THE DEVELOPMENT OF STATIONARY PHASES FROM ADDITION COPOLYMERS

by

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Submitted in partial fulfilment of
the requirements for the degree

MASTER OF SCIENCE

in the

FACULTY OF MATHEMATICS AND
NATURAL SCIENCE
UNIVERSITY OF PRETORIA

PRETORIA MAY 1981

SUMMARY

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Four new gum stationary phases suitable for use in glass capillary columns have been prepared by radiation-induced copolymerization of chlorotrifluoroethylene with the following comonomers: ethyl vinyl ether, butyl vinyl ether, vinyl acetate, and vinyl pentanoate. The polarity of each was classified, using the five basic McReynolds constants. A wide range of polarities was achieved by altering the functional group and the length of the side chain of the comonomers. The minimum and upper operating temperatures were determined. The minimum operating temperature was found to be 100 °C higher than the corresponding glass-transition temperature.

SAMEVATTING

DIE ONTWIKKELING VAN STASIONêRE FASES VAN ADDISIE-KOPOLIMERE

deur

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Vier nuwe stasionêre gomfases wat in kapillêre glaskolomme gebruik kan word, is deur straling-geïnduseerde kopolime=risering van chlorotrifluooretileen voorberei met die volgende komonomere: etielvinieleter, butielvinieleter, vinielasetaat en vinielpentanoaat. Die polariteit van elk is geklassifiseer deur middel van die vyf basiese McReynolds-konstante. 'n Wye reeks polariteite is verkry deur die komonomere te verander. Die minimum en bo-bedryfstemperature is bepaal. Die minimum bedryfstempera=tuur was 100 °C hoër as die ooreenstemmende glasoorgangs=temperature.

ACKNOWLEDGEMENTS

The author is greatly indebted to the following people:

1. The Director of Chemistry, Dr W.J. de Wet, of the Atomic Energy Board for permission to do the experimental work in the laboratories of the Chemistry Division, as a full-time employee, for degree purposes.

2. The promotor of this thesis, Prof. R.G. Böhmer of the Department of Chemistry, University of Pretoria, for his support, direction, and critical evaluation of this study.

3. The co-promotor of this thesis, Dr N.G. Schnautz, for his advice and encouragement.

4. Mrs A. van der Laan for the editing of this thesis.

5. Messrs H.C. Ridder, P. Cusens, and D. Terblanche for glass blowing.

6. Mrs H. Roesch for the drawings.

7. Last but not least, I wish to thank my wife Dot for her help, advice, and efficient typing of this thesis.

LIST OF SYMBOLS

1.	$\bar{M}_n$	number-average molecular mass
2.	CTFE	chlorotrifluoroethylene
3.	EVE	ethyl vinyl ether
4.	BVE	butyl vinyl ether
5.	VA	vinyl acetate
6.	VP	vinyl pentanoate
7.	k_{nm}	rate constant
8.	r_n	monomer reactivity ratio
9.	Q_{nm}	reactivity of various monomers
10.	e_n	electrostatic interaction of permanent charges on the substituents in polarizing double bonds
11.	T_g	glass-transition temperature
12.	DSC	differential scanning calorimetry
13.	GC	gas chromatography
14.	TG	thermogravimetry
15.	DTG	differential thermogravimetry
16.	Bq	Becquerel
17.	kGy	kilogray
18.	OD	outside diameter
19.	ID	inside diameter
20.	t_R	retention time
21.	t_M	gas holdup time
22.	t'_R	adjusted retention time
23.	T	absolute temperature K
24.	I_x	Kováts retention index
25	ΔI_x	McReynolds phase specific constant
26.	$b_{0,5}$	peak width at half height
27.	n_{eff}	effective plate number

