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OXYGEN AND WATER VAPOUR PERMEABILITY  
OF COMPRESSION MOULDED POLYKETONE FILMS

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## SUMMARY

Oxygen permeability, under both wet and dry conditions, and water vapour transmission measurements have been made on compression moulded films of 8 experimental ethylene/propene - carbon monoxide terpolymers (1:1 alternating olefin : CO). The polymers, prepared at BPC, Hull, covered a range of composition from 1-8 mole % propene incorporation, corresponding to a range of melting point of 240-193°C and density 1.270 - 1.220 gcm<sup>-3</sup>.

The oxygen permeability range measured was comparable to that of other barrier polymers : Barex, amorphous polyamide and EVOH. Oxygen permeability increased with increasing incorporation of propene units in the polymer (i.e. decreasing density and melting point). Oxygen permeability was sensitive to moisture, increasing with increasing relative humidity. Permeability was also somewhat sensitive to the moulding conditions, especially cooling rate. The permeability range which can be exploited in practice will depend on optimisation of polymer structure, morphology, stabilisation and processing. The water vapour transmission rate was relatively high compared to other moisture sensitive barrier polymers and apparently insensitive to polyketone composition.

These results confirm earlier data that polyketones have potentially useful barrier properties, and combined with their relatively low cost and good mechanical properties, they are a new class of materials worthy of more detailed study to see if they can be exploited commercially.

## RECOMMENDATIONS

1. Develop an understanding of how fabrication history affects polymer morphology and barrier properties.
2. Investigate in more detail how moisture affects barrier performance.
3. Identify and evaluate means to improve water barrier performance.
4. Investigate the effect of controlled orientation on barrier properties.
5. Measure permeability of processed materials.

## 1. INTRODUCTION

Highly alternating ethylene carbon monoxide copolymers, known to have high density and high degree of crystallinity<sup>1,2</sup> might be expected to have useful barrier properties. The Permachor calculation<sup>3</sup> predicts high barrier properties for these ethylene-carbon monoxide copolymers, Figure 1, which rank them alongside EVOH. High molecular weight polymers of this type, which until recently could only be made by a free radical route<sup>4</sup>, are high melting (260°C), degrade rapidly on heating above their melting point and have not been commercialised. No reliable permeability data has been published.

Recent advances in catalyst technology has enabled a more general polymerisation of  $\alpha$ -olefins with carbon monoxide to produce high molecular weight strictly 1:1 alternating copolymers (polyketones)<sup>4,5</sup>. Partial replacement of ethylene units with propene units gives lower melting polymers than the basic ethylene-carbon monoxide copolymer, which, although still prone to thermal degradation, are more tractable for processing and have attracted interest. Shell International are leaders in this field and have a number of patents<sup>6</sup> disclosing permeability data indicating they are moderate to good barrier polymers.

Work at RCS has made these polyketones available to BP Chemicals. Initial evaluation in PSB<sup>7,8</sup> also indicated, despite poor reproducibility, low oxygen permeability but relatively high water vapour permeability. This report describes a more comprehensive study of oxygen permeability, under dry and wet conditions, and water vapour permeability of polyketones for a number of polymers to confirm the earlier results and reveal how permeability is influenced by polyketone composition.

## 2. EXPERIMENTAL

### 2.1 Materials

Polyketones were prepared on the ~1kg scale using a 7l autoclave at BPC, Hull, to procedures described previously elsewhere<sup>9</sup>. The polymers were freed from residual catalyst impurities by washing with methanol and Soxhlet extraction over refluxing methyl ethyl ketone and then dried under vacuum at 70°C. The composition of the polymer was determined by <sup>13</sup>C nmr in m-cresol solution. The intrinsic viscosity was obtained from a single point measurement of dilute solution viscosity in m-cresol. (Both <sup>13</sup>C nmr and intrinsic viscosity measurements were made at RCS). The polymer density was measured on compression moulded film using a density gradient column. The melting point of the compression moulded film was determined as the peak of the DSC endotherm on scanning at 10°C min<sup>-1</sup>. The basic characterisation of the polymers studied is summarised in Table 1.

## 2.2 Preparation of Compression Moulded Films

The powder material as received, without further drying or addition of stabilisers, was compression moulded into film using a manually operated hydraulic press. The sample was contained in a 130mm<sup>2</sup> x 120µm picture-frame mould between PFTE sheets supported by aluminium backing plates. The pressing conditions were largely determined by the composition (i.e. melting point) and molecular weight (i.e. intrinsic viscosity) of the material. It is known that these polymers crosslink in the melt so the temperature and time at high temperature during pressing were minimised. The polymers were moulded 15-30°C above the DSC peak melting point. Although it is desirable to produce thin films for permeation measurements the use of high force during moulding was avoided as much as possible since it is known this can induce uncontrolled orientation in the films disrupting crystallinity. It was found (see Appendix 1) that cooling the films with air in the press at 10-15°C min<sup>-1</sup> to below the polymer's crystallisation point was beneficial compared to faster water cooling (~150°C min<sup>-1</sup>) and this procedure was followed for all materials. The pressing conditions and typical film thicknesses achieved are given in Table 2 for each polymer evaluated.

## 2.3 Oxygen Permeability

Measurements were made using the Oxtran 1000 O<sub>2</sub> TR test apparatus. Tests were made on between 3 to 10<sup>2</sup> films for each material. Each film had a test area of 80mm diameter. Measurements were made at 25°C in a 0% and ~90% relative humidity. Samples were conditioned in the rig during testing. ASTM D3985-81 was followed for dry conditions. Wet conditions of ~90%RH were obtained by bubbling the oxygen through tubes containing water and glass beads.

## 2.4 Water Vapour Transmission

The films were stored at 50% RH and 23°C and conditioned for 2 days at 90-100% RH and 38°C prior to testing at these conditions. At least 3 films were tested for each material. The films were masked leaving an area of 25mm diameter for testing. Tests were made to 40 hours. The apparatus was calibrated against a Mylar film.

### 3. RESULTS & DISCUSSION

#### 3.1 Oxygen Permeability

The measured values of oxygen permeability coefficient for all the films tested of the 8 polymers included in this study are collected in Table 3. The permeability coefficient data at 0%RH and 90%RH are correlated against polyketone composition in Figs 2 and 3 respectively. The solid lines on the graphs correspond to the measured range of values of the permeability coefficient for each polymer and the broken lines serve as a guide to the eye illustrating the trend. There was a general trend of increasing permeability coefficient with increasing incorporation of propene units in the polyketone. This was anticipated since polyketone crystallinity decreases with increasing incorporation of propene units and crystalline regions are less permeable.

