*Figure 3a*); moreover, $SO_3$ was not detected qualitatively.

Thus chemical reactions, which were already suggested by different authors[1,5], are responsible for the decrease in exchange capacity and weight. These reactions are the hydrolysis of sulpho groups by traces of moisture after drying, resinification of the polymer under the influence of sulphuric acid ($SO_2$ formation), and additional crosslinking of the resin due to the formation of sulphones.

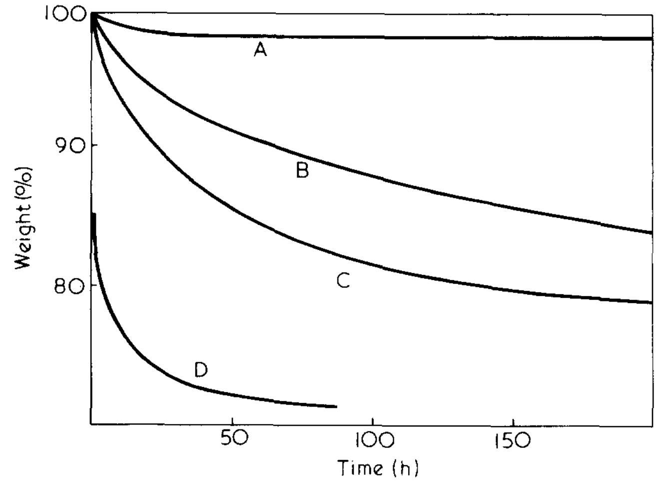

*Figure 2* Effect of temperature on the weight loss of Amberlyst 15, H-form. A, 150°C; B, 180°C; C, 200°C; D, 240°C

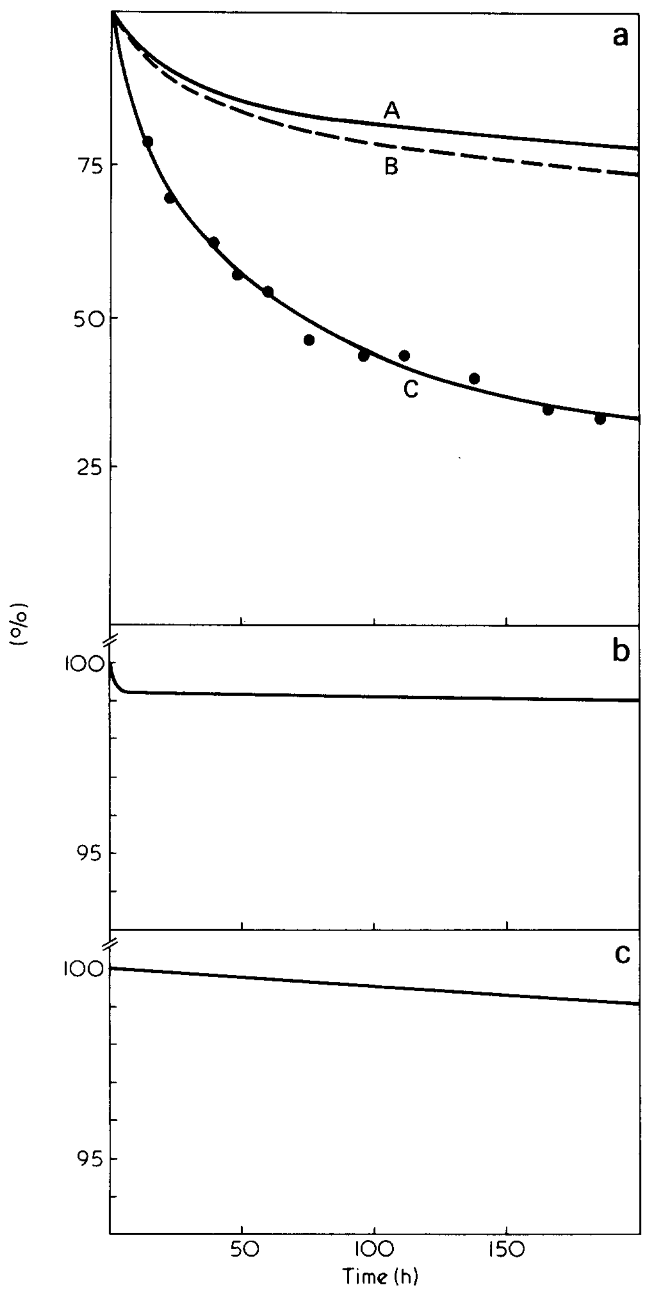

*Figure 3* Weight and capacity loss in the gas phase at 200°C (a) Amberlyst 15, H-form, A, measured weight loss, B, weight loss calculated from capacity loss, C, capacity loss (b) Amberlyst 15, Na-form, (c) Styrene/18% DVB-copolymer

