

Chemical modification of styrene–divinylbenzene copolymers by dialkyl phosphites

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Chloromethylated styrene–divinylbenzene copolymers were treated with dialkyl phosphites to obtain cation exchangers with phosphorus-containing acid groups. The gel and macroporous styrene–divinylbenzene (St–DVB) copolymers of Wofatit type were used. The influence of the phosphite ($R = CH_3, C_2H_5$) as well as of the copolymer structure (gel, macroporous) on the course of the phosphorylation and of the ester bond hydrolysis was investigated. The cation exchangers with $-PO(OH)(OR)$ functional groups were obtained and their main properties (density, swelling, ion exchange capacity, pK_a , thermal stability, i.r. spectra) were determined.

(Keywords: chloromethylated St–DVB copolymers; chemical modification; dimethyl and diethyl phosphite; cation exchangers; phosphorus-containing resins)

INTRODUCTION

Styrene–divinylbenzene copolymers are widely used for manufacturing many commercial ion exchange resins. The copolymers may have a gel or macroporous structure, the content of divinylbenzene in each being *ca.* 2–8% or 15–20%, respectively. The introduction of a chloromethyl group into the St–DVB polymeric matrix modifies its properties, and owing to the high mobility of the chlorine atom many further chemical reactions can easily be made^{1–4}. That is why the chloromethylated St–DVB copolymers have often been used in the laboratory for the preparation of many special ion exchangers.

In our previous studies we investigated the chemical modification of St–DVB copolymers of Wofatit type by the Friedel–Crafts reaction, using PCl_3 in the presence of $AlCl_3$ ⁵. The use of trimethyl and triethyl phosphites to obtain phosphonic cation exchangers was also successful⁶. No reports in the literature on the use of dialkyl phosphites in this reaction have been found.

EXPERIMENTAL

Materials

Chloromethylated St–DVB copolymers produced by VEB 'Chemie-kombinat Bitterfeld' (GDR) were used. They serve as intermediates for the production of ion exchange resins of Wofatit type on an industrial scale. The properties of the initial copolymers are given in Table 1. No additional purification of the phosphites (Fluka) was attempted.

Chemical modification

The modification was achieved by treating the starting chloromethylated St–DVB copolymers with an excess of dialkyl phosphite at the boiling temperature of the heterogeneous reaction mixture (copolymer + phosphite), i.e. 169°C–172°C and 174°C–177°C for dimethyl and diethyl phosphite, respectively.

To control the course of the modification reaction, samples of the copolymer were taken. After washing them with water and drying, phosphorus and chlorine contents were estimated. In this way the optimum time for the phosphorylation reaction to occur was found. The modified copolymers were called 'estronits', with the proper symbols indicating the phosphite used (DM, dimethyl phosphite; DE, diethyl phosphite) and the structure of the copolymer (G, gel structure; M, macroporous structure).

The phosphorylated copolymers were then treated with KOH or HCl to develop their ion exchange capacity (i.e.c.) by saponification of the ester bonds. Various concentrations of KOH (6% and 17%, by volume) and HCl (11.6% and 21%) solutions were examined. The course of the hydrolysis reaction was controlled by means of pH-metric titration of resin samples. The final products

Table 1 Characteristics of the initial St–DVB copolymers

Properties	Structure of the copolymer	
	gel	macroporous
Chlorine content (%)	17.7	17.8
Crosslinking (%DVB)	4	<i>ca.</i> 20
Shape of the granule	spherical	spherical
Colour of the granule	beige-yellow	beige-white
Particle-size distribution (mm)	d_{95} 0.42 d_5 1.20	d_{95} 0.40 d_5 1.20
Pores characteristics		
diameter (nm)	No	40–80
surface (cm^2/g)	geometric	20–30
volume (cm^3/g)	pores	0.35–0.50
Swelling (%vol.)		
water	0	5
methyl alkohol	10	20
toluene	110	60
saturated brine	0	10
dimethyl phosphite	14	32
diethyl phosphite	120	30
Bulk density (kg/dm^3)	0.67	0.37

(after hydrolysis) were called 'cation exchangers', with the same symbols as for the proper 'estronits'.

