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CORRELATION BETWEEN CHEMICAL AND PHYSICAL CHARACTERISTICS AND ADSORPTION PROPERTIES OF SOME STYRENE COPOLYMERS

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SUMMARY

The gas chromatographic retention properties of Chromosorb 103 under different thermal treatment conditions are reported. The behaviour is compared with that of similar previously studied polymers, Porapak Q and Chromosorb 101 and 102.

The gas chromatographic data are discussed in relation to chemical and physical results obtained by X-ray diffraction, differential thermogravimetric analysis, differential scanning calorimetry and surface area measurements.

INTRODUCTION

Porous polymers have been used extensively as adsorbents of organic compounds in air. Developments in the manufacture of such materials have led to a wide range of possibilities for the selection of a suitable trapping medium for a given determination of volatiles and therefore the study of polymer properties and characteristics is necessary for anyone working in this field. Methods for the preconcentration of organics on porous polymers have been reviewed¹, but some aspects of their use are not well defined.

In a previous paper² it was pointed out that different thermal treatments influence the adsorption properties of some styrene copolymers. Only when adsorbents were conditioned at the temperature limit suggested by the manufacturer was linearity of the relationship $\ln V_g$ vs. $1/T$ (where V_g is the specific retention volume and T is the absolute column temperature) completely achieved. Moreover, such treatment was particularly suitable for good cleaning of the polymeric surface³.

In this paper, a study of the influence of thermal pre-treatment on the adsorption properties of Chromosorb 103 is reported. The correlation between physical and chemical characteristics and adsorption properties as a function of conditioning temperature is discussed for Porapak Q and Chromosorb 101, 102 and 103. The chemical and physical characteristics were evaluated by X-ray diffraction analysis, differential scanning calorimetry (DSC), thermogravimetry and surface area measurements by the BET nitrogen adsorption method.

EXPERIMENTAL

Chromosorb 101, 102 (60–80 mesh), 103 and Porapak Q (80–100 mesh) were supplied by Supelchem (Milan, Italy). Analytical-reagent grade solvents (*n*-hexane, benzene, acetone and 2-propanol) were used without further purification, with vapour-phase injection.

The gas chromatographic apparatus, columns, carrier gas, experimental conditions for evaluation of V_g and the computation procedure have been described previously². The analysis of volatile products was performed as described earlier³.

For X-ray analysis, Cu $K\alpha$ radiation was employed. The DSC measurements were carried out with a Du Pont 910 calorimeter and thermogravimetric analysis with a Mettler thermobalance; both the analyses were performed in a dynamic nitrogen atmosphere. For scanning electron microscopy a Siemens Autoscan was utilized.

RESULTS AND DISCUSSION

Chromosorb 103 was conditioned at 150, 200 and 275°C, the temperature limit suggested by the manufacturer.

The specific retention volumes of model adsorbates, *viz.*, acetone, 2-propanol, *n*-hexane and benzene, were determined at different column temperatures. The V_g values were the means of at least three measurements carried out under different ageing conditions and their repeatability was better than $\pm 1\%$. Fig. 1 shows plots of retention volumes against treatment temperature.

The retention volumes increased with increasing pre-treatment temperature for all the adsorbates. This increase does not appear to be linked to the nature of the adsorbate, as it was similar for all the model molecules.

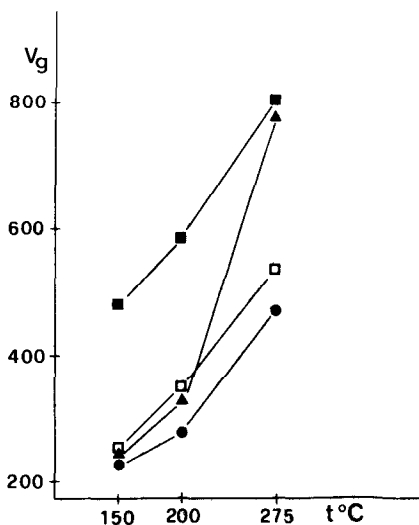


Fig. 1. Plots of specific retention volumes, V_g (ml g^{-1}), versus pre-heating temperatures, t (°C). ■ Benzene, column temperature 80°C; ▲ 2-propanol, column temperature 60°C; □ *n*-hexane, column temperature 80°C; ● acetone, column temperature 60°C.

The relationship between $\ln V_g$ and the reciprocal of the column temperature was examined as a function of different conditioning temperatures. Linearity was achieved for all the adsorbates, independent of the thermal treatment. In Table I the regression parameters are reported. The errors in the values of the slope and the intercept at a confidence level of 95%, the correlation coefficient, ρ , and the residual variance, s_{yx}^2 , are also given.

