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Surface Chemistry of Polymers
The Influence of Thermal and Chemical Treatments on the Surface Properties of Polyvinylchloride

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Summary. The influence of thermal and chemical treatments (tetrahydrofuran and dioxane) on the adsorption properties of polyvinylchloride is investigated by gas chromatographic methods. It is shown, that heating to the glass-transition temperature has an erasing effect. Methanol was used as the main molecular probe.

1. Introduction. – It was shown [1] that heating PVC. to its glass-transition temperature (near 354 K), did not affect the isosteric heat of adsorption of N_2 at low temperature, for surface coverages θ between 0.2 and 1. However, the surface area of a typical sample of unstabilised PVC. would decrease from 2.05 to 1.80 $m^2 g^{-1}$ and its density at room temperature (in nitrogen gas) changed from (1.46 ± 0.01) g cm^{-3} to (1.40 ± 0.02) g cm^{-3}.

The effects of thermal and chemical treatments on the surface of PVC. have now been investigated by using gas-solid chromatography (GSC.). This method gives reliable results for the heats of adsorption at low coverage, as shown by *Kiselev et al.* [2]. Some significant changes, reversible and irreversible, have been detected, and in some cases they were checked against static adsorption measurements at low pressure.

2. Experimental. – The measurements were carried out with a *Carlo Erba* (Fractovap Mod D) chromatograph, having a double column and a thermal conductivity detector.

The powdered polymer (PVC., type G unstabilized from *Lonza AG.*) was packed in tubes of diameter 0.4 cm and of lengths varying between 25 and 80 cm.

Before the runs, the apparatus was flushed for a minimum of 24 h with the carrier gas (helium). In view of the low surface energy of the polymer, it was assumed that the surface was virtually clean after the treatment.

The adsorbates were methanol (*Siegfried*, p.a., $>99\%$), neopentane (*Fluka*, $>99\%$), tetrahydrofuran (*Merck*, p.a., $>99\%$), dioxane (*Merck*, Uvasol) and sulfur dioxide (*Fluka* puriss, $>99{,}97\%$). The quantities of adsorbate injected into the chromatograph varied between 0.2 and 20 µl for liquids and between 0.05 and 0.25 ml for gases, and the flow rate was usually of about 6 cm^3/min. In a typical experiment, the temperature was gradually increased from room temperature to 365 K, and then decreased. The flow rate w of the carrier gas was measured after the column, and at room temperature (it was the same for all temperatures). For every temperature the corrected retention volume V'_{Rc} was determined from the corresponding retention times by using the relation (1) [2]:

$$V'_{Rc} = (t_R \cdot w \cdot j)\ (T_c/T_o) \qquad (1)$$

where t_R is the net retention time of the adsorbate, T_c and T_o are the temperatures in the column and in the flow-meter,

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w is the flow-rate of carrier gas measured at T_o, and j is the correction of *Martin* given by

$$j = (3/2)\,[(p_i/p_o)^2 - 1]/[(p_i/p_o)^3 - 1] \qquad (2)$$

where p_i and p_o are the pressures at the entrance and at the exit of the column.

Static measurements of isotherms were carried out in a standard volumetric B.E.T. apparatus, described earlier [1] [3]. Accurate pressure measurements between 10^{-3} and 1 Torr were taken with a *Pirani* gauge (L.K.B. *Autovac* type 2394B).

3. Results and discussion. – The standard theory of GSC. [2] leads to the fundamental equation

$$\ln V'_{Rc} = -\Delta H_{ads}/RT + \text{constant} \qquad (3)$$

where V'_{Rc} is the corrected volume of retention for the adsorbate under investigation, and ΔH_{ads} is a quantity practically equal to the isosteric heat of adsorption at low coverage ($\theta \to 0$).

