

Principal Factors in Preparing Columns for Inverse Gas Chromatography

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ABSTRACT: The principal factors in preparing columns for inverse gas chromatography (IGC) were investigated, with particular interest in obtaining a distinct Z-shaped retention diagram which can be seen near at the glass transition or melting temperature of a polymer by using a small amount of the polymer. The use of a silane-treated support of a relatively large surface area was found to be favorable. It was also found effective to use a casting solvent that gives a smooth and glassy polymer film. The Z-shaped retention curve became more distinct as the column was loaded with more polymer. The solute retention mechanism at an extremely low polymer loading may differ from that at an ordinary polymer loading. Plots of $\log V_N$ vs. $1/T$ (V_N , net retention volume, T , column temperature) for the columns prepared at various polymer loadings were examined to find the best polymer loading. The retention diagram of the initial heating-up measurement was different from that of the subsequent measurement, and this may be attributed to thermal hysteresis.

KEY WORDS Inverse Gas Chromatography / Z-Shaped Curve / Glass Transition Temperature / Melting Temperature / Poly(methyl methacrylate) / Poly(ethylene oxide) / Chromosorb / Column Preparation / Thermal Hysteresis / Retention Mechanism /

Inverse Gas Chromatography (IGC) is a very simple and useful method for obtaining information on polymers, such as the glass transition temperature, the melting temperature, the degree of crystallinity, and the solubility parameter.¹⁻⁹ IGC has also been used to characterize multicomponent polymer systems such as block copolymers or polymer blends.¹⁰⁻¹⁴ We have already reported a morphological study on the physical blends of poly(ethylene oxide) with polystyrene by IGC.¹⁵

The effects of the following factors on IGC diagram have been reported: thickness of coated polymer,^{6,16, 17} flow rate of a carrier gas,⁶ and the injection size of a solute.¹⁸ However, very few studies have been made on the conditions for the preparation of columns for IGC.

In the IGC study of a polymer, a clear Z-shaped retention diagram, attributable to the intrinsic properties of the polymer, can be expected with a small loading polymer. Because complexity such

as a diffusion process would also come about, loading of a large amount of the polymer was not preferable.

It is not easy to prepare small loading columns and we have focused our attention on this problem. In this paper, we discuss the principal factors in preparing IGC columns, to include the surface nature of solid supports, solvent, thermal hysteresis, polymer loading, and the mechanism of solute retention.

EXPERIMENTAL

Materials

All the reagents were used as received. Benzene, chloroform, ethylene glycol monomethyl ether, and acetone were used to disperse a polymer on solid supports. *n*-Dodecane and *n*-octane were used as solutes for gas chromatography. Various kinds of Chromosorb (60—80 mesh) purchased from Johns-

Manville Co. were employed as solid supports of gas chromatographic columns: G NAW, G AW-DMCS, W NAW, W AW-DMCS, P NAW, and P AW-DMCS, where NAW and AW-DMCS stand for Non Acid Washed and Acid Washed-Dimethylchlorosilane-treated, respectively. Poly(methyl methacrylate) (PMMA) was prepared by radical polymerization in benzene at 60°C ($M_n = 70.4 \times 10^3$ by gel permeation chromatography), with AIBN as the initiator. Poly(ethylene oxide) (PEO) was a commercial product, PEO #6000, $M_n = 4600$, Nakarai Chemicals).

Columns

A solution was made by dissolving calculated amount of a polymer in a solvent. A known portion of a Chromosorb was immersed in this solution. The solvent was allowed to evaporate at room temperature with gentle stirring, and the Chromosorb was completely dried at 45°C under slightly reduced pressure. The amount of the polymer load was determined by the weight increase in the Chromosorb before and after this procedure. A weighed amount of the polymer-loaded Chromosorb was tightly packed into a 1.5 m × 3 mm i.d.

stainless steel column by means of a mechanical vibrator. The column was dried for 5 h at 45°C under a constant stream of helium. The columns prepared under various conditions are summarized in Table I.

The BET-surface area of each support was measured by the one-point N_2 -adsorption method using a gas chromatograph by the continuous flow technique at the temperature of liquid nitrogen. The BET-surface areas of various Chromosorbs are summarized in Table I.