Analytic control of the modification reaction

The quantitative determination of the phosphorus and the chlorine contents was made for the samples that had previously undergone a mineralization with Eschka mixture at 750°C. To determine the phosphorus content (PO₄³⁻) the molybdenum-vanadium-phosphoric acid spectrophotometric method was applied⁷. The chlorine content (Cl⁻) was determined by means of an ion-selective electrode and a 'Radelkis' pX-meter (Hungary).

Characteristics of the resins

The following properties of the phosphorus-containing resins obtained were examined: bulk density and swelling in some solvents (Table 2); ion exchange capacity and pK_a of functional groups (Table 3) derived from titrimetric curves that have been published elsewhere⁸; thermal stability by means of derivatographic analysis on a Thermal Analyser Model 1100-OC (MOM, Hungary); i.r. spectra on an M-621 Perkin-Elmer Spectrophotometer (USA).

RESULTS AND DISCUSSION

As our studies have shown, the dialkyl phosphites applied are useful reagents for effecting the modification of chloromethylated St-DVB copolymers. The substitution of the chlorine atom in the -CH₂Cl group by a phosphorus-containing organic group can easily be achieved with these reagents. The introduction of phosphorus-containing ionogenic groups into the crosslinked matrix gave some cation exchange resins and sorbents with valuable properties.

As can be seen from Figures 1 and 2, the phosphorus content in the modified copolymers is influenced both by

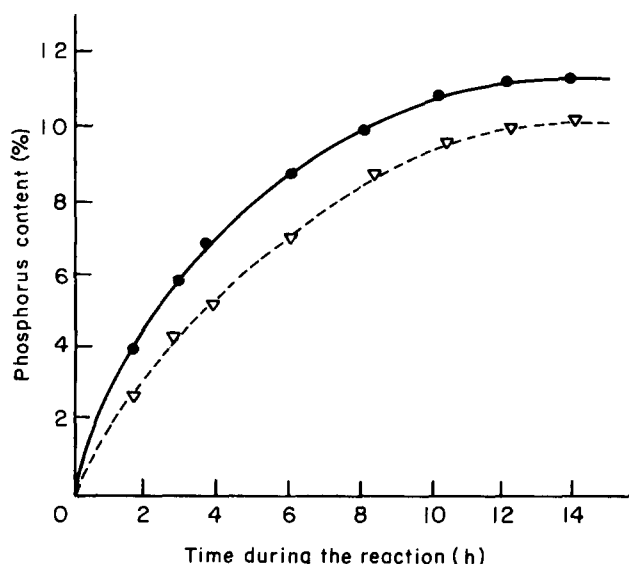


Figure 1 Modification of St-DVB copolymers by dimethyl phosphite: ●, gel; ▽, macroporous

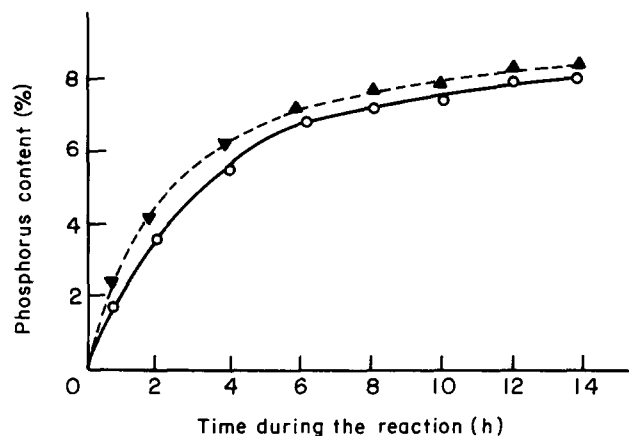


Figure 2 Modification of St-DVB copolymers by diethyl phosphite: ○, gel; ▽, macroporous

Table 2 Characteristics of the cation exchangers obtained

Properties	Cation exchange resin			
	DM-G	DM-M	DE-G	DE-M
Bulk density (kg/dm ³)	0.74	0.65	0.72	0.61
Swelling (%vol.)				
water	80	10	0	4
methyl alcohol	56	12	20	33
toluene	0	-10	40	50
saturated brine	30	32	10	20

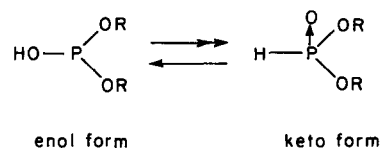
Table 3 Phosphorus content and ion exchange capacity of the modified St-DVB copolymers