Consequently, a plot of ln (V'_{Rc}) against (1/T) should yield a straight line with a slope equal to $-\Delta H_{ads}/R$. Equation (3) is valid for a temperature range of about 60 degrees, if ΔH_{ads} does not vary too much with temperature. *Thermal treatment:* Fig. 1 shows the result for a sample of PVC. (type G, unstabilised), which had never been heated before. One obtains *two* values for the heat of adsorption of methanol:

$$\Delta H_{ads} = -(42.7 \pm 1.2)\ \text{kJ/mol} \quad \text{(first temperature increase).}$$

and

$$\Delta H_{ads} = -(29.4 \pm 0.8)\ \text{kJ/mol} \quad \text{(temperature descent, and all subsequent runs)}$$

These results suggest that during the *first* heating to the glass-transition temperature, the polymer changes its structure irreversibly, from a slightly unstable form to a more stable form.

This is also suggested by heat capacity measurements on PVC., carried out by *Alford & Dole* [4]. These authors found that the C_p curve for the *first* temperature increase was different of those obtained for all subsequent runs.

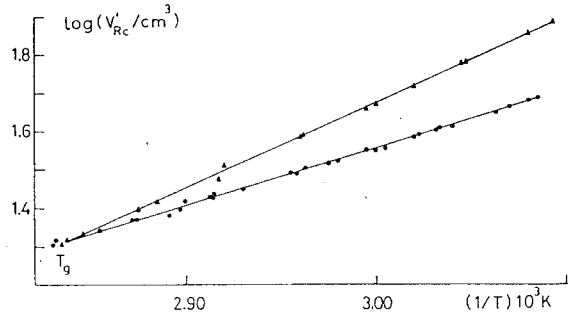

Fig. 1. *Gas-solid chromatography of methanol on PVC., between 298 and 355 K.* (▲) First temperature increase. (●) Temperature decrease and all subsequent runs. Each point is the average of 2–4 independent measurements.

A plausible explanation is the possibility of some chain rearrangement occurring as the polymer reaches T_g for the first time (it is manufactured near room temperature).

The change does not occur exclusively at T_g, as revealed by series of runs, where the upper temperature was gradually increased from about 320 to 365 K. The changes in the slopes (and hence in ΔH_{ads}) show that the degree of transformation is temperature-dependent, and complete at T_g.

The change in heat of adsorption at low coverage was confirmed by static measurements of methanol adsorption on PVC. Fig. 2 shows the low pressure isotherms

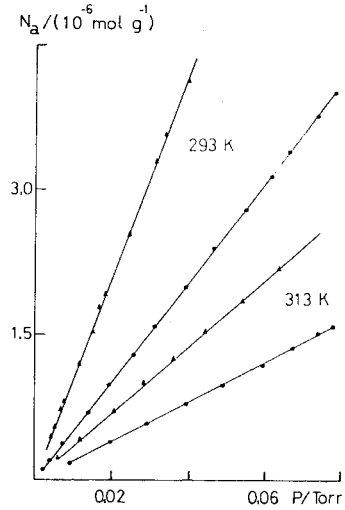

Fig. 2. *Static isotherms for the adsorption of methanol on PVC., at 293 and 313 K.* (▲) Untreated and (●) thermally treated sample.

measured at 293 and 313 K, for a sample before and after heating to T_g. These linear isotherms give the following isosteric heats of adsorption [3]:

$Q^{st} = -41.0 \pm 1.0$ kJ/mol (before heating)

$Q^{st} = -33.0 \pm 1.0$ kJ/mol (after heating)

With sulfur dioxide, the same effect was observed by GSC., and the results were

$\Delta H_{ads} = -(41.8 \pm 0.8)$ kJ/mol (first run, temp. increase)

$\Delta H_{ads} = -(25.5 \pm 0.5)$ kJ/mol (temperature descent)

Similar experiments performed with neo-pentane did *not* reveal any change in the heats of adsorption before and after the thermal treatment of PVC. The insensitivity of this molecule to the modifications in the polymer may be related to the rather large cross-sectional area of neo-pentane (40 Å²) [5] against 22 Å² for methanol and 20 Å² for SO_2 [6].