Gas Chromatography

Gas chromatograms were recorded on a Yanaco G1800 equipped with a thermal conductivity detector, using helium as a carrier gas and air as a noninteracting marker. In all measurements, the carrier gas flow rate and the injection temperature were fixed at 20 ml-N.T.P. min^{-1} and 100°C, respectively. 0.6 μl of *n*-dodecane or *n*-octane and 0.4 μl of air were injected simultaneously. The net retention time t_R (min) from the air peak to the front side of the solute peak was measured. The t_R is defined in terms of the specific retention volume V_g (ml g^{-1}) and the net retention volume V_N (ml) by^{6,13}

Table I. Gas chromatographic columns

Column No.	Polymer	Chromosorb		BET surface area $\text{m}^2 \text{g}^{-1}$	Polymer loading wt%	Solvent
		Sort				
1	PMMA	G	NAW	0.5	2.5	Benzene
2	PMMA	G	AW-DMCS	0.5	5.0	Benzene
3	PMMA	W	NAW	1.1	5.0	Benzene
4	PMMA	W	NAW	1.1	10.0	Benzene
5	PMMA	W	AW-DMCS	1.0	5.0	Benzene
6	PMMA	P	NAW	3.7	18.6	Benzene
7	PMMA	P	AW-DMCS	3.1	5.0	Benzene
8	PMMA	P	AW-DMCS	3.1	9.1	Benzene
9	PMMA	P	AW-DMCS	3.1	18.7	Benzene
10	PMMA	P	AW-DMCS	3.1	8.7	Acetone
11	PMMA	P	AW-DMCS	3.1	9.6	EGME ^a
12	PEO	P	AW-DMCS	3.1	1.0	Chloroform
13	PEO	P	AW-DMCS	3.1	5.0	Chloroform
14	PEO	P	AW-DMCS	3.1	10.0	Chloroform
15	PEO	P	AW-DMCS	3.1	20.0	Chloroform
16	—	P	AW-DMCS	3.1	0	—

^a Ethylene glycol monomethyl ether.

$$V_g = \frac{V_N}{w} = \frac{t_R F}{w} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \cdot \frac{3}{2}$$

where F is the flow rate of the carrier gas at N.T.P. measured with a soap-film flow meter (ml min^{-1}), w is the polymer loading weight (g), P_i and P_o are the column inlet and outlet pressures, respectively. The measurement was usually carried out by heating-up the column temperature T (K), but when necessary the cooling-down measurement was also carried out. The retention diagram was obtained by plotting $\log V_g$ vs. $10^3/T$.

RESULTS AND DISCUSSION

The Effect of the Support Surface Area

Figure 1 shows the retention diagrams for the columns No. 1 (G NAW: $0.5 \text{ m}^2 \text{ g}^{-1}$), 3 (W NAW: $1.1 \text{ m}^2 \text{ g}^{-1}$), and 6 (P NAW: $3.7 \text{ m}^2 \text{ g}^{-1}$), where the weights of PMMA per unit area were nearly the same ($\approx 0.05 \text{ g m}^{-2}$). In these three columns, the thicknesses of the polymer layer on the supports

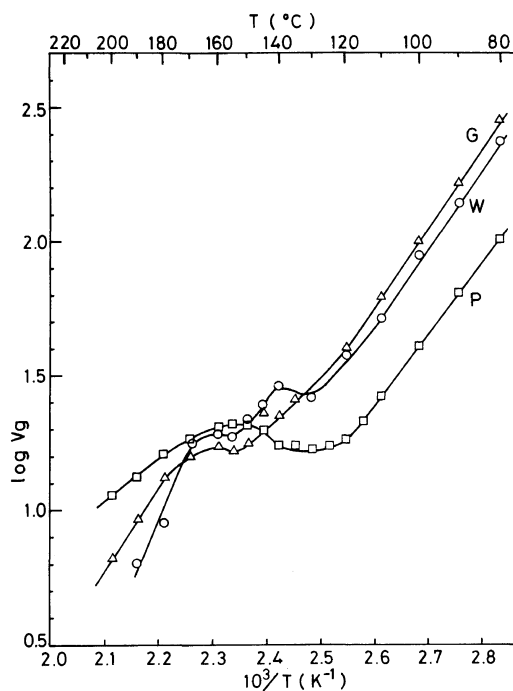


Figure 1. Effect of the surface area of Chromosorb on the retention diagram: *n*-dodecane, PMMA; (Δ) No. 1 (G NAW; 2.5% PMMA); (\circ) No. 3 (W NAW, 5.0%); (\square) No. 6 (P NAW, 18.6%).