TABLE I

VALUES OF THE CONSTANTS IN THE EQUATION $\ln V_g = (A/T) - B$ ON CHROMOSORB 103 PRE-HEATED AT DIFFERENT TEMPERATURES

Compound	Pre-heating temperature (°C)	Column temperature range (°C)	A	B	ρ	s_{yx}^2
Acetone	150	60-130	5759 ± 24	11.9 ± 0.1	0.9996	6.17 · 10 ⁻⁴
2-Propanol		60-130	5925 ± 38	12.4 ± 0.1	0.9991	1.42 · 10 ⁻³
Benzene		80-150	6478 ± 42	12.1 ± 0.1	0.9990	1.32 · 10 ⁻³
n-Hexane		80-150	6712 ± 44	13.4 ± 0.1	0.9990	1.34 · 10 ⁻³
Acetone	200	60-130	5821 ± 34	11.9 ± 0.1	0.9992	1.01 · 10 ⁻³
2-Propanol		60-130	6140 ± 40	12.7 ± 0.1	0.9993	8.11 · 10 ⁻⁴
Benzene		80-150	6452 ± 39	11.9 ± 0.1	0.9992	8.52 · 10 ⁻⁴
n-Hexane		80-150	6739 ± 45	13.2 ± 0.1	0.9991	1.11 · 10 ⁻³
Acetone	275	60-130	6669 ± 107	13.8 ± 0.3	0.9948	6.70 · 10 ⁻³
2-Propanol		60-130	7029 ± 76	14.5 ± 0.2	0.9975	3.93 · 10 ⁻³
Benzene		80-150	6622 ± 31	12.1 ± 0.1	0.9995	4.66 · 10 ⁻⁴
n-Hexane		80-150	7035 ± 35	13.7 ± 0.1	0.9995	5.25 · 10 ⁻⁴

The values of the A parameter indicate that an increased interaction occurs when the conditioning temperature is increased.

The chromatograms of volatile products released on heating Chromosorb 103 and trapped as described previously³ are shown in Figs. 2 and 3.

Good cleaning of the adsorbent surface was obtained by conditioning the polymer at the temperature limit for at least 3 h; however after 48 h the chromatogram showed only a few peaks.

The results indicate that the retention behaviour of Chromosorb 103 as a function of its thermal pre-treatment is similar to that of other polymers studied previously^{2,3}. A difference is that for Chromosorb 103 the relationship $\ln V_g$ vs. $1/T$ is linear even when the conditioning temperature is lower than the limit. However, it must be remembered that Chromosorb 103 is a cross-linked polystyrene polymer⁴. Non-linear relationships were obtained for Porapak Q and Chromosorb 101 and 102, as reported in a previous paper².

The above behaviour may be attributed to glass transitions taking place in the adsorbents in the temperature range examined. It is well known that chromatographic techniques can be employed to study glass transitions in polymers⁵⁻⁷.

To investigate this aspect, X-ray diffraction and DSC analyses were performed on Porapak Q and Chromosorb 101, 102 and 103. The X-ray diffraction curves

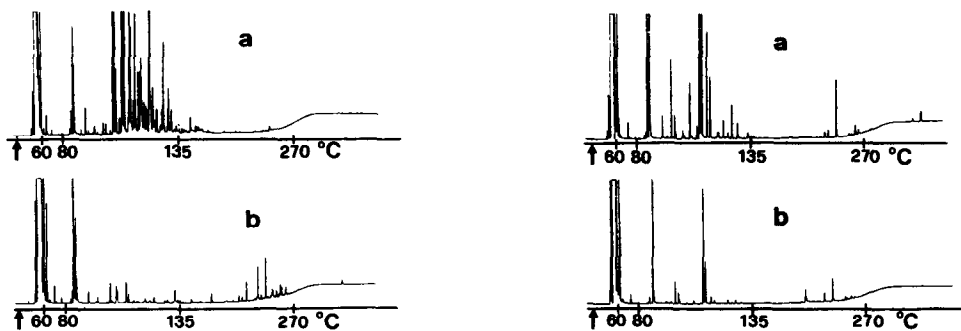


Fig. 2. Glass capillary chromatogram of Chromosorb 103 volatile products at (a) 150°C and (b) 200°C. Temperature: isothermal at 60°C for 3 min, programmed from 60 to 80°C at 8°C min⁻¹, from 80 to 135°C at 4°C min⁻¹ and from 135 to 270°C at 10°C min⁻¹. Injection mode: on-column. Detector temperature, 320°C, attenuation × 32.

Fig. 3. Glass capillary chromatogram of Chromosorb 103 volatile products at (a) 275°C and (b) 275°C after heating for 48 h. Experimental conditions as Fig. 2.

showed that all the polymers were amorphous, both before and after treatment at the temperature limit. Only for Chromosorb 103 did the diffraction curves show any characteristic peaks, as shown in Fig. 4. This polymer probably has some regions of crystallinity related to its higher degree of cross-linking. However, the diffractogram peaks disappeared when Chromosorb 103 was conditioned at the temperature limit.