28.	n_{theor}	theoretical plate number
29.	n_{real}	real plate number
30.	h_{theor}	height equivalent to a theoretical plate
31.	h_{real}	height equivalent to a real plate
32.	TZ	separation number
33.	TZ_{10}	number of peaks which can be separated between $k = 0$ and $k = 10$
34.	V_g	specific retention volume
35.	ΔH_e	differential heat of evaporation
36.	TF	tailing factor
37.	ΔI_B	base-line shift during temperature programming
38.	T_{max}	temperature where the base-line deviates by more than 3×10^{-12} amps from the initial base-line
39.	A:B	acid:base ratio
40.	DMA	dimethylanaline
41.	DMP	dimethylphenol
42.	S	2-ethylhexanoic acid
43.	am	dicyclohexylamine
44.	ol	1-octanol
45.	al	n-nonanal
46.	D	2,3-butanediol
47.	Π	osmotic pressure
48.	s.d.	standard deviation
49.	d_f	film thickness (μm)

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1. INTRODUCTION

The aim of this study was -

a. to produce gum stationary phases that would coat glass capillary columns;

b. to produce a family of stationary phases that would cover the whole polarity range required by chromatographers; and

c. to characterize the polarity of these stationary phases.

1.1 Gum Stationary Phases

The development of glass capillary columns has been hampered by the lack of adherence of the stationary phase to the glass surface. Three approaches have been used to try to improve film stability and adhesion to the capillary wall:

1. Improvement of the wettability of the glass surface.
2. Roughening of the column wall.
3. The use of gum stationary phases.

Commercially, a limited number of gum stationary phases is available. Three years ago when only four gum stationary phases were available, Grob[1] called polymer chemists' attention to the need of developing new and especially more polar, gum phases. A more recent review by Versele[2] has shown that four more gum phases have become available. He stresses that gums should be selected in preferance to liquid stationary phases for the following reasons:

1. Gums coat readily by the static method.
2. Gums give consistently higher plate numbers, particularly after extensive conditioning.

Grob and Versele attribute the higher plate number to better film homogeneity of gum phases. Versele has emphasised that column wall modification has lost much of its importance and that more research should be concentrated on gum phases.

The silicone stationary phases are produced from a variety of homo- or comonomers. In order to initiate the copolymerization of these monomers, catalysts must be added[3]. When the desired degree of polymerization has been obtained, the catalyst must be removed to prevent depolymerization of the stationary phase at high temperatures. The degree of polymerization determines whether a stationary phase is a gum or an oil; for example, according to Miller and Hawkes[4], the polydimethylsilicone oil SF-96-2000 has a number-average molecular mass ($\bar{M}_n$) of $3{,}5\text{x}10^4$ while the polydimethylsilicone gum SE-30 has a $\bar{M}_n = 4\text{x}10^5$.

Polymerization initiated by means of gamma radiation offers a unique method of preparing gum stationary phases without entraining catalyst in the gum. The basic requirements for new gum stationary phases may be summarized as follows:

a. High average molecular mass, which confers low bleed.

b. Stability to high temperatures.

c. The capacity to alter the polarity to achieve the separations required.

1.2 The Family of Copolymers Studied

Chlorotrifluoroethylene (CTFE) was considered as a potential basis for a family of stationary phases for the following reasons:

a. Polychorotrifluoroethylene has been used for many years as the stationary phase Kel F.

b. The copolymers of chlorotrifluoroethylene exhibit high thermal stability.

c. The copolymers can be prepared with a high molecular mass.

d. The polarity of the alternating CTFE-based copolymers may be altered by selection of a comonomer of suitable polarity.

e. The copolymers can be prepared with a known structure that can be reproduced from batch to batch.

Recently Klein and Widdecke[5] showed that more attention should be paid to polymeric blends and copolymers as non-volatile mixed stationary phases. They showed that the equation of Purnell and co-workers[6-9] for mixed stationary phases could be applied to copolymers and polymeric blends of the two homopolymers.

The variation in the composition of the copolymer provides a useful additional method for varying the polarity of a stationary phase. When a stationary phase has to be manufactured, it is essential that the polarity can be reproduced from batch to batch. Indeed it is desirable that the copolymer be homogeneous in composition rather than having a broad distribution of compositions.