Product	Phosphorus content (%)	Ion exchange capacity (meq/g)			
		Analytic	Static	pH-metric*	pK _a
Estronits					
DM-G	11.0	0-3.5	2.4	2.6	3.8
DM-M	9.8	0-3.2	2.1	2.2	3.1
DE-G	8.1	0-2.6	0.0	-	-
DE-M	8.4	0-2.7	0.4	-	-
Cation exchange resins					
DM-G	6.8	2.2-4.4	3.3	3.5	3.8
DM-M	6.7	2.2-4.4	2.9	3.2	3.3
DE-G	1.5 (P ^{III})	0.5	0.0	-	-
DE-M	2.0 (P ^{III})	0.6	0.5	-	-

* up to pH=9.0

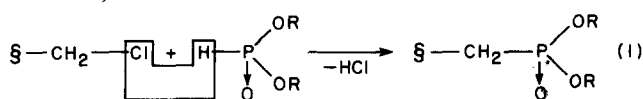
the kind of the dialkyl phosphite and by the copolymer structure. The products contained: 11.0 and 9.8% P when dimethyl phosphite was used; 8.1 and 8.4% P for diethyl phosphite (for gel and macroporous structure, respectively). When (CH₃O)₂POH was applied, a higher phosphorus content was attained in gel than in macroporous copolymer. This points to the fact that there is no steric hindrance and the reaction proceeds in a kinetic region. A quite different observation was made when (C₂H₅O)₂POH was used: the diffusion of diethyl phosphite into the polymeric matrix was decisive because of the molecular size of the reagent.

Considering the following structure of dialkyl phosphite



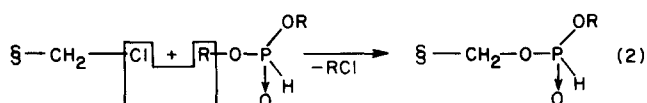
four various types of phosphorylation reaction have been taken into account.

'Acid', with C-P bond formation

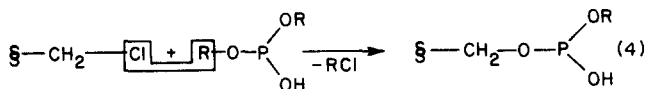
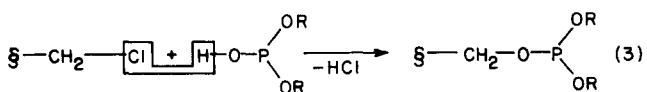


(where ξ is used to represent the St-DVB macromolecular matrix).

'Alkyl', with C-O-P bond formation



It can also be expected that the enol form of dialkyl phosphite can react according to the schemes



From Table 3 it may be seen that after hydrolysis the phosphorus content in DE products was diminished. By means of iodometric titration it was established that DE cation exchangers contained phosphorus as P^{III} . When diethyl phosphite was applied as a modifying agent the products showed no (or very little) ion exchange capacity.

For dimethyl phosphite, the resins obtained practically did not contain P^{III} and their ion exchange capacities were in good agreement with the expected ones (analytic ion exchange capacity). These observations, as well as the analysis of the gaseous reaction products (HCl, RCl), show that the manner of dialkyl phosphites addition to the chloromethylated St-DVB copolymers depends on the alkyl radical of phosphite. For dimethyl phosphite, the modification proceeds mainly according to scheme (1). When diethyl phosphite is applied, the same reaction proceeds mainly according to scheme (3). Although it is known that in standard conditions dialkyl phosphites occur in the keto form⁹, in the conditions of the modification reaction a displacement of the tautomeric equilibrium is possible. The different tautomeric equilibrium in dimethyl and diethyl phosphites is probably the reason for the various ways in which the modification can occur.

Our investigations on hydrolysis of estronits showed that the reaction proceeds in acidic media only. By using hydrochloric acid with concentrations 11.6% and 21.0%, the hydrolysis reaction was accomplished after 13 and 3 h, respectively. On the basis of titrimetric curves⁸, it was established that, in the conditions described, only half the ester groups were saponified. The hydrolysis of both O-R bonds was achieved by heating estronits with 30% HCl for 24 h at 98°C–100°C. But in these conditions a considerable degradation of the resin particles was observed.