Fig. 3 shows the isotherms obtained from GS. chromatograms, following the method of *Kiselev et al.* [2].

The three isotherms (T = 273, 283 and 293 K) are practically identical for the samples, before and after heating to T_g. The various results for neo-pentane are listed in Table 1.

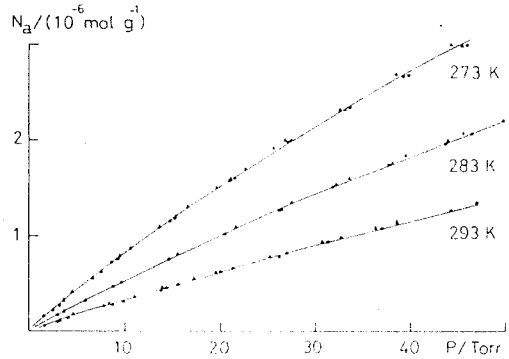

Fig. 3. *Isotherms for the adsorption of neopentane on PVC., determined by GSC. at 273, 283 and 293 K.* (▲) Untreated and (●) thermally treated sample.

Table 1. *Heats of adsorption at low coverage for neo-pentane on PVC.* (in kJ/mol)

	Untreated	Treated sample
ΔH_{ads} (eqn 1)	−27.6 ± 0.4	−26.9 ± 0.4
Q^{st} (isotherms)	−33.0 ± 1.0	−33.0 ± 1.0

The two sets of results differ by 6 kJ/mol. This corresponds to the observation made by *Kiselev et al.* [2], that the results derived from the isotherms are usually higher (this applies to isotherms derived from chromatographic measurements, as above, and not to static isotherms).

Chemical treatments. PVC., previously heated to the glass-transition temperature, was submitted at 323 K to a chemical treatment from the gas phase, by injecting small amounts of tetrahydrofuran (THF) and dioxane into the chromatograph. After the solvent was passed through the column, the apparatus was flushed with the carrier gas for at least 24 hours, and the adsorption of methanol was investigated, as described above. Table 2 shows the results for the heats of adsorption.

Table 2. ΔH_{ads} *of methanol on PVC., for various chemical treatments* (values in kJ/mol)

treatment	temp. increase	temp. decrease
blank runs	−29.4 ± 0.8	−29.4 ± 0.8
12 × 10 µl THF	−30.5 ± 0.8	−29.0 ± 0.8
15 × 20 µl THF	−35 ± 1	−28.5 ± 0.8
40 × 20 µl THF	−36 ± 1	−28 ± 1
15 × 20 µl dioxane	−35.1 ± 0.9	−30.1 ± 0.8

The results show clearly the effect of THF and of dioxane, two solvents for PVC. The most striking feature is the reversibility of the effect, which is erased after the first passage at T_g. Hence, we may assume that the solvents cause some perturbations in the ordering of the polymer chains at the surface, which disappear when the solid reaches the glass-transition temperature. The phenomena is similar to the case of the original polymer described above.

Both results illustrate the particular interest in using methanol as a molecular probe, in order to detect by chromatography, small effects on the surface of PVC. The method will be extended to other polymers.

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REFERENCES

[1] *E. A. Perret, H. F. Stoeckli & C. Jeanneret*, Helv. *55*, 1987 (1972).
[2] *A. V. Kiselev & Ya. I. Yashin*, 'La Chromatographic Gaz-Solide', Masson & Cie, Paris 1969; *L. D. Belyakova, A. V. Kiselev & N. B. Kovaleva*, Bull. Soc. chim. France *1967*, 285.
[3] *H. F. Stoeckli*, Helv. *55*, 101 (1972).
[4] *S. Alford & M. Dole*, J. Amer. chem. Soc. *77*, 4774 (1955).
[5] *P. G. Hall & H. F. Stoeckli*, Trans. Farad. Soc. *65*, 3334 (1969).
[6] *A. L. McClellan & H. F. Harnsberger*, J. Colloid Interface Sci. *23*, 577 (1967).