were the same, since nonuniformity of the polymer was not observed by a scanning electron microscope irrespective of the difference in polymer loading per support weight. In these retention diagrams, the temperature at the first deviation of the curves from the straight line for lower temperatures corresponds to the glass transition temperature (T_g) of PMMA ($\approx 115^\circ\text{C}$). A typical single Z-shaped curve around the T_g of PMMA was clearly observed in the retention diagram for the column No. 6, in which Chromosorb P was employed. On the other hand, no such curve was observed for the columns of Chromosorb G and W. The double Z-shaped curve for Chromosorb W suggests that some nonuniformity exists in the polymer distribution on the support surface.

The retention diagrams for the columns prepared with various Chromosorbs at the same polymer loading (5.0% PMMA, columns No. 2, 5, and 7) are shown in Figure 2. The Z-shaped curve in the retention diagram for the column prepared with Chromosorb P ($3.1 \text{ m}^2 \text{ g}^{-1}$, No. 7) was more distinct than that prepared with Chromosorb W ($1.0 \text{ m}^2 \text{ g}^{-1}$, No. 5) or Chromosorb G ($0.5 \text{ m}^2 \text{ g}^{-1}$, No. 2).

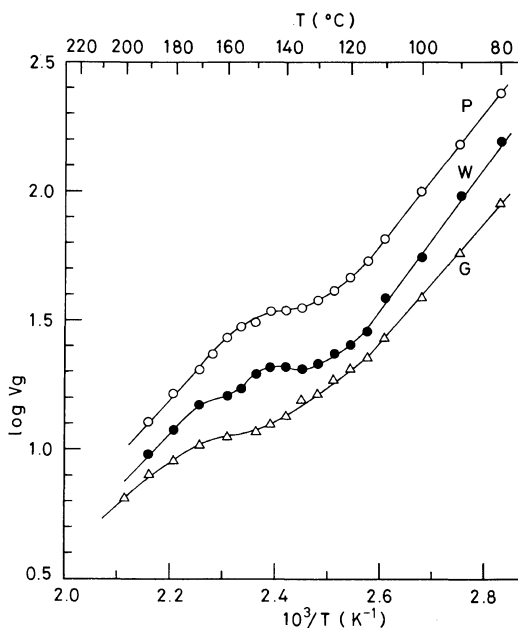


Figure 2. Effect of the surface area of Chromosorb on the retention diagram: *n*-dodecane, 5.0% PMMA; (\circ) No. 7 (P AW-DMCS); (\bullet) No. 5 (W AW-DMCS); (Δ) No. 2 (G AW-DMCS).

It may be concluded from these results that in an IGC study the use of a support having a relatively large surface area is desirable for obtaining a clearer Z-shaped curve with a small amount of a polymer.

The Effect of Silane-Treatment on a Support

The surface of Chromosorb NAW was treated with an acid and dimethyldichlorosilane (Chromosorb AW-DMCS). Figure 3 shows the retention diagrams for columns prepared with Chromosorb P NAW (18.6% PMMA, No. 6) and P AW-DMCS (18.7%, No. 9). Although the polymer loading for each column was nearly the same, the Z-shaped curve was more distinct in the retention diagram for Chromosorb P AW-DMCS (No. 9) than for Chromosorb P NAW (No. 6). Since the BET surface areas of Chromosorb P AW-DMCS ($3.1 \text{ m}^2 \text{ g}^{-1}$) and P NAW ($3.7 \text{ m}^2 \text{ g}^{-1}$) were of the same order, this difference can be attributed to the silane-treatment of the support. Consequently, the use of a silane-treated Chromosorb as a solid support is preferable in an IGC study.