*Table 2* Amberlyst 15 (H-form) – data of elemental analysis before and after thermal treatment in the gas phase at 200°C for 186 h

| Capacity (meq $-SO_3H/g$) | Carbon (%) | Hydrogen (%) | Oxygen (%) | Sulphur (%) |
|---|---|---|---|---|
| 4.8 | 53.3 | 4.8 | 25.1 | 17.1 |
| 2.0 | 64.1 | 4.4 | 17.2 | 14.1 |

Data of the elemental analysis of Amberlyst 15 before and after its thermal treatment in vacuum support these conclusions (*Table 2*). One can calculate from the S/O that *ca.* one-third of the original sulphur leaves the polymer as $SO_2$, one-third remains bound as $-SO_3H$, and one-third remains with a S/O ratio of 1:2, which indicates sulphone formation in the ion-exchange resin during thermal treatment.

In the same way Lewatit sulphonic acid resins were examined (*Figures 4*). As the nature of the matrix and the ionic groups are always the same, differences in the thermal stability may be explained by different divinylbenzene contents and pore structures. Furthermore, the ionic group concentration and its local position in the aromatic ring have to be considered. Detailed studies are in progress.

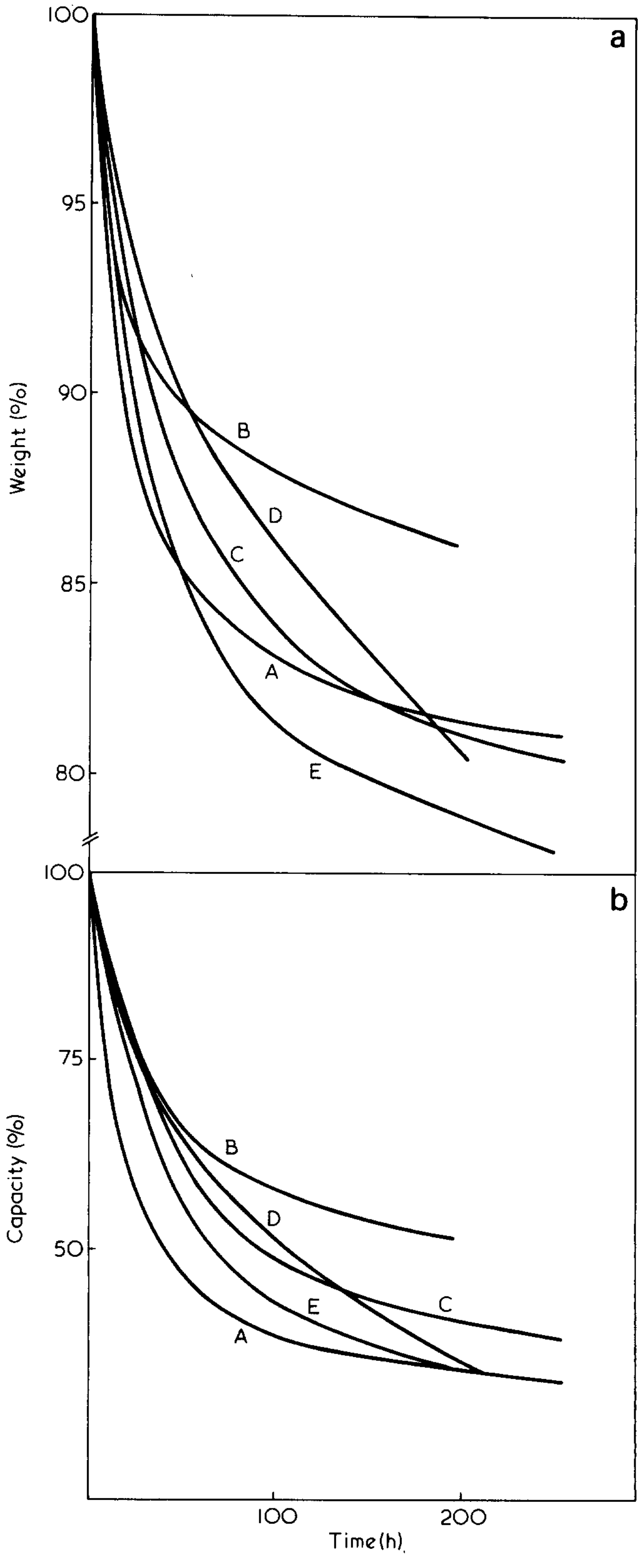

*Figure 4* (a) Weight and (b) capacity loss of different polymeric sulphonic acids at 200°C in nitrogen (A) Lewatit SPC 118 (B) Lewatit SPC 112 (C) Lewatit SPC 108 (D) Lewatit SC 108 (E) Amberlyst 15