The permeability increased under wet conditions compared to dry conditions for each film as reported for Hull 7 before. For most of the films the permeability coefficient increased by a factor of 2-8 times, but for a few larger increases were observed. There was no clear trend between sensitivity to moisture of oxygen permeability and polyketone composition. For each polymer, the values of the permeability coefficient measured under wet conditions for different films showed less scatter than those measured under dry conditions and are thought to be more reliable. The values measured under dry conditions are likely to be sensitive to the conditioning history of the polymer prior to testing. The sensitivity of the oxygen permeability of polyketone to moisture is expected since polyketones are known to absorb water which has a plasticising effect and will facilitate the transport of small molecules.

Figs. 2 and 3 show the polyketones to fall into two groups with different oxygen permeability for a given propene incorporation. The reason for this is not known, but it apparently indicates the influence of some other factor(s), perhaps distribution of propene units or molecular weight distribution. Strictly, it was anticipated that the permeability coefficient would vary with polyketone crystallinity and Figure 4 shows the correlation with film density (which increases with increasing crystallinity). The data for all the polymers lie around a single curve of decreasing permeability with increasing density. A similar result is obtained when the permeability coefficient is plotted against the temperature of the peak of the DSC melting endotherm (Figure 5). There is, however, greater scatter of the data than can be accounted for by error in density or DSC measurements suggesting some other factors may be having an influence. According to general correlations for many polyketones of density and melting point against polymer composition only Hull 7 appears anomalous. Hull 6 which is particularly attractive having lower permeability for its melting point or density than the general trend is a lower molecular weight polymer. It may be that the film preparation conditions are having an influence.



These measured values of oxygen permeability coefficient for polyketones are comparable to the range covered by barrier polymers such as EVOH and amorphous polyamide and lower than the values published by Shell for polyketones, Figure 1 and Table 4. Although melt degradation, in the absence of the development of more effective stabilisers, prohibits processing of polyketones above 235°C (i.e polyketones with melting point above ~ 215°C) oxygen permeability coefficients of the order of  $10^{-12}$  -  $10^{-13}$  cc cm cm<sup>-2</sup> s<sup>-1</sup> (cmHg)<sup>-1</sup> should be readily achievable and  $10^{-14}$  cc cm cm<sup>-2</sup> s<sup>-1</sup> (cmHg)<sup>-1</sup> may be achievable with optimisation of the polymer and fabrication route.

### 3.2 Water Vapour Transmission

The measured water vapour permeability data are shown in Figure 6 for all the different films of the 8 polymers tested. There was a spread of values obtained for different films of each polymer although they were prepared under nominally the same conditions. Somewhat surprisingly, unlike the behaviour for oxygen permeability, no strong dependence on polymer composition was evident, despite the wide range of crystallinity covered. This may in some way be related to the material's propensity to absorb moisture (up to ~2% at 25°C), but further work is required to understand this.

The effect of water uptake was explored briefly for polyketone 030590 and the results are presented in Figure 7. This shows that for a film tested to the 'standard' procedure (section 2.4) the transmission rate increases with time beyond the 40 hours 'standard' measurement time. Conditioning the film longer at 100%RH or soaking it in water prior to testing resulted in double the transmission rate and the rate varying less with test duration. Further work is needed to confirm this behaviour for other polyketones and to define a useful 'standard' procedure.

Comparison of these measured values of WVTR for polyketones can be made with literature data for other barrier polymers, Table 4. The values reported here for polyketones are higher than those of other moisture sensitive barrier polymers and higher than the values quoted by Shell for polyketones. However, bearing in mind the sensitivity of the measured value to the test procedure, as discussed above, comparisons would better be made to the same procedure. It may be possible to improve the water vapour permeability of polyketones, if necessary, and Shell have patented improvement by fluorination, but other routes such as compounding with appropriate fillers, orientation or co-extrusion with a water barrier polymer, for instance a random ethylene-carbon monoxide (low CO content) copolymer.

4. CONCLUSIONS

- i) Polyketones have low oxygen permeability and rank with other barrier polymers such as amorphous polyamides, Borex and EVOH.
- ii) Oxygen permeability of polyketones increases with increasing incorporation of propene units in the polymer (which leads to reduced crystallinity, density and melting point).
- iii) Oxygen permeability of polyketones is sensitive to moisture: increasing with increasing relative humidity.
- iv) The measured water vapour transmission of polyketones is relatively high, even compared with other water sensitive barrier polymers.
- v) Water vapour transmission seems to be fairly insensitive to the polyketone composition (i.e. propene monomer incorporation).

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Table 1

Basic Characterisation of Polyketone Samples

Reference Code	Mole % Composition			Intrinsic Viscosity (dlg <sup>-1</sup> )	Film Density (gcm <sup>-3</sup> )	DSC Peak Melting Point (°C)
	Ethene	Propene	CO			
090290	42.3	7.7	50	1.9	1.220	193
130390	44.3	5.7	50	1.65	1.232	208
HULL 7	44.0	6.0	50	1.4	1.233	218
HULL 6	45.0	5.0	50	1.1	1.233	214
260490	46.5	3.5	50	3.5	1.233	220
220590	47.7	2.3	50	3.1	1.245	227
175090	48.8	1.2	50	2.0	1.269	242
030590	48.9	1.1	50	2.9	1.270	241

Table 2

Moulding Conditions for Polyketone Films

Reference Code	Press Set Temp. (°C)	Time Before Cooling (min)	Applied Force (ton)	Temp. at End of Air Cooling (°C)	Typical Film Thickness (µm)
090290	220	3	6	140	210
130390	235	3	6	160	135
HULL 7	240	3	6	170	140
HULL 6	235	3	6	170	180
260490	250	1	6	180	330
220590	240	1	10	180	300
170590	260	1	6	180	210
030590	260	1	6	190	300

Table 3

## Measured Oxygen Permeability of Polyketone Films

FILM REFERENCE	THICKNESS ( $\mu\text{m}$ )	OXYGEN PERMEABILITY $10^{13}/\text{cc cm cm}^{-2} \text{s}^{-1} (\text{cmHg})^{-1}$		WET/DRY
		90% RH	0% RH	
090290	207	16.6	9.46	1.8
	206	24.3	1.44	17
	214	26.2	9.42	2.8
	213	27.6	10.4	2.6
	216	27.9	17.4	1.6
130390	92	27.2	17.5	1.6
	148	28.2	14.3	2.0
	162	30.1	14.2	2.1
	166	32.1	17.1	1.9
	146	32.5	18.2	1.8
	84	35.1	20.6	1.7
HULL 7	158	2.00	0.29	6.9
	128	2.51	0.37	6.8
	147	-	0.29	-
	131	3.21	0.60	5.4
	139	4.02	0.93	4.3
HULL 6	149	0.118	0.036	3.2
	186	0.255	-	-
	213	0.324	-	-
	204	0.559	-	-
	150	0.999	0.187	5.3
	205	1.35	0.968	1.4
	154	1.36	0.304	4.5
	157	1.42	0.355	4.0
260490	339	2.33	0.465	5.0
	327	2.45	0.369	6.6
	328	2.63	0.400	6.6
	329	3.31	0.461	7.2
	341	3.53	0.748	4.7
220590	298	0.906	<0.01	-
	286	1.43	0.156	9.2
	312	2.90	0.275	10.5
170590	230	0.385	0.231	1.7
	202	0.400	0.197	2.0
	206	0.458	0.169	2.7
030590	264	0.425	<0.01	-
	310	0.584	0.014	41
	292	2.75	0.159	17