Solvent Effect

The surface feature of a polymer film may be

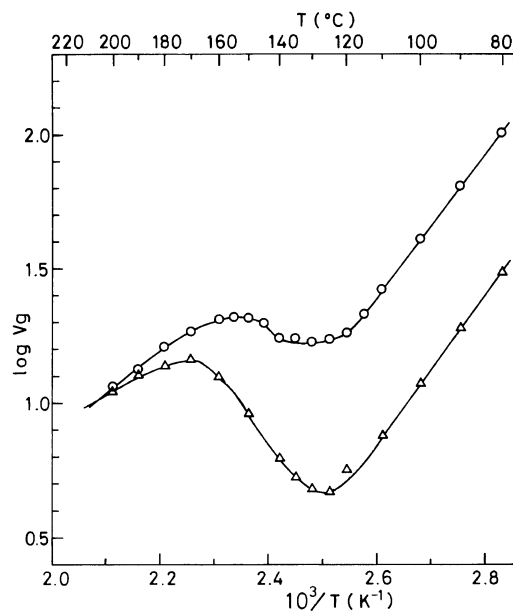


Figure 3. Effect of the silane-treatment for Chromosorb on the retention diagram: *n*-dodecane, PMMA; (\circ) No. 6 (P NAW, 18.6% PMMA); (\triangle) No. 9 (P AW-DMCS, 18.7%).

varied by changing the solvent. In order to observe the difference in film formation from various solutions, PMMA films were cast onto glass plates. Optical-microscope photographs of these plates were taken and are shown in Figure 4. The film cast from acetone (a) or ethylene glycol monomethyl ether (b) solution was inhomogeneous, whereas that from benzene solution (c) was smooth and glassy.

In Figure 5 are shown the retention diagrams for columns prepared using various solvents (acetone in

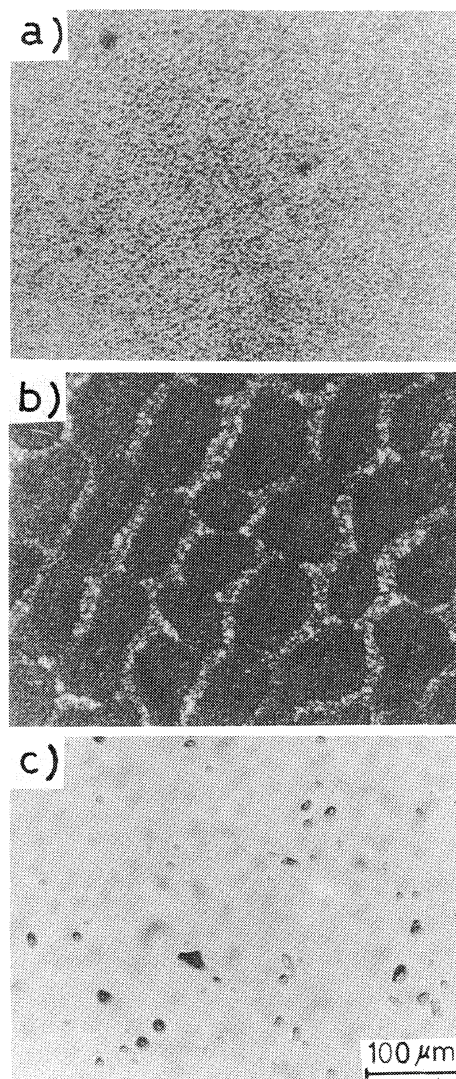


Figure 4. Optical microscope photographs of PMMA films cast from various solutions: (a) acetone; (b) ethylene glycol monomethyl ether; (c) benzene.

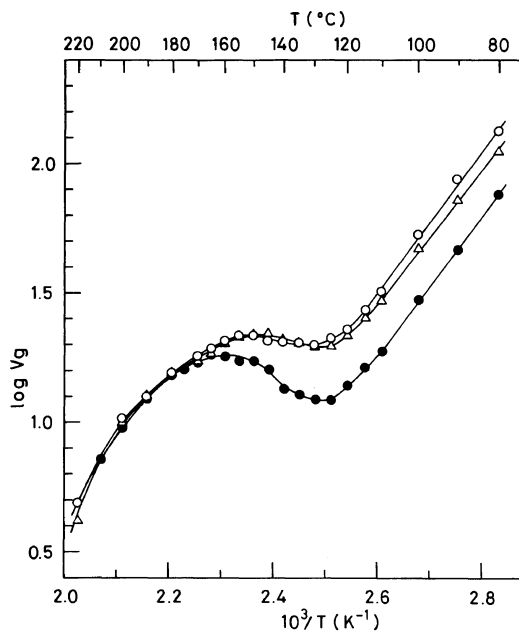


Figure 5. Effect of solvent on the retention diagram: *n*-dodecane, PMMA, Chromosorb P AW-DMCS; (○) No. 10 (acetone, 8.7% PMMA); (△) No. 11 (ethylene glycol monomethyl ether, 9.6%); (●) No. 8 (benzene, 9.1%).