1.2.1 Theory of polymerization

Kinetic expressions can be derived for gamma-ray-induced free radical copolymerization. This provides information on the reactivities of a variety of radicals towards a single monomer, or on the relative reactivities of a series of monomers towards a reference radical. Thus the monomers M_1 = CTFE and another vinyl monomer M_2 form radicals when irradiated. The four possible propagation reactions are:

Reaction	Rate
$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot$	$k_{11} \lvert M_1\cdot\rvert \lvert M_1\rvert$
$M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot$	$k_{12} \lvert M_1\cdot\rvert \lvert M_2\rvert$
$M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot$	$k_{21} \lvert M_2\cdot\rvert \lvert M_1\rvert$
$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot$	$k_{22} \lvert M_2\cdot\rvert \lvert M_2\rvert$.

For the formation of high molecular mass polymer, the composition of a copolymer being formed at any instant is given by the Mayo and Lewis[10] equation:

$$\frac{d\lvert M_1\rvert}{d\lvert M_2\rvert} = \frac{\lvert M_1\rvert}{\lvert M_2\rvert} \; \frac{r_1\lvert M_1\rvert + \lvert M_2\rvert}{\lvert M_1\rvert + r_2\lvert M_2\rvert}$$

$r_1 = k_{11}/k_{12}$ r is the reactivity ratios.

$r_2 = k_{22}/k_{21}$

When $r_1 > 1$, the radical $M_1\cdot$ reacts preferentially with M_1, while when $r_1 < 1$, the radical $M_1\cdot$ reacts preferentially with M_2. It must be emphasised that the regular alternation of two monomer units requires that the reactivity ratios be small, i.e. r_1 and r_2 should be small.

The monomer reactivity ratios r_1 and r_2 may be determined from experimental data, using one of the following methods: Finemann and Ross[11], Tosi[12] or Braun, Brendlein and Mott[13]. These data are available in tables[14] or in publications[15,16]. The monomer reactivity ratios for some of the monomer studies, are shown in Table I.

TABLE I

Monomer reactivity ratios				
M_1	M_2	r_1	r_2	t/°C
CTFE	Vinyl Acetate (VA)	0-0,1	0,36-0,56	0
CTFE	Ethyl Vinyl Ether (EVE)	0,008-0,012	0	20

From Table I the EVE/CTFE and VA/CTFE copolymers are seen to be predominantly alternating systems.

When the problem is encountered where the comonomers have not been copolymerized experimentally and the reactivity ratios determined, recourse must be made to the theoretical equations of Alfrey-Price[17]:

$$r_1 = \frac{Q_1}{Q_2} \exp - e_1(e_1-e_2)$$

$$r_2 = \frac{Q_2}{Q_1} \exp - e_2(e_2-e_1) \;.$$

Q_1 and Q_2 are the reactivity, and e_1 and e_2 are proportional to the electrostatic interaction of the permanent charges on the substituents in polarizing the double bond. Tables[14] are available for the Q-e values. Using these values, the reactivity ratios were calculated for the various vinyl monomers that were copolymerized with CTFE as shown in Table II.

TABLE II

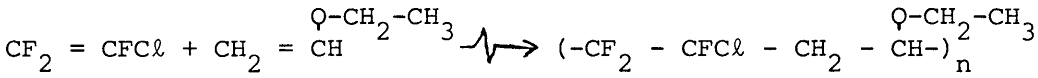
Monomer reactivity ratios calculated by the Alfrey-Price method

Monomer 1	Monomer 2	r_1	r_2
CTFE	Ethyl Vinyl Ether (EVE)	0,12	0,072
CTFE	Butyl Vinyl Ether (BVE)	0,004	0,064
CTFE	Vinyl Acetate (VA)	0,06	0,89
CTFE	Vinyl Pentanoate (VP)	0,056	1,11

The experimental reactivity ratios for the VA/CTFE and VP/CTFE copolymers in Table I compare well with the calculated values shown in Table II. The VP/CTFE copolymer can be expected to be enriched with respect to the VP; however, this copolymer remains essentially alternating.