Table 4

Literature Permeability Data for Some Barrier Polymers

POLYMER TYPE	GRADE	$10^{13} P (O_2)$		WVTR gcm <sup>m</sup> - <sup>2</sup> dy <sup>-1</sup>
		cc cm cm <sup>-2</sup> s <sup>-1</sup> (cmHg) <sup>-1</sup>		
		Dry	Wet	
EVOH	EVALCO, EVAL K	0.15	1.2	0.13 - 0.34
	, EVAL F	0.08	1	0.06
	DU PONT, SELAR OH	0.07	1.5	-
AMORPHOUS POLYAMIDE	MITSUBISHI, N-MXD6	9.4	1.4	0.2
ACRYLIC-IMIDE COPOLYMER	ROHM & HASS, KAMAX	30	-	0.2
ACRYLONITRILE POLYMER	BP, BAREX 210	4.8	-	0.2
	, BAREX 218	9.1	-	0.3
PET	-	5.4	-	0.12
PVDC	DOW, SARAN	0.04-0.09	-	0.001-0.008
POLYKETONE	SHELL, CARILON	12 - 29	-	0.12 - 0.7

FIG 1

OXYGEN PERMEABILITY OF SOME BARRIER POLYMERS

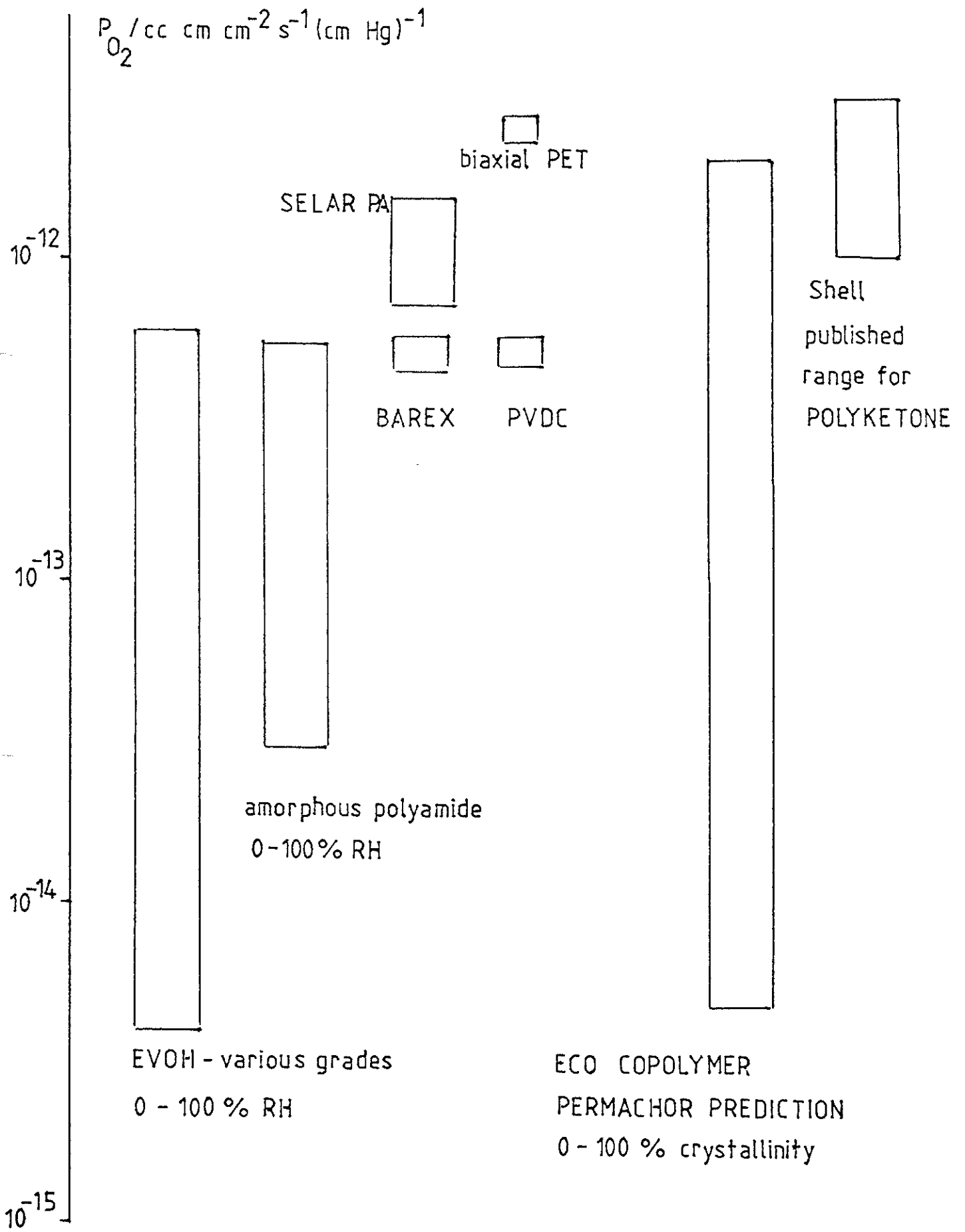