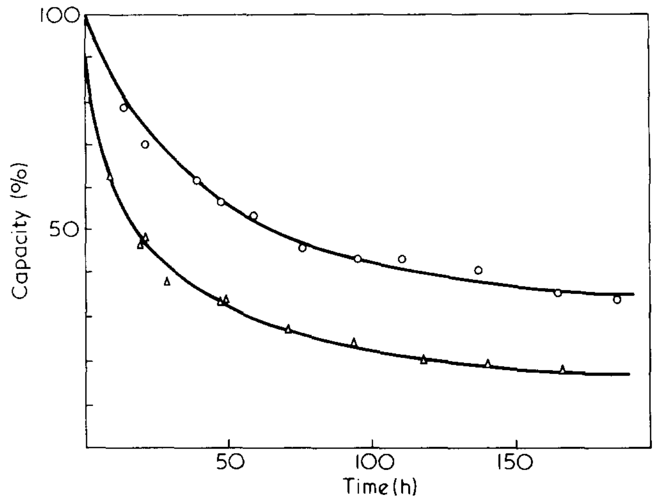

*Figure 5* Capacity loss of Amberlyst 15, H-form, in nitrogen (○) and water (△) at 200° C

### *Isothermal decomposition in water*

The measurements in an inert medium should give information about those decomposition effects which are only due to the nature and properties of the ion-exchange resins. However, it was shown that catalytic traces of moisture, which are present in the hygroscopic resins even after thorough drying[10], influence the decomposition considerably.

In the presence of an excess of water the decomposition rate increases (*Figure 5*). In contrast to the experiments in the gas phase, the capacity loss of Amberlyst 15 (H form) in water is caused solely by the hydrolysis of the ionogenic groups thus reversing the sulphonation reaction:

$$R - H + H_2SO_4 \rightleftharpoons R - SO_3H + H_2O$$

The split-off ionogenic groups can be titrated in the water phase. The total quantity of sulphuric acid was always molecularly equivalent to the losses in capacity.

### *Isothermal decomposition in 10 N $H_2SO_4$ and benzene*

The capacity loss of Amberlyst 15 (H form) in $H_2O$, 10 N $H_2SO_4$ and benzene at 190°C is shown in *Figure 6*. The decomposition effects in sulphuric acid are analogous to those in water; only the desulphonation rate increases caused by the increased proton concentration. Resulphonation of the matrix with sulphuric acid can be neglected because sulphonation occurs only at higher acid concentrations[11]. The styrene–divinylbenzene copolymer was not sulphonated detectably after heating for 60 h at 190°C in 10 N sulphuric acid.

The heat treatment of the polymeric acid in both water and sulphuric acid leads only to hydrolysis of the ionic group whereas the decomposition in benzene proved to be a more complex process. This was shown by elemental analysis of Amberlyst 15 (H form) after heating for 250 h in benzene (*Table 3*). With regard to a weight loss of 27%, 63% of the original sulphur has left the resin and the capacity decreases from 4.8 to 0.6 milliequivalent $-SO_3H$ groups/g. From this it can be concluded that, in addition to the residual $SO_3H$-groups, sulphur is bound in the resin with a molar ratio of S:O = 1:1.5. Therefore, it can be assumed that the hydrolysis of the ionic groups is accompanied by intramolecular (a) and intermolecular (b) formation of sulphones:

(a) $\text{Resin}-SO_3H + HO_3S-\text{Resin} \rightarrow \text{Resin}-SO_2-\text{Resin} + H_2SO_4$
or $\text{Resin}-SO_3H + \text{Resin} \rightarrow \text{Resin}-SO_2-\text{Resin} + H_2O$
(b) $\text{Resin}-SO_3H + C_6H_6 \rightarrow \text{Resin}-SO_2-C_6H_5 + H_2O$

It is known from literature[12] that monomeric arylsulphonic acids form sulphones during the reaction with aromatic hydrocarbons.