No. 10, ethylene glycol monomethyl ether in No. 11, and benzene in No. 8) to disperse PMMA onto Chromosorb. The reproducibility of the column preparation reflecting to the Z-shaped curve in the retention diagram of first heating-up measurement was very good. So the effect of the solvent on the Z-shaped curve was examined. The Z-shaped curve in the retention diagram for the column prepared with benzene as the solvent was more distinct than that prepared with either acetone or ethylene glycol monomethyl ether. Thus, for obtaining a distinct Z-shaped curve around the T_g of a polymer, we used a casting solvent which gave a smooth and glassy polymer film. The surface features of a polymer film could be correlated to the solubility parameter, the evaporation rate of the solvent, and the adsorption of polymer on the surface of the support.

Thermal Hysteresis

Figure 6 shows the retention diagrams from successive heating-up and cooling-down measurements for the column No. 4. After the first heating-up measurement, the first cooling-down and the

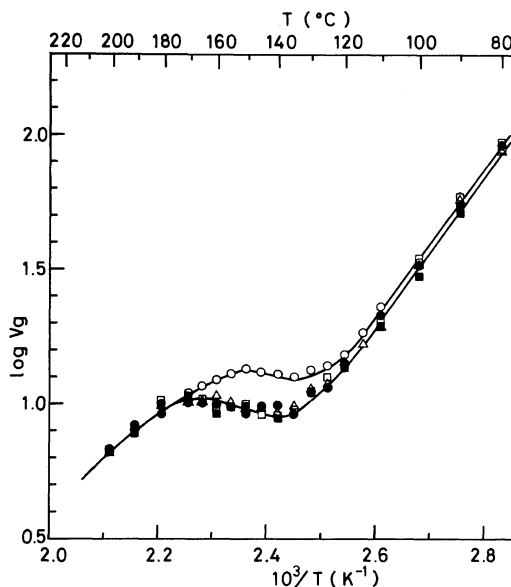


Figure 6. Retention diagrams of successive heating-up and cooling-down measurements for the column No. 4 (W NAW, 10.0% PMMA): *n*-dodecane; (○) 1st heating-up; (●) 1st cooling-down; (△) 2nd heating-up, 5 days later; (□) 3rd heating-up; (■) 2nd cooling-down.

second heating-up measurements were successively carried out. The third heating-up measurement and the successive second cooling-down measurement were carried out five days later. The retention diagram for the first heating-up measurement (○) was different from those of subsequent measurements which were almost the same. This hysteresis may be due to the thermal spreading of the polymer layer on the support. In IGC, the column should be thermally treated at a suitable temperature under an inert atmosphere to obtain reproducible results. It should be noted that in an IGC study of multicomponent polymer systems such as polymer blends the surface structure of the polymer on a support may be changed by thermal treatment.¹⁵ In such a case, the results of the first heating-up measurement should be discussed separately from those of subsequent measurements.

Polymer Loadings and Retention Mechanism

The retention diagrams for columns prepared at various PMMA loadings are shown in Figure 7. The larger the polymer load, the clearer the Z-shape of the curve. This tendency was also observed in the