FIG. 2

OXYGEN PERMEABILITY AT 0%RH FOR POLYKETONE

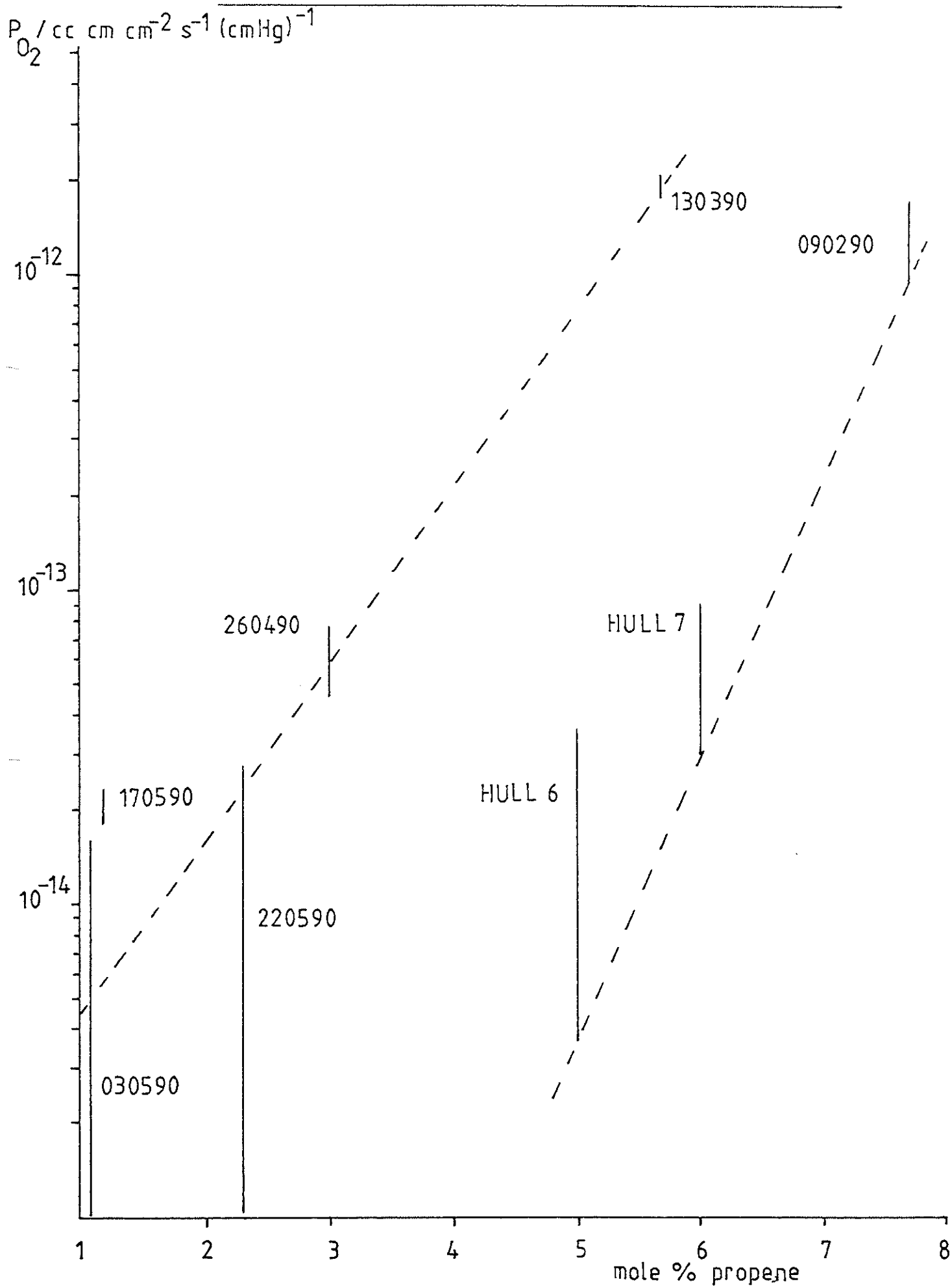




FIG. 3

OXYGEN PERMEABILITY AT 90%RH FOR POLYKETONE

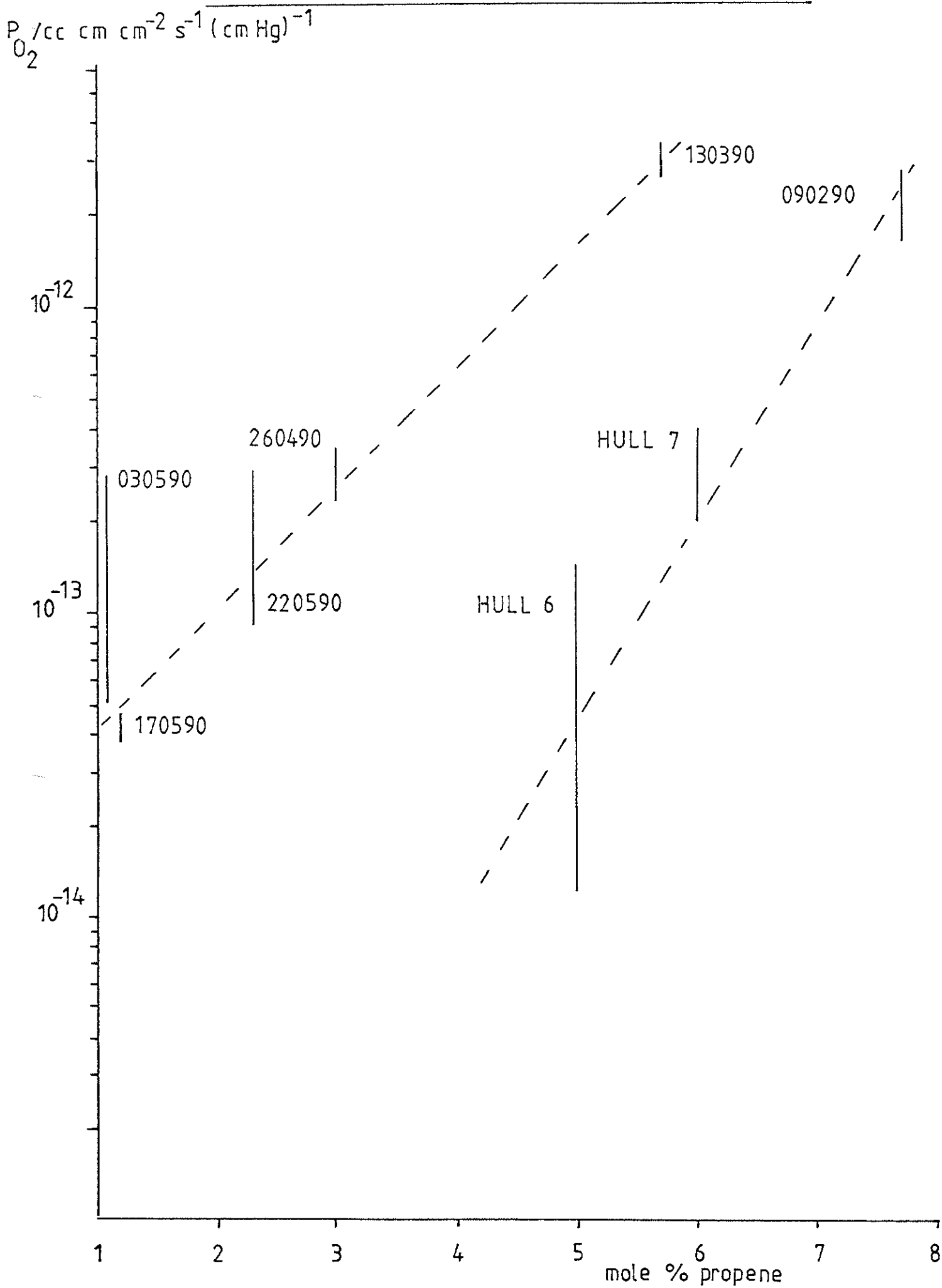


FIG. 4

POLYKETONE 90% RH OXYGEN PERMEABILITY vs DENSITY

$P_{O_2} / \text{cc cm cm}^{-2} \text{s}^{-1} (\text{cm Hg})^{-1}$

