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Transitions in Semi-Crystalline Polymers

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SUMMARY

Transition studies in polymers by inverse gaschromatography showed a characteristic pressure-jump in the carrier with constant flow-rate, which may be related to the dilatometric behaviour of the polymer in the transition region.

INTRODUCTION

Starting with the first work published by SMIDSRØD and GUILLET, the "inverse gaschromatography" imposed more and more as a method to evidence transitions in polymers and in present it may be considered as overall recognized (BRAUN-GUILLET, 1976 and GRAY, 1977).

Even in our first investigations we observed beside the well known modifications in the retention diagram also a characteristic pressure-jump in the carrier at the column inlet by maintaining the flow-rate constant and the present study deals with this phenomenom.

First and second order transitions were investigated using the following semi-crystalline polymers: Poly(propylene) "Malen", $\bar{M}_{visc}$=227.900 and "Daplen", $\bar{M}_{visc}$=150.000; poly (ε-caprolactam), M_n=25.000 and a copolyesther of ethyleneterephthalate with ethyleneglycole and 15% polyglycol 4ooo (CO-ETPG), $\bar{M}_{visc}$= =25.000.

DTA-measurements in nitrogen were performed on a

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METTLER thermobalance, using samples of 40 mg and a heating rate of 10°/min, while the gaschromatographic determinations on a PYE 104 Series gaschromatograph with a GOW-MAC detector, equipped with a sensitive manometer to measure the pressure of the carrier (Ar) at the column inlet.

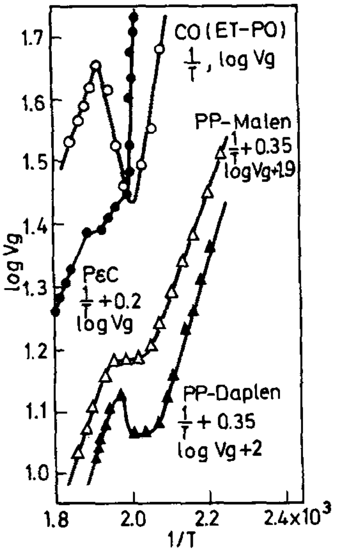
EXPERIMENTAL

Preparation of the columns: the polymers, using amounts of respective 0.0561 g Malen, 0.1237 Daplen, 0.57 g PεC and 0.264 g CO-ETPG were solved in an adequate solvent and coated on 7 g Cellite C22 (60/80 mesh). Total removal of the solvent was assured by gentle heating for 4-5 h in vacuum. Chromatographic glasscolumns of 1.52 length and 4 mm internal diameter were then packed with polymer coated on support and subsequently thermally treated.

For measurements of the melting transition, the columns were heated for 3 h at 20° above the respective Tm's and then very slowly cooled to assure crystallization of the polymer. For Tg-measurements, the above Tm heated polymer samples were quick cooled to room temperature.

The retention times were determined, using as molecular probes n-heptane for the Tg- and n-hexadecane for the Tm-measurements, while the flow-rate of the carrier was maintained constant between 10 and 35 cc/min, depending on the used column, by increasing correspondingly the inlet pressure.

RESULTS AND DISCUSSION



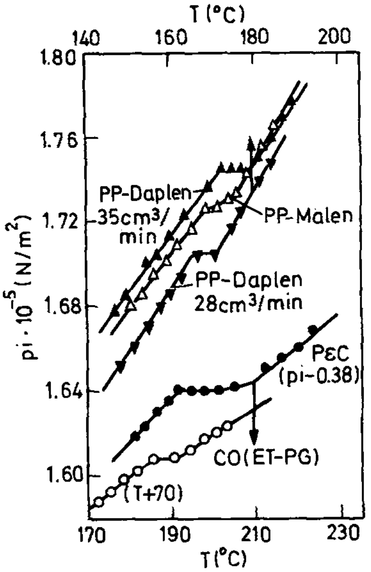


Fig.1 Retention diagrams Fig.2 Pressure diagrams

The figures show semi - crystalline polymers in the Tm-range Flow-rates of the carrier: PP-Daplen 35; Malen 29; PεC 10 and CO-ETPG 21 cc/min.

The melting transitions of the polymeric stationary phases are shown in the retention diagrams in Fig. 1. To comprise, the coordinates were shifted by the amounts noted on the respective curves.

The corresponding modifications of the pressure of the carrier at the column inlet, by maintaining the flow-rate constant, are illustrated in Fig. 2. Again the curve for CO-ETPG is shifted with 70° to lower temperature.

For PP-Daplen experiments with (flow-rate of the carrier 35 cc/min) and without (flow-rate 28 cc/min) molecular probe in the carrier were performed, the agreement of the measured pressure-jumps being quite acceptable.

We mention that the step of constant pressure is as larger, as greater the amount of the coated on polymer in the chromatographic column.

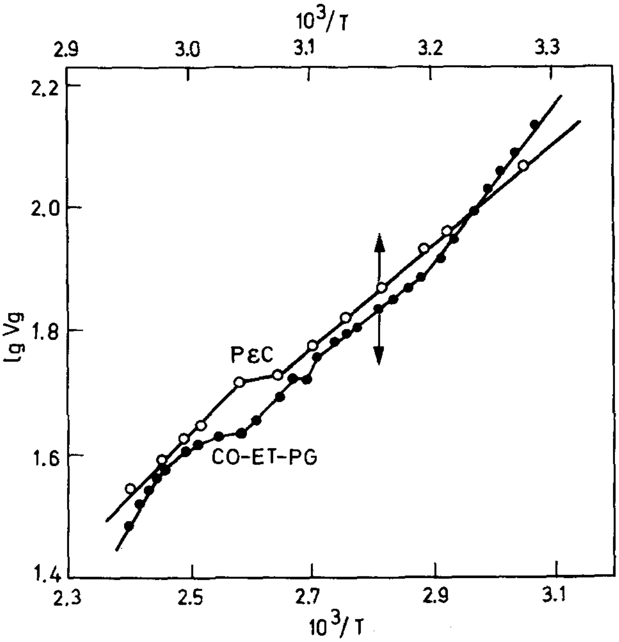


Fig.3 Retention diagram of the semi-crystalline polymers in the Tg-range. Flow-rate of the carrier: 15 cc/min

The retention diagrams of the glass-transitions for PεC and CO-ETPG are shown in Fig. 3. As seen, the plots for CO-ETPG evidence also two l,l-transitions (at 368 and 386 K) similar to the homopolymer PET (SCHNEIDER-CALUGARU, 1978). The Tg's are also evidenced in the inlet-pressure diagrams, even if they are less visible for the copolymer.

Finally in Table I are given the obtained values of the investigated transitions. The values for PεC and CO-ETPG are in good agreement, taking into account their molecular weight, with those reported elsewhere (SCHNEIDER-CALUGARU, 1977 and 1978).

Table I. Transition temperatures of semi-crystalline polymers

Polymer	Melting, K			Glass-transition, K		
	Retention	Press.	DTA	Retn.	Press.	DTA
Malen	438	441	444	-	-	-
	436	445	441	-	-	-
		439*				
PεC	478	465	483	325	322	323
CO-ETPG	525	529	532	346	340	325

*without molecular probe in the carrier

It seems therefore possible to evidence transitions in polymers also only by measuring the pressure of a carrier at the inlet in a column packed with a polymer coated on support, if during heating the flowrate is maintained constant. It may be that this behaviour is related to the respective dilatometric behaviour of the coated on polymer and to the modifications of the "frozen in" free volumen.

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