The copolymerization of the various monomers with CTFE leading to alternating copolymers, is shown below:

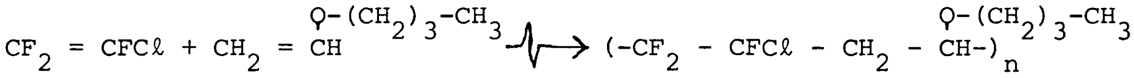
a.



$$CF_2 = CFCl + CH_2 = \overset{O-CH_2-CH_3}{\overset{|}{CH}} \longrightarrow (-CF_2 - CFCl - CH_2 - \overset{O-CH_2-CH_3}{\overset{|}{CH}}-)_n$$

(CTFE) (EVE - ethyl vinyl ether)

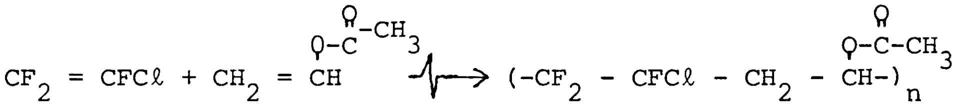
b.



$$CF_2 = CFCl + CH_2 = \overset{O-(CH_2)_3-CH_3}{\overset{|}{CH}} \longrightarrow (-CF_2 - CFCl - CH_2 - \overset{O-(CH_2)_3-CH_3}{\overset{|}{CH}}-)_n$$

(CTFE) (BVE - butyl vinyl ether)

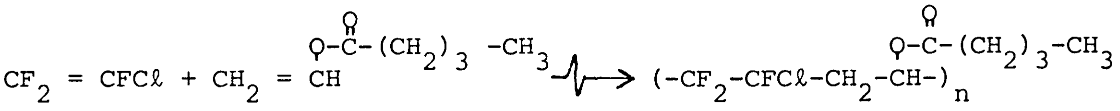
c.



$$CF_2 = CFCl + CH_2 = \overset{O-\overset{O}{\overset{\|}{C}}-CH_3}{\overset{|}{CH}} \longrightarrow (-CF_2 - CFCl - CH_2 - \overset{O-\overset{O}{\overset{\|}{C}}-CH_3}{\overset{|}{CH}}-)_n$$

(CTFE) (VA - vinyl acetate)

d.



$$CF_2 = CFCl + CH_2 = \overset{O-\overset{O}{\overset{\|}{C}}-(CH_2)_3-CH_3}{\overset{|}{CH}} \longrightarrow (-CF_2-CFCl-CH_2-\overset{O-\overset{O}{\overset{\|}{C}}-(CH_2)_3-CH_3}{\overset{|}{CH}}-)_n$$

(CTFE) (VP - vinyl pentanoate)

From the kinetic data all the copolymer systems to be studied can be seen to be predominantly alternating, therefore, no difficulty should be encountered in reproducing the structure of the copolymers. The polymeric product of these reactions contains a broad distribution of molecular masses; the lower molecular mass fraction of the copolymers (which causes column bleed) may be removed by fractionating the polymers by solubility differences. Fractional precipitation is carried out by adding the non-solvent to a dilute solution of the polymer until a turbidity develops.

1.2.2 Limitation of copolymer materials

1.2.2.1 Limitations to the minimum operating temperature

The minimum operating temperature of a stationary phase that exhibits a crystalline melting point has usually been taken at a few degrees above the melting point. Schwartz and Mathews[18] have shown that stationary phases with relatively high melting points do not yield efficient columns at their melting points. They have shown that in some cases stationary phases become efficient at 75 °C above their melting points. Crystalline melting points are usually encountered in stationary phases that are homopolymers, e.g. poly-CTFE consists of only CTFE units. Stationary phases that are manufactured from two different monomer units usually do not exhibit crystalline melting points. These copolymer stationary phases exhibit glass transitions characteristic of amorphous polymers[19]. Below the glass-transition temperature (T_g), these copolymers exhibit the characteristics of glasses, i.e. hardness, stiffness, and brittleness. The minimum operating temperature of a copolymer stationary phase may be expected to be considerably higher than the glass-transition temperature.

When designing a new stationary phase, the prediction of the T_g's of polymers from their chemical structures can be seen to have remarkable practical importance. Marcinčin and Romanov[20,21] have proposed empirical equations expressing the T_g of polymers as a function of cohesive energy and a steric factor. The T_g of copolymers was shown to be lowered by increasing the methylene side chain. Therefore, the BVE and VP/CTFE copolymers can be expected to have glass transitions at temperatures lower than the EVE and VA/CTFE copolymers.