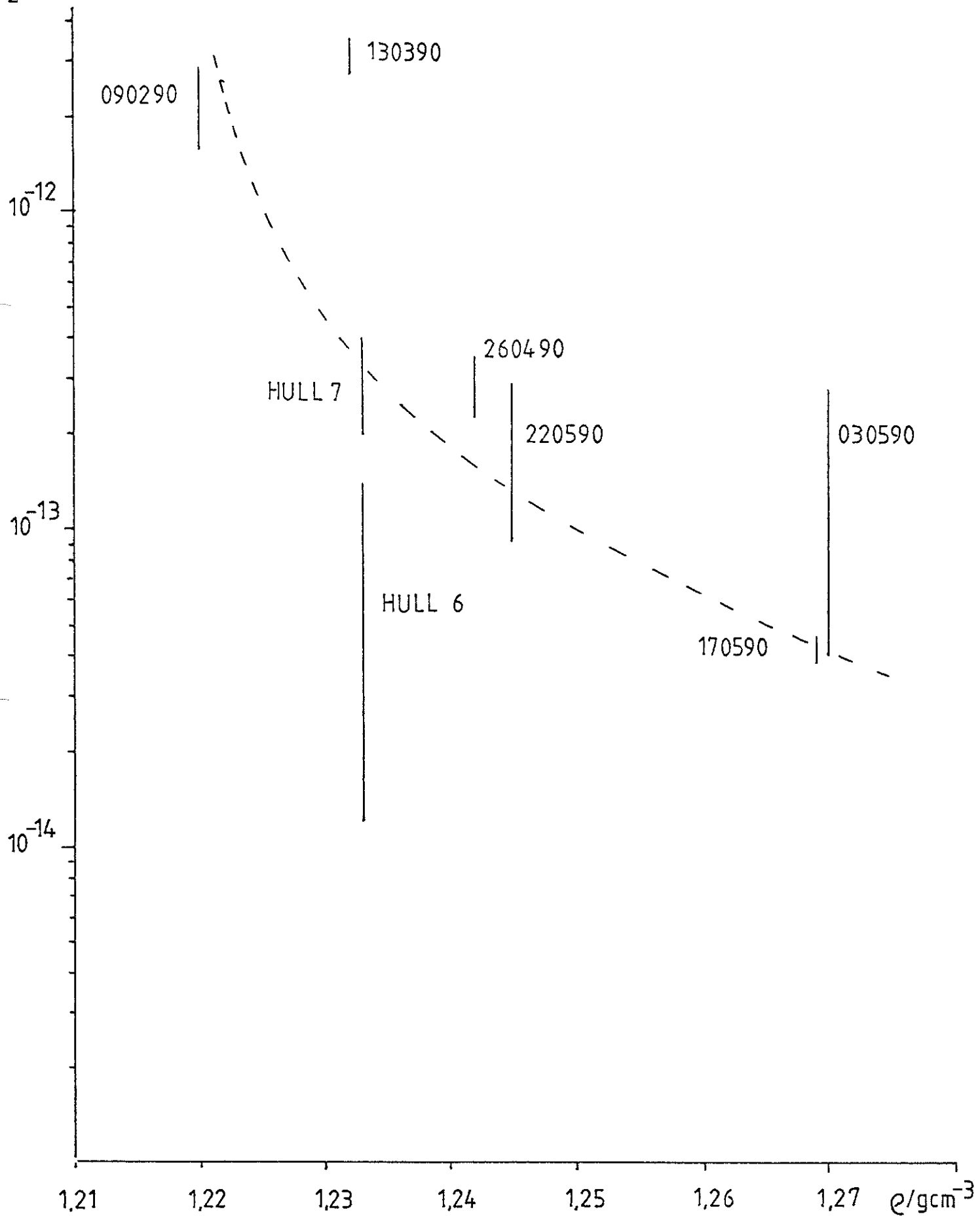


FIG. 5

POLYKETONE 90%RH OXYGEN PERMEABILITY vs MELTING POINT

$$P_{O_2} / \text{cc cm cm}^{-2} \text{s}^{-1} (\text{cm Hg})^{-1}$$

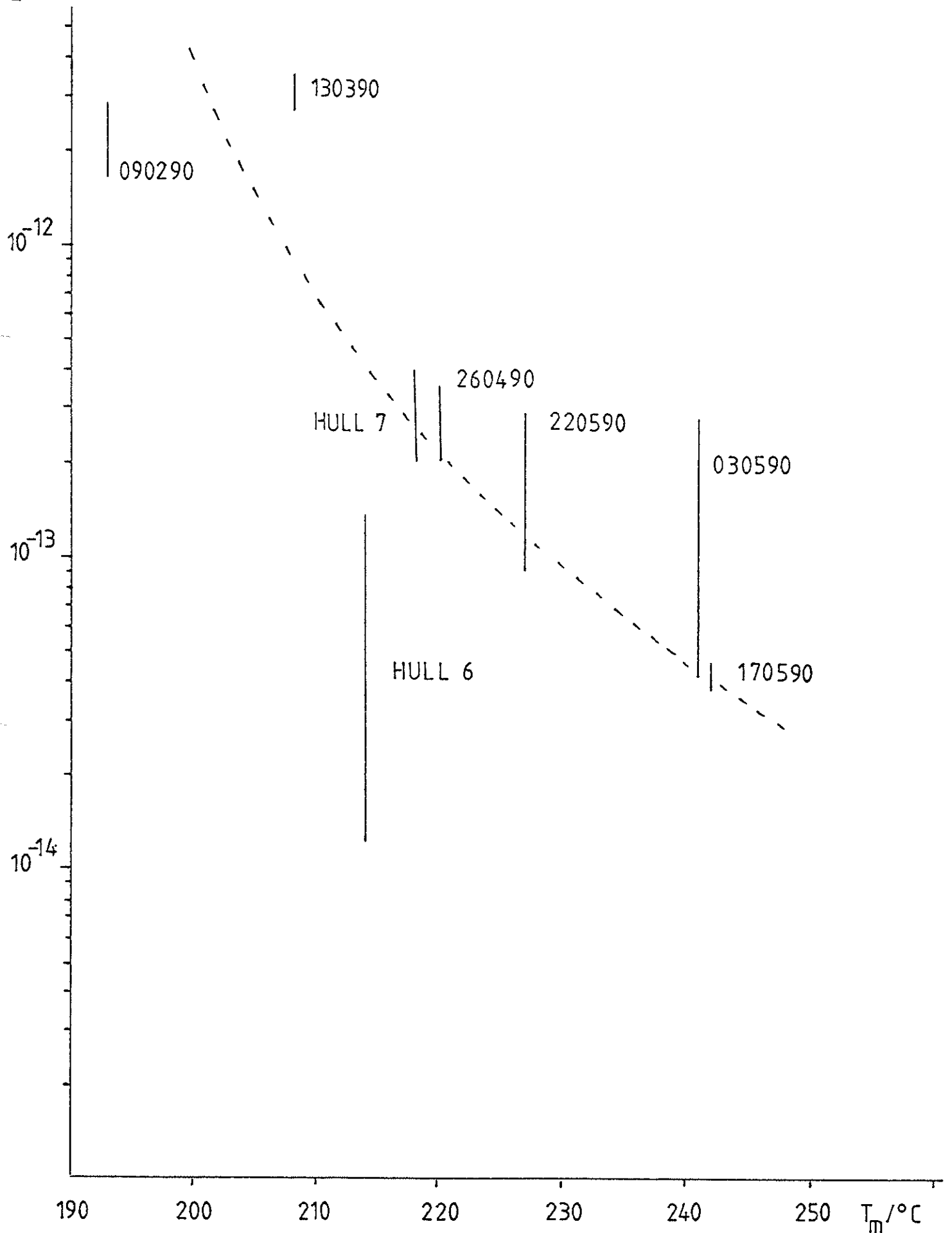


FIG. 6

WATER VAPOUR TRANSMISSION RATE FOR VARIOUS POLYKETONES

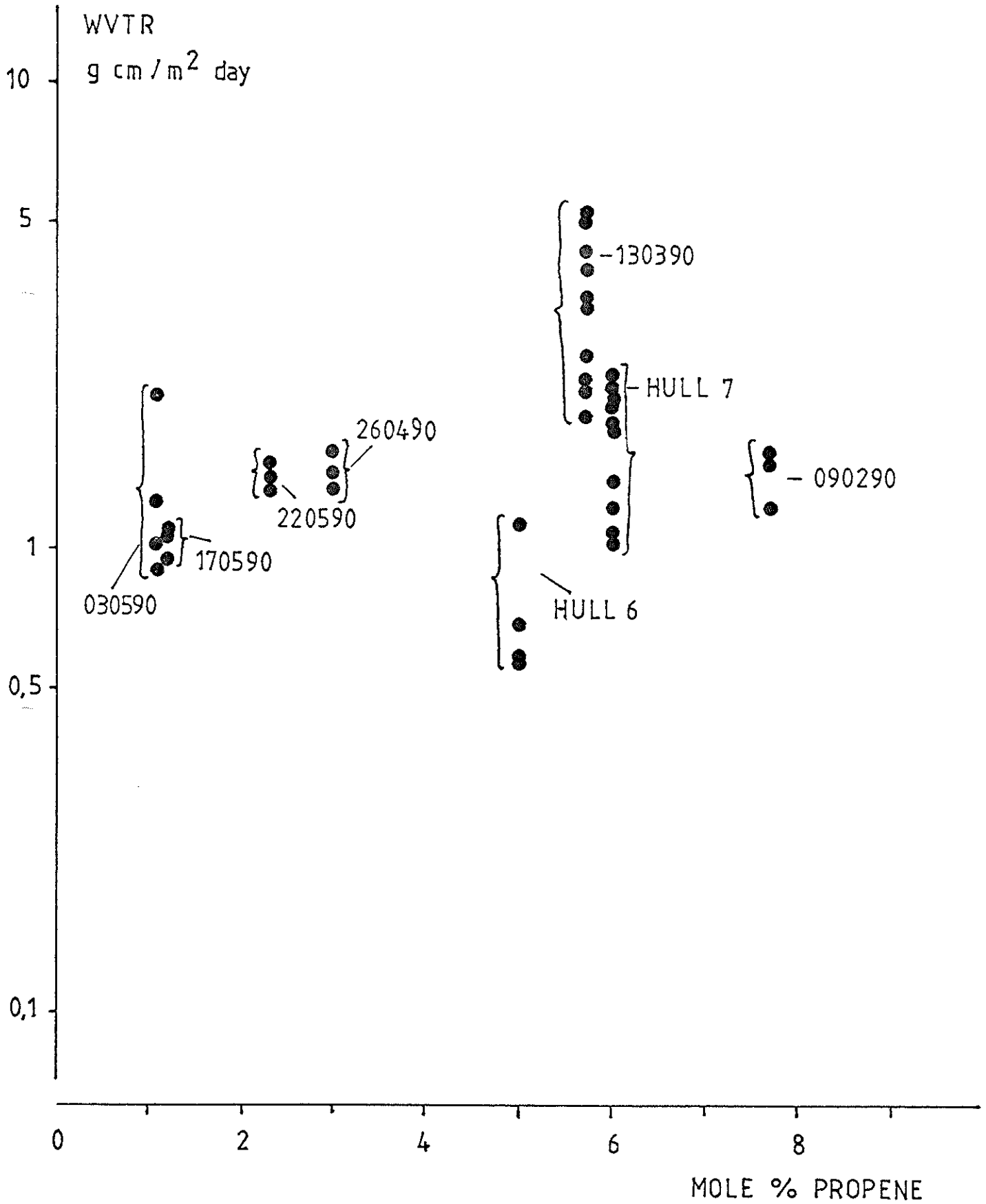
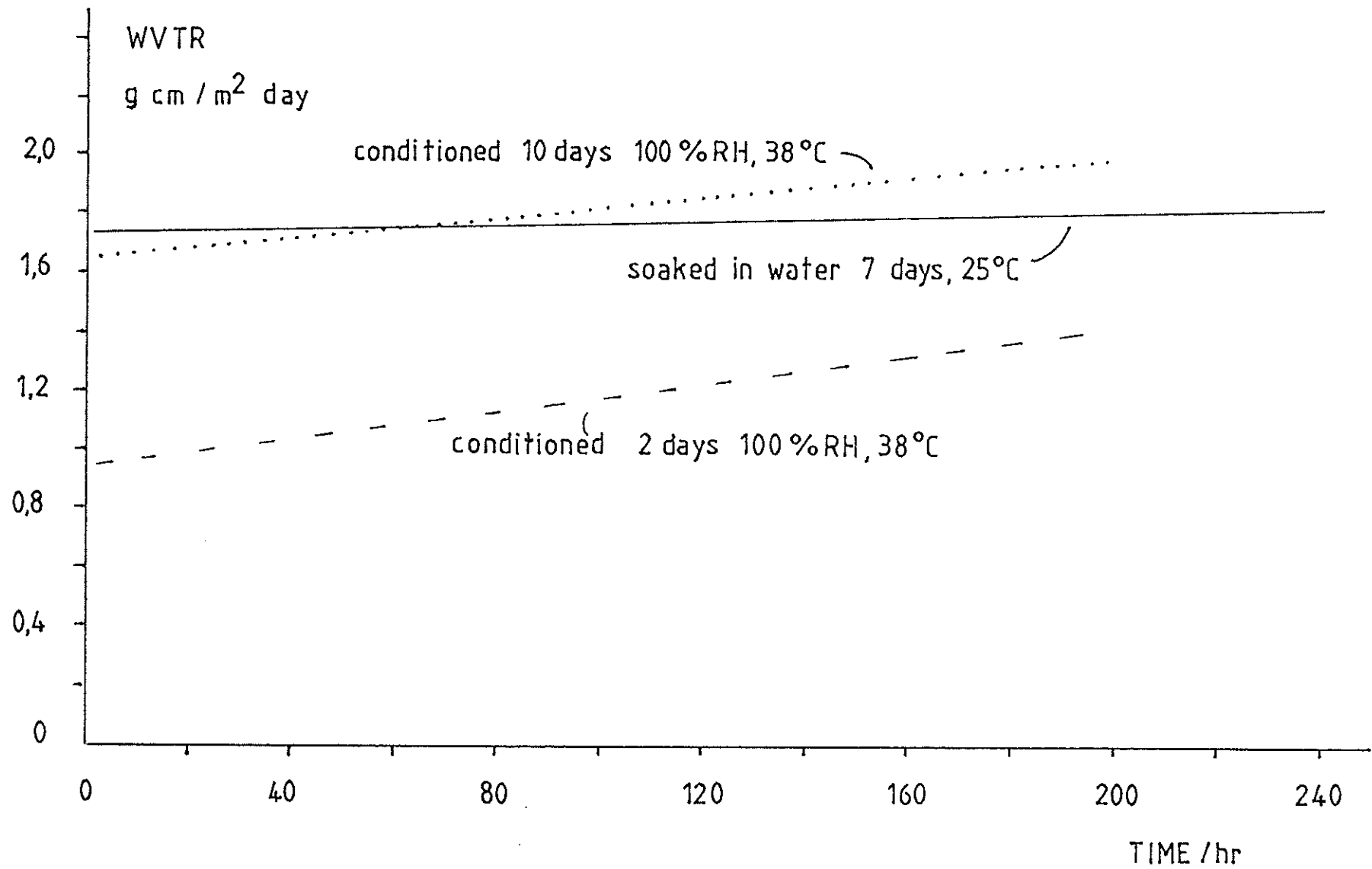