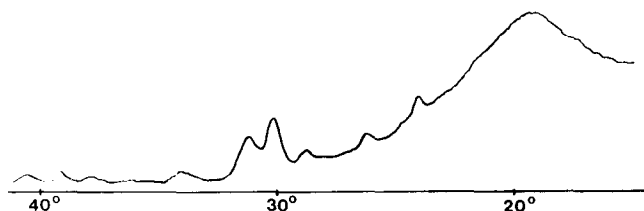


Fig. 4. X-ray diffraction curve of Chromosorb 103. Cu K α radiation.

DSC results are presented in Figs. 5 and 6. Porapak Q and Chromosorb 101 and 102 did not show phase transitions in the temperature range used. According to X-ray diffraction, only Chromosorb 103 produced phase transitions between 180 and 200°C, which disappeared after treatment at the temperature limit. It is important to note that for Chromosorb 103 the $\ln V_g$ vs. $1/T$ relationship is linear, independent of the thermal treatment. Moreover, it is interesting that the temperature limits suggested by the manufacturers are largely below the decomposition temperatures (Figs. 5 and 6).

These results do not prove the existence of any glass transition. However, Hradil and Švec⁸ obtained a negative result in experiments involving DSC for a styrene-divinylbenzene copolymer. They observed deviations from linearity of the retention diagrams at a temperature (T_g) corresponding to the glass transition of amorphous polystyrene. Furthermore, on heating the copolymer above T_g sintering

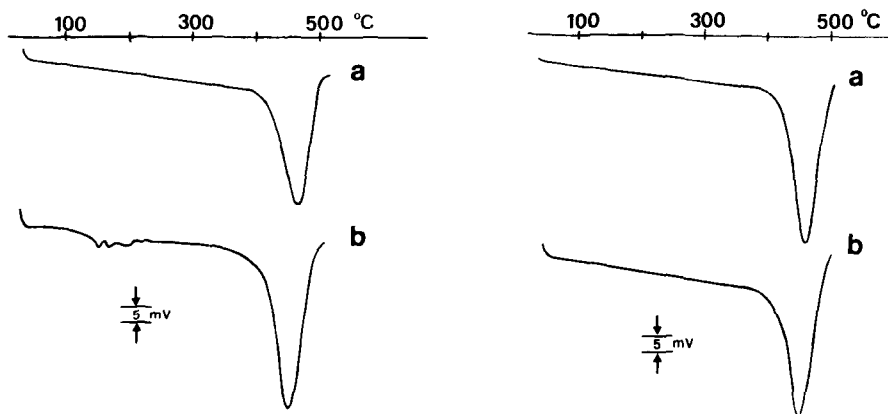


Fig. 5. DSC thermogram of (a) Porapak Q and (b) Chromosorb 103. Sample, 10 mg; heating rate, $20^{\circ}\text{C min}^{-1}$.

Fig. 6. DSC thermogram of (a) Chromosorb 101 and (b) Chromosorb 102. Experimental conditions as in Fig. 5.

of the porous structure occurred, which was reflected by a decrease in the specific surface area. Table II shows the specific surface area measured by the BET nitrogen adsorption method before and after conditioning at the temperature limit. Polymer samples were treated under vacuum at room temperature for a long period (several days) before the measurements. The surface area values were invariant for all the polymers, the variations being within the limits of experimental error. Moreover, scanning electron microscopy did not reveal any changes in the porous structure. Therefore, it is concluded that no glass transitions take place for Porapak Q and Chromosorb 101, 102 and 103.

Anomalies in the retention parameters may be caused by the release of volatile products on heating. Chromatograms of these materials have been presented in a previous paper³ and their nature was investigated by gas chromatography-mass spectrometry⁹. Most of the compounds were alkyl derivatives of benzene, styrene, divinylbenzene and naphthalene.

The weight losses obtained from thermogravimetric analysis between 20°C and the temperature limits were as follows: Porapak Q, 0.05; Chromosorb 101, 1.53;

TABLE II

SPECIFIC SURFACE AREAS OF THE SORBENTS BEFORE AND AFTER CONDITIONING AT THE TEMPERATURE LIMIT

Polymer	S_g (m^2/g)*	
	A	B
Porapak Q	557	537
Chromosorb 101	11	10
Chromosorb 102	314	334
Chromosorb 103	19	18

* Surface area: A, before heating; B, after heating.

Chromosorb 102, 0.12; and Chromosorb 103, 3.80%. Such losses vary according to the type of polymer, but are not very large and are in agreement with an unchanged surface area.

The released organics are probably physically adsorbed on the polymer surface. Vacuum treatment, carried out before area measurements, was able to remove these impurities like thermal treatment at the temperature limit. Such organics occupy some adsorption sites, which become available after thermal treatment at the temperature limit for at least 3 h. Therefore, the adsorption properties may be fully explained only under such conditions.

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