The T_g of a copolymer can easily be determined on a differential scanning calorimeter (DSC), or the T_g may be determined on the GC by the Littlewood[22] method. This entails the determination of the specific retention volume of a substance at a number of different temperatures. This method is time-consuming and requires operation of the GC at subambient temperatures. Wasik[23] has shown that these two methods give comparable results.

1.2.2.2 Limitations to the upper temperature limit

With the increasing use of polymeric materials as stationary phases, the decomposition temperature, rather than volatility, is of greater importance when designing a new stationary phase, since volatility can be controlled by increasing the molecular mass of the polymeric material and fractional precipitation to remove the lower molecular mass constituents. The mass loss due to evaporation and/or pyrolitic destruction is best determined thermogravimetrically. The wall of the glass capillary column together with oxygen in the carrier gas can catalyse the decomposition of a stationary phase even at relatively low temperatures. It was decided that the columns should be conditioned in the GC at the following temperatures: 200 °C, 250 °C, and 275 °C, for twenty hours. When a column failed to separate a C_6-C_{12} hydrocarbon series after conditioning, this temperature was taken as the upper temperature limit.

1.3 The Characterization of the Polarity of the New Stationary Phases

The trend today is to define the polarity of stationary phases by the five basic McReynolds[24] probes: benzene, butanol, 2-pentanone, nitropropane, and pyridine. In order to make sure that the phase alone was being defined, all the columns were deactiviated with Carbowax 1000, prior to coating with thick films of the stationary phases.

The quality of the columns coated with the new stationary phases compared to columns coated with commercial stationary phases of similar polarity was judged by determining the real plate number and separation number according to the method described by Kaiser[25], in combination with the test procedures developed by Cram[26] and Grob[27] Finally a perfume was injected onto the columns and the separation achieved while temperature programming was compared to separations achieved on columns coated with commercial stationary phases.

2. EXPERIMENTAL

2.1 Copolymer Preparation

2.1.1 Materials

Vinyl acetate (Merck 99 %), ethyl vinyl ether (Merck 99 %) and butyl vinyl ether (Fluka 97 %) were distilled in order to remove the inhibitors present. Chlorotrifluoroethylene (Matheson Gas Products 99 %) was used directly from the cylinder.

Vinyl pentanoate was prepared by the vinyl exchange reaction between pentanoic acid and vinyl acetate using mercuric acetate/fuming sulphuric acid as the catalyst[28]. Purification was by double vacuum distillation at 85 ^{o}C and a pressure of 120 mm H_g.

2.1.2 Procedure for copolymer preparation

The monomers were degassed by three freeze-pump-thaw cycles on a vacuum line prior to storage in glass vessels attached to the vacuum manifold. This manifold had a calibrated known volume in which the pressure could be accurately measured. Half mole fraction mixtures of the required monomers were condensed into the glass ampoules using liquid nitrogen. The frozen ampoules were then sealed off with a flame.

The ampoules were irradiated at 0 °C until a conversion of 20-30 % was achieved. The ampoules were immediately placed in liquid nitrogen and then opened. The copolymer formed was dissolved in acetone and then precipitated with ethanol. The reprecipitation was carried out three times and approximately 90 % was recovered after each precipitation. The final precipitate was dried overnight in a vacuum oven at 60 °C and a pressure of 5 mm Hg.

2.1.3 Irradiation source

Irradiations were carried out in an Atomic Energy of Canada Limited Gamma Cell 220 irradiator with a nominal capacity of $4,1 \times 10^{14}$ Bq(s^{-1}). The dose rate of 3,4 kGy was determined by Fricke dosimetry[29].