Finally, the strong decrease in capacity in benzene possibly results from the formation of a $\pi$-complex of the aromatic benzene ring and the sulpho-groups, thus polarizing the C–S bond and facilitating the decomposition.

### *Kinetics*

It has been shown that the decomposition in the gas phase and in benzene is caused by more than one reaction and

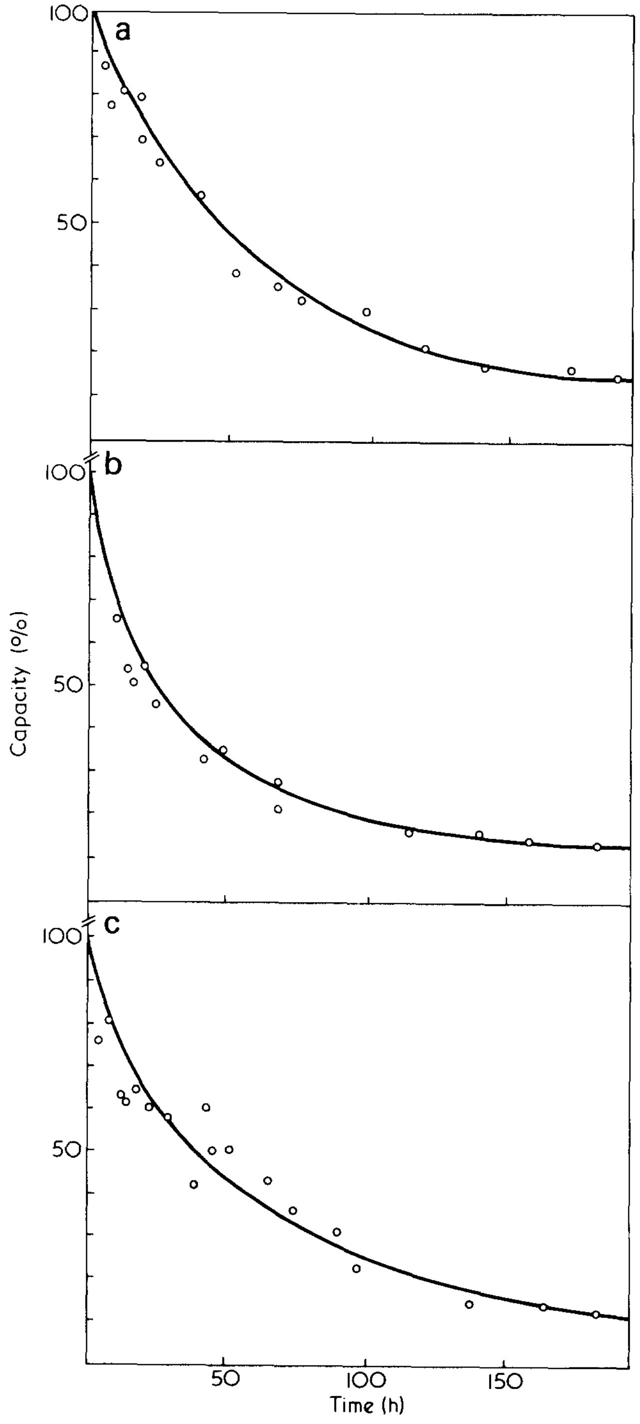

*Figure 6* Capacity loss of Amberlyst 15, H-form, in different media at 190°C (a) water (b) 10n sulphuric acid (c) benzene

*Table 3* Amberlyst 15 (H-form) – data of elemental analysis after thermal treatment in benzene at 190°C for 250 h

| Carbon (%) | Hydrogen (%) | Oxygen (%) | Sulphur (%) |
|---|---|---|---|
| 78.1 | 5.9 | 8.6 | 8.6 |

therefore no simple kinetic scheme was found. This is not true for the thermal treatment in the water phase. A second-order dependence on the sulphonic acid group concentration (capacity) is to be expected:

$$\text{rate} = k[\mathrm{RSO_3}^-]\ [\mathrm{H_3O^+}] \text{ and } [\mathrm{RSO_3}^-] = [\mathrm{H_3O^+}]$$

In *Figure 7* second-order kinetics is found. At high concentrations of sulphuric acid deviations from the linear curve are observed as was to be expected.

Summarizing the above results, it was shown that the thermal stability of sulphonated styrene divinylbenzene copolymers is limited by the chemical reactivity of the sulphonic acid groups which leads to hydrolytic cleavage of the C–S bond and, in other media than water, to the formation of sulphones.