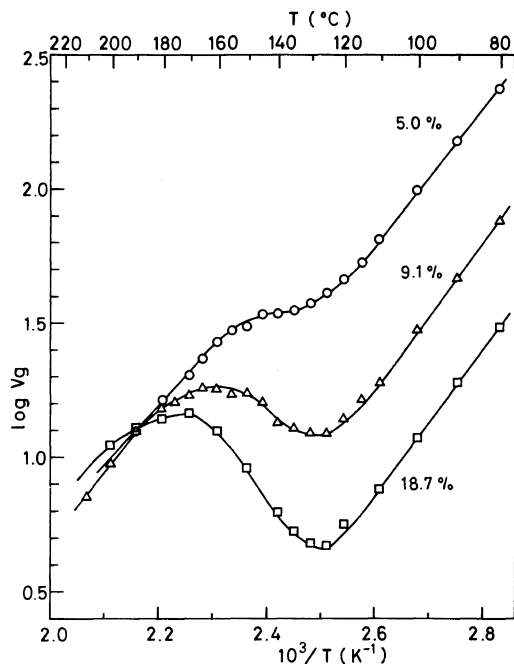


Figure 7. Effect of loading of PMMA on the retention diagram: *n*-dodecane, Chromosorb P AW-DMCS; (○) No. 7 (5.0% PMMA); (△) No. 8 (9.1%); (□) No. 9 (18.7%).

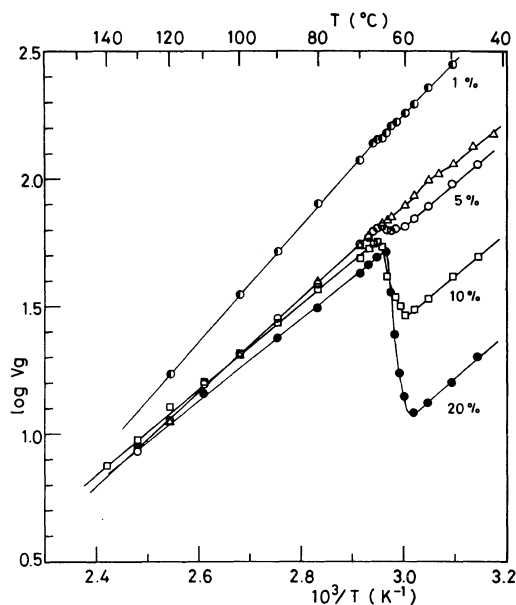


Figure 8. Effect of PEO loading on the retention diagram: *n*-octane, Chromosorb P AW-DMCS; (●) No. 12 (1.0% PEO); (△) No. 13 (5.0%, cooling-down); (○) No. 13 (heating-up); (□) No. 14 (10.0%); (●) No. 15 (20.0%).

retention diagrams at the melt-transition of PEO.^{16,17} In Figure 8 are shown the retention diagrams for the columns No. 12–15, in which PEO was loaded onto Chromosorb P AW-DMCS from chloroform at different polymer loadings. In the heating-up measurement on the column No. 13, a Z-shaped curve due to the transition corresponding to melting of PEO was observed around 60°C. In the cooling-down diagram, the transition corresponding to the crystallization of PEO was slightly observed around 55°C. This discrepancy may be due to a cooling rate (0.1 K min⁻¹) faster than that of the crystallization of PEO. The changes in log V_g before and after melting of PEO were nearly proportional to the amount of PEO loaded onto the support in the range from 5 to 20%. Thus, the change in log V_g at the glass transition or melting point of a polymer increases with an increase in the polymer load.

In the retention diagram for column No. 12 prepared at a 1% loading of PEO, no Z-shaped curve was observed at all, and the straight line above the melting temperature of PEO ($T_m \approx 60^\circ\text{C}$) appeared far below those of the other three cases. This suggests that the retention mechanism of *n*-octane at 1% loading is different from that above

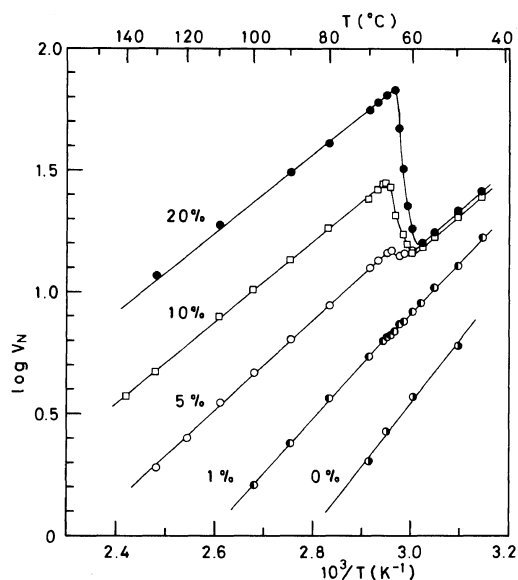


Figure 9. Effect of PEO loading on the relation between V_N and T : *n*-octane, Chromosorb P AW-DMCS; (●) No. 12 (1.0% PEO); (○) No. 13 (5.0%); (□) No. 14 (10.0%); (●) No. 15 (20.0%); (●) No. 16 (0%).