2.2 Preparation of Capillary Columns

2.2.1 Surface roughening and column drawing

The quartz powder method[30,31] for surface-roughening the column was used. A mixture consisting of 6 ml methanol, 3 ml of 96 % ethanol, and 2 g of 5 µm quartz powder was placed in an ultrasonic bath for 15 min. The suspension was poured down clean Pyrex glass tubes (6 mm OD x 3 mm ID) held in a vertical position. The tube was immediately dried by flushing it with nitrogen at a rate that advanced the drying front at approximately 1 cm/s. The quartz-coated tubes were then drawn at an 80:1 draw ratio with an oven temperature of 800 °C on a Shimadzu GDM1 glass-drawing machine. This yielded a capillary tube with an ID of 0,3 mm, which was broken into twenty-metre lengths.

The capillaries were washed by passing a number of solvents through the column in the following order: chloroform, acetone, methanol, water, concentrated nitric acid, water, 25 % ammonia solution and water. The capillaries were finally dried with acetone.

2.2.2 Column deactivation

Each of the capillary tubes was deactivated with Carbowax 1000 in the following way:

- 5 ml of a 20 mg/cm^3 solution of Carbowax 1000, dissolved in methylene chloride, was passed through the tubing, using nitrogen pressure. The tubes were dried by blowing nitrogen through them overnight.
- After both ends of the capillary tubes had been sealed off in a flame, they were placed in an oven at 270 °C for 20 h.
- After the baking the sealed ends of the tubes were broken off and the Carbowax 1000 not bonded to the glass was removed by washing with 10 ml methylene chloride.

2.2.3 Static coating

A 5 mg/cm^3 solution of the copolymer in question dissolved in acetone was forced into a capillary tube under nitrogen pressure. The end seal[32] was effected by placing the end of the capillary in a bath of ethanol and slipping a plug over the end. The plug consisted of a piece of PVC tubing 10 mm long, which had a piece of rounded capillary tube inserted halfway into it whilst submerged in the ethanol bath. The integrity of the seal was tested immediately by applying a vacuum of 50 mm Hg to the open end.

The filled column was placed in a water bath that was left to equilibrate to a room temperature of 22 °C. The open end of the column was connected to a vacuum pump, and the vacuum gradually improved until the acetone started to evaporate.

As the meniscus moved down the column, the vacuum was slowly improved so as to maintain the initial rate of evaporation as closely as possible. When the column was empty it was removed and placed in the gas chromatograph.

2.3 Chromatography

A Varian 1400 gas chromatograph modified for capillary columns, fitted with a flame ionization detector, was used.

2.3.1 Carrier gas

Nitrogen (Air Products High Purity) was used as the carrier gas for all the tests, except in the case of the Grob test, where helium (Fedgas 99,995 %) was used. The linear flow rate, using methane, was set at 12 cm/s when nitrogen was the carrier gas and 28 cm/s when helium was the carrier gas. Generally a split ratio of 100:1 was used.

2.3.2 Column conditioning

All the columns were initially temperature-programmed from 30 °C up to 120 °C at a rate of 2 °C/min while purging with nitrogen. Further conditioning was done isothermally at specified temperatures for 20 h.

2.3.3 Quantity of sample injected

The samples were diluted in hexane to a concentration of 5 μℓ/100 μℓ. Using a 1 μℓ syringe, 0,2 μℓ of the solutions were injected.

2.3.4 Measurement of retention times

A stop-watch, set in a wooden block, was activated with the foot as the injection was made. The watch was stopped by hand when the pen on the recorder reached a peak. The recorder was run at a chart speed of 160 mm/min. The retention time of all subsequent peaks was measured with a ruler.

2.3.5 Determination of the McReynolds constants

The principle of characterizing stationary phases and the participation of each of the authors in developing the system has been covered in reviews by Ettrie[33,34,35].

The retention index (I) is a characteristic parameter of a substance (x) at a given temperature (T), on a given stationary phase. The retention index (I) may be calculated by the general Kováts equation[36,37]:

$$I_x^{(\text{Stationary phase})}(T) = 100 \left| n\left(\frac{\log t'_{R(x)} - \log t'_{R(Z)}}{\log t'_{R(z+n)} - \log t'_{R(Z)}}\right) + Z \right| \quad \ldots 1$$

T = temperature of the column (K)

t_R = retention time of a substance

t'_R = $t_{R(x)} - t_M$ = adjusted retention time

t_M = retention time of an unretained substance

x = symbol for the unknown substance

(