## CONCLUSIONS

From this it can be concluded that the synthesis of polymeric sulphonic acids of higher thermal stability is possible only, if the ionic group is not bound directly to the aromatic ring thus avoiding hydrolysis.

Therefore, new ion-exchange resins have now been synthesized[13] possessing alkyl-spacer-groups between the aromatic polystyrene ring and the sulpho groups. In fact, a higher thermal stability was observed with them compared to standard commercial resins studied in this work.

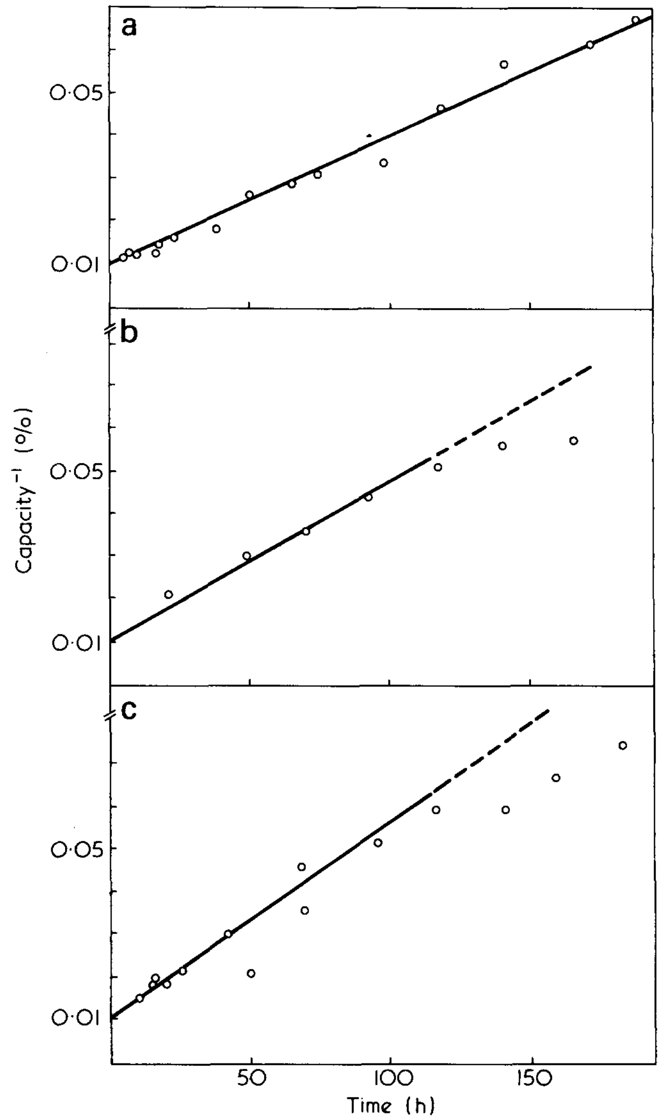

*Figure 7* Kinetics of desulphonation of Amberlyst 15, H-form (a) water at 190°C, (b) water at 200°C, (c) 10n sulphuric acid at 190°C

## REFERENCES

1 Polyanskii, N. G. and Tulupov, P. E. *Russ. Chem. Rev.* 1971, **40**, 1030
2 Polyanskii, N. G. *et al.*, *Russ. J. Phys. Chem.* 1971, **45**, 1615
3 Tulupov, P. E. and Karpov, O. N. *Russ. J. Phys. Chem.* 1973, **47**, 800
4 Leikin, Yu, A. et al. *Vysokomol. Soedin.* 1968, **A10**, 157
5 Karpov, O. N. et al. *Russ. J. Phys. Chem.* 1971, **45**, 995
6 Hall, G. R. et al. 'Ion Exch. Proc. Ind.', Pap. Conf. London 1969, 62
7 Kunin, R. et al. *J. Am. Chem. Soc.* 1962, **84**, 305
8 Kunin, R. et al. *Ind. Eng. Chem. Prod. Res. Dev.* 1962, **1**, 140
9 Gates, B. C. and Sherman, J. D. *Chem. Eng. Educ.* 1975, **9**, 124
10 Mohorcic, G. et al. *Ion Exch. Membr.* 1975, **2**, 107
11 Tulupov, P. E. et al. *Russ. J. Phys. Chem.* 1973, **47**, 81
12 Meyer, H. *Ann. Chem.* 1923, **433**, 327
13 Döscher, F. and Klein, J. in prep.