5% loading. The dependence of $\log V_N$ (V_N , net retention volume) on $1/T$ for columns No. 12—16 is shown in Figure 9. When the loading was above 5%, the retention diagrams below T_m of PEO nearly overlapped with each other, while the retention diagram for 1% loading came close to that for 0% loading. The mechanism of solute retention below and above the T_m of PEO was analyzed by considering the contribution of both adsorption on the polymer surface and sorption into bulk of the polymer.^{16,17} When the surface of support is completely covered by the polymer, the surface area of the polymer layer should be almost constant regardless of the amount of polymer loading. In general, therefore, the contribution of surface adsorption to V_N below T_m should be constant regardless of the polymer loading. The difference in the values of $\log V_N$ below T_m can be ascribed to the difference in the contribution of bulk sorption. As can be seen from Figure 9, the contribution of bulk sorption below the T_m was negligible when the loading was higher than 5%. Thus, the crystallinity of PEO on the Chromosorb surface is regarded as nearly 100%.

Since the crystallinity is zero above T_m , the depth

of a Z-shaped curve is roughly proportional to the thickness of the polymer-bulk layer, *viz.*, polymer loading. At 1% loading, the contribution of adsorption at the polymer-support interface or at the surface of the support uncovered with polymer should be taken into consideration as well as surface adsorption and bulk sorption at the polymer layer.

The dependence of $\log V_N$ on $1/T$ for columns No. 7—9 and 16 is shown in Figure 10. Below the T_g of PMMA the retention proceeds exclusively by surface adsorption, and above the T_g , the penetration of the solute into the bulk of the polymer (bulk sorption) begins in the amorphous domains of the polymer.⁷ If the polymer completely covers the surface of the support, the amount of surface adsorption should be constant regardless of the polymer loading. As can be seen in Figure 10, below the T_g of PMMA the values of $\log V_N$ for columns prepared at 9.1% (No. 8) and 18.7% (No. 9) loadings agree well at the same temperature, while the value at 5.0% loading was different from these two values and rather close to the value at 0% loading. It is probable that PMMA did not cover the entire surface of the support in the column prepared at 5.0% loading (No. 7). In the study of the physical properties of a polymer by IGC, therefore, it is necessary to find a minimum amount of polymer loading which can cover the whole surface of a support, since, if any part of the surface is not covered, interaction between solute and surface will add to the complexity. The $\log V_N$ vs. $1/T$ diagrams for the columns prepared at various polymer loadings are required to find suitable polymer loading.

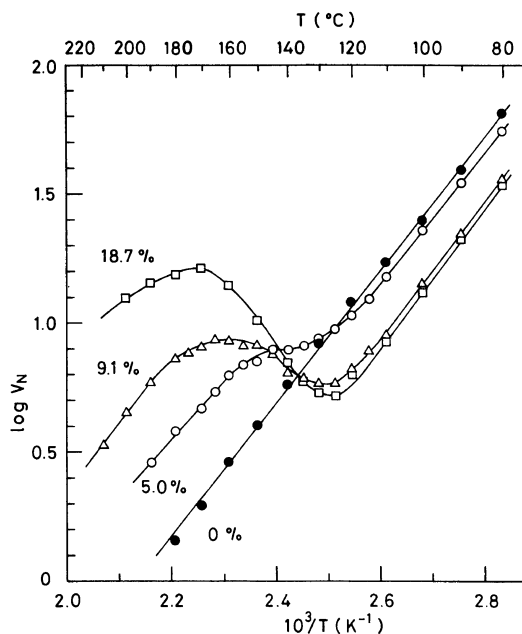


Figure 10. Effect of PMMA loading on the relation between V_N and T : *n*-dodecane, Chromosorb P AW-DMCS; (○) No. 7 (5.0% PMMA); (△) No. 8 (9.1%); (□) No. 9 (18.7%); (●) No. 16 (0%).

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