The absorption bands in the i.r. spectrum of the initial macroporous copolymer (Figure 3A) correspond to vibrations of the groups listed in Table 4. In the spectra of estronits (Figures 3B, C) there are no absorption bands at 670 cm^{-1} , due to the absence of C-Cl bonds, while the vibration at 830 cm^{-1} is too broad and too strong to be assigned to C-Cl only. In this region bending vibrations of C-H can also be observed. The absorption at 1180 and 1150 cm^{-1} was assigned to the stretching vibrations of P-OCH₃ and P-OC₂H₅, respectively. Estronits show very strong bands in the range 1080–900 cm^{-1} and 1300–1200 cm^{-1} . These bands can also be observed in the spectra of the proper cation exchangers, but here the

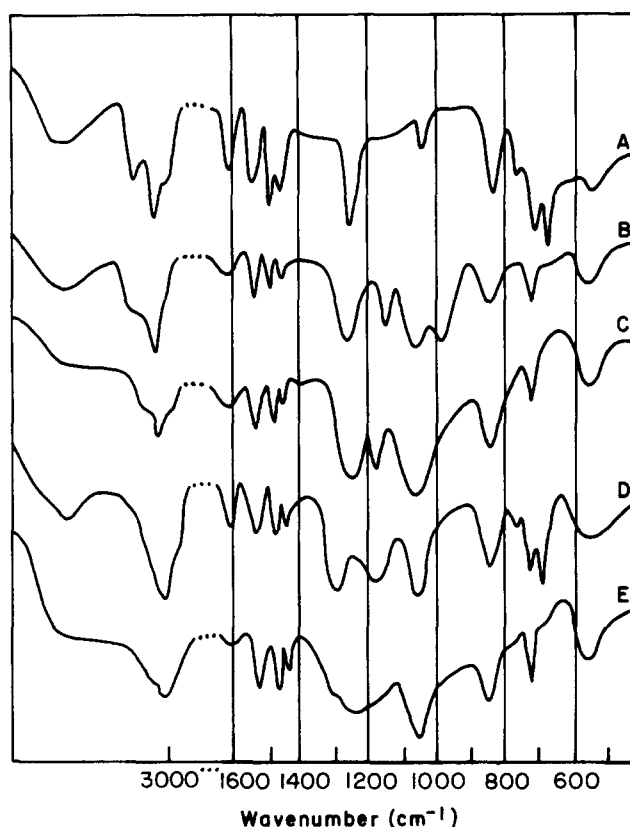


Figure 3 Infra-red spectra (in KBr) of the macroporous chloromethylated St-DVB copolymer (A), estronits DE-M (B) and DM-M (C), cation exchangers DE-M (D) and DM-M (E)

Table 4 Groups producing the absorption bands in the i.r. spectra of the initial copolymer

Group	Vibration	Wavenumber (cm^{-1})	
C-Cl	stretching	830, 670	
C-H	side chain	bending	1020, 830, 690, 530
		wagging	1270
CH ₂	scissoring	1455, 1430	
C-C	aromatic stretching	1520	
C-H	ring stretching	3020	

bands are sharper. The clear difference appears in the spectrum of DE estronits where the absorption at 950 cm^{-1} can be assigned to the C-O-P group. This band is not found in the spectra of DE cation exchangers (Figure 3D), so this can prove that the hydrolysis causes a cleavage of the C-O-P bond. In the spectra of DE cation exchangers the absorption at 690 cm^{-1} was also recorded. This is a result of C-Cl bond formation during the hydrolysis and it was proved by chlorine detection in DE cation exchangers. The analysis showed 13.1 and 12.7% Cl in gel and macroporous products, respectively. In the spectra of estronits and cation exchangers some changes at 1180 and 1150 cm^{-1} can also be seen. In the spectra of cation exchangers (Figure 3D, E) the broader absorption bands in this range are observed because the strong P=O vibrations overlap part of the spectrum and part of the P-OR bands cannot be observed.

The thermal properties of the products obtained were studied by means of a Paulik-Paulik-Erdey derivatograph system, and t.g., d.t.g. and d.t.a. curves were recorded simultaneously. The measurements were made

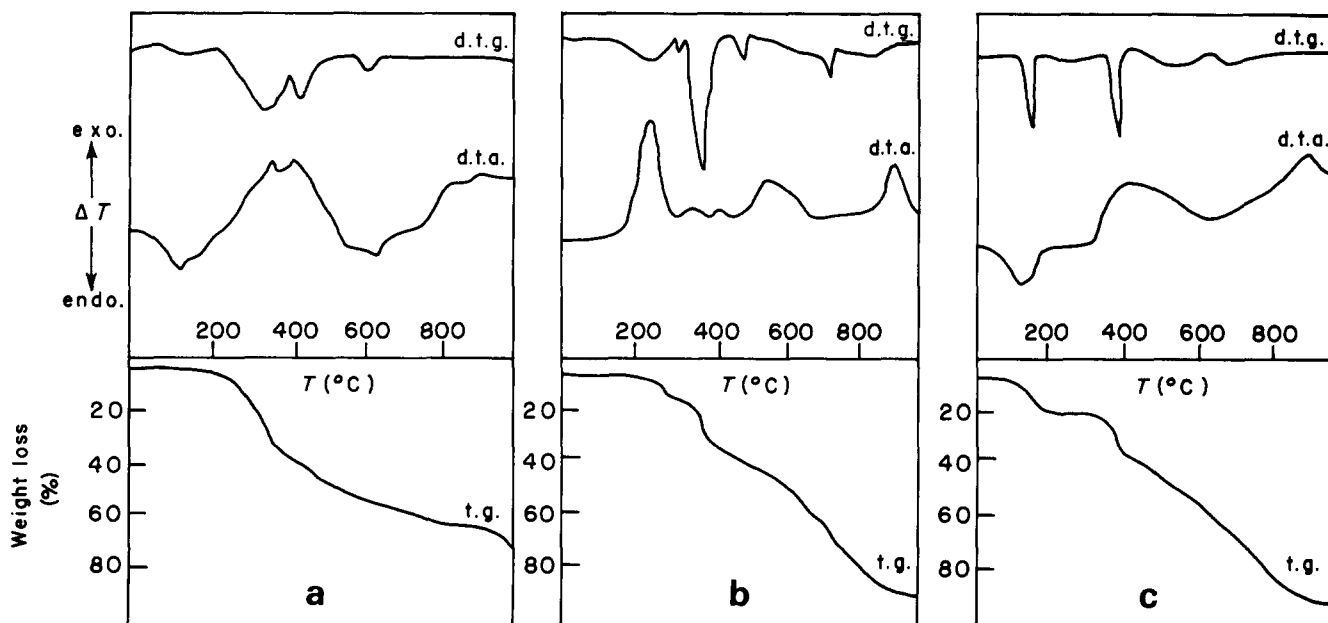


Figure 4 Thermal analysis curves for (a) chloromethylated St-DVB copolymer, (b) estronit DM-M, (c) cation exchanger DM-M

in an atmosphere of air (20 l/h) in a temperature range of 20°C–1000°C at the heating rate of 5 K/min.

Thermal examination of the resins reveals their high stability. The thermal behaviour of DM-M estronit and DM-M cation exchanger in comparison with initial St-DVB copolymer are discussed below. The more detailed thermal studies of the other phosphorus-containing resins will be published elsewhere.

For the chloromethylated St-DVB copolymer as well as for the DM-M cation exchanger (Figure 4a, c), a marked endothermic effect is observed on the d.t.a. curve in the range 65°C–180°C. The t.g. curves show 2.2% (St-DVB) and 17.7% (DM-M cation exchanger) loss of weight, respectively. The effect is due to the loss of water. The transformation described is not observed for DM-M estronit (Figure 4b). It may be explained by strong hydrophobic properties of the $-\text{PO}(\text{OCH}_3)_2$ groups. For DM-M cation exchanger, the main degradation process is seen in the temperature range 350°C–400°C; the maximum point of degradation rate is at 380°C. The t.g. curve shows 17.1% weight loss in this range. This exothermic effect can be attributed to the splitting off of some phosphoric compounds. The same transformation

is also observed for DM-M estronit, but in this case it proceeds by the degradation process in the range 155°C–300°C. The higher thermal stability of DM-M cation exchanger than for proper estronit is probably due to the more stable acidic groups P-OH. For both resins, the conversion at the temperature above 400°C is caused by destructive oxidation processes. This exothermic effect is observed up to 1000°C and is accompanied by over 90% weight loss.

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