FIG. 7

INFLUENCE OF WATER UPTAKE (CONDITIONING & TEST TIME) ON WVTR FOR 030590



## APPENDIX 1

### INFLUENCE OF MOULDING CONDITIONS

It was reported previously (Tech. Memo. 06-28-0789) that the oxygen permeability coefficient of polyketone Hull 7 apparently varied with film thickness, over the range 70-150 $\mu$ m. The permeability coefficient increased with decreasing film thickness. Compression moulding conditions were not strictly controlled in that work, but, in general, high forces were applied to produce as thin films as possible whilst the moulding temperature was kept just above the melting point and rapid cooling was used to minimise thermal degradation. These moulding conditions, may, however, have led to detrimental effects on the film morphology. Indeed DSC showed the films to have multiple melting endotherm peaks (Figure A1). It was noted that the films with the higher oxygen permeability coefficient [ $\sim 10^{-12}$  cc cm cm<sup>-2</sup> s<sup>-1</sup> (cmHg)<sup>-1</sup>] showed a DSC melting endotherm at lower temperature, 202-207°C, than the main endotherm at 210-220°C which was not so prominent for the films with better performance [ $P(O_2) \sim 10^{-13}$  cc cm cm<sup>-2</sup> s<sup>-1</sup> (cmHg)<sup>-1</sup>]. It may have been that the thickness dependence was an artefact of the moulding conditions.

A short programme of work was carried out to find moulding conditions which would give more reproducible good barrier performance. Films of polyketone 130390 were compression moulded under a range of applied force (6, 10 and 18 ton) for 1 to 3 min at 235°C,  $\sim 25^\circ$ C above the DSC melting endotherm peak, with slow cooling ( $\sim 15^\circ$ C min<sup>-1</sup>) and fast cooling ( $\sim 150^\circ$ C min<sup>-1</sup>) cycles. None of the films of 130390 showed the multiple melting endotherm peaks seen for Hull 7. The films prepared with the slower cooling rate had the peak of the DSC melting endotherm at higher temperature (Figure A2) and had lower permeability coefficient. An apparent correlation between the permeability coefficient and the DSC melting endotherm peak temperature for 130390 and Hull 7 is shown in Figure A3. The dependence was much stronger for Hull 7 than 130390. The effect of cooling rate on permeability was also found for polyketone 260490, which has a lower propene content and higher melting point than 130390. It was a lower permeability material and more, perhaps, sensitive to cooling rate. At 0% relative humidity the permeability of a slowly cooled film was  $7 \times 10^{-14}$  cc cm cm<sup>-2</sup> s<sup>-1</sup> (cmHg)<sup>-1</sup> compared to  $1.4 \times 10^{-13}$  cc cm cm<sup>-2</sup> s<sup>-1</sup> (cmHg)<sup>-1</sup> for a rapidly cooled film.

Since this work was carried out, Shell have published data (US 4892697) claiming the benefit of moderate cooling rates for producing polyketone films with enhanced barrier properties.

There remain features of the effects of moulding conditions on polyketone film permeability to be understood. However, for the purposes of investigating the influence of polyketone composition on barrier properties, controlling the pressing conditions (applied force, temperature, time and cooling rate) was deemed sufficient to give consistent and reproducible results.

FIG. A1

DSC OF HULL 7 POLYKETONE FILM

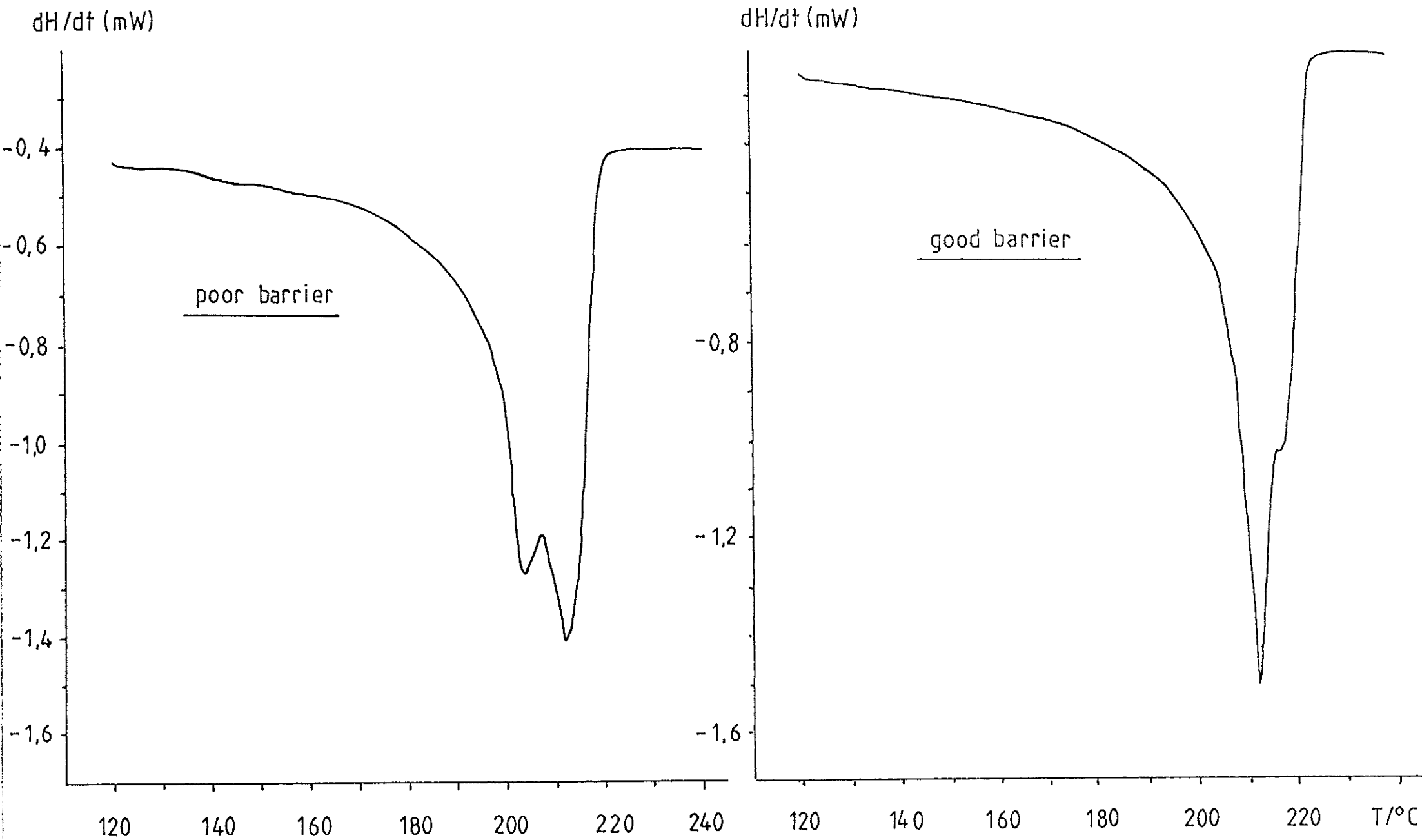


FIG. A2

DSC OF 130390 POLYKETONE FILM

dH/dt (mW)

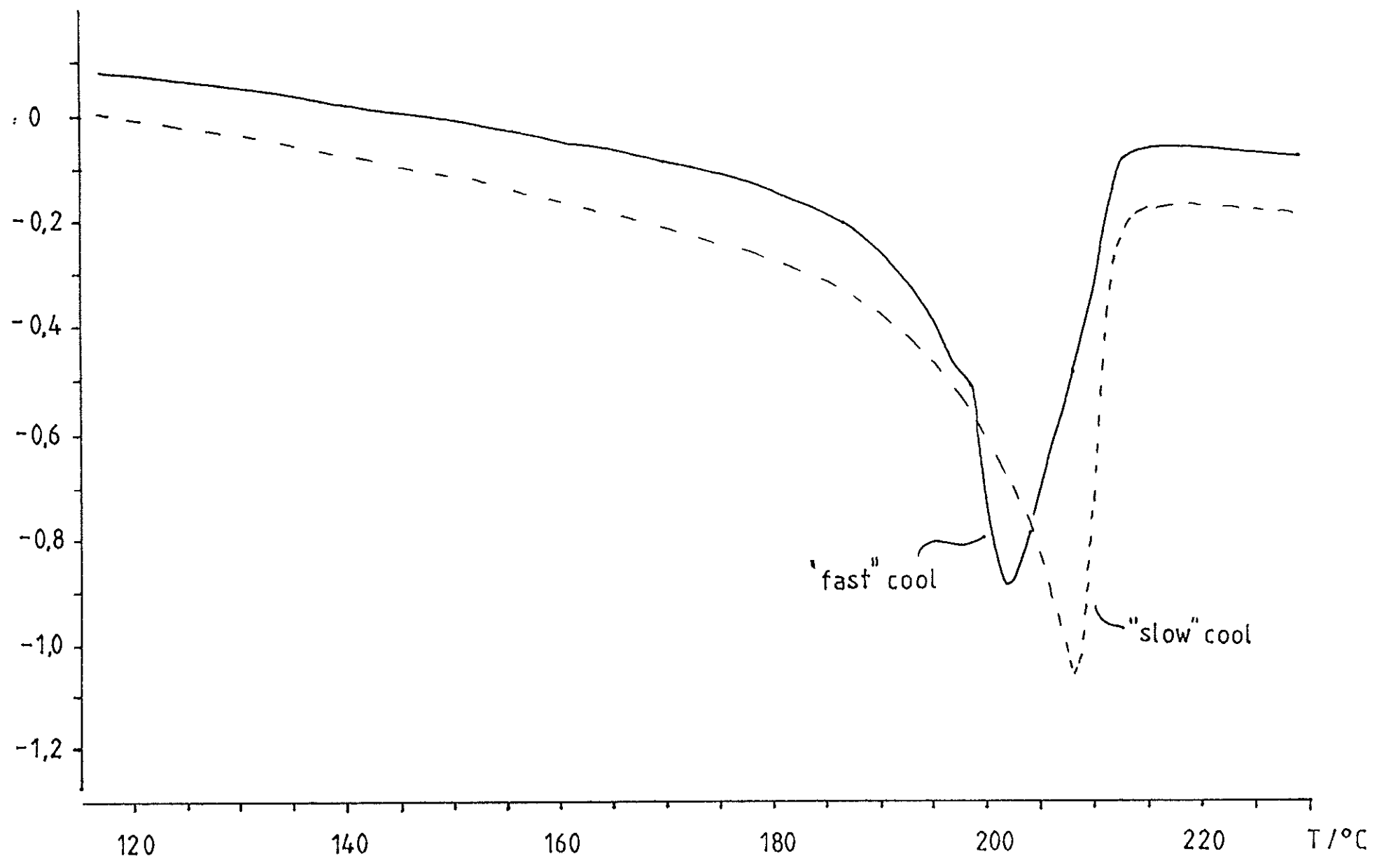




FIG. A3

OXYGEN PERMEABILITY vs MELTING POINT

$P_{O_2} / \text{cc cm cm}^{-2} \text{s}^{-1} (\text{cm Hg})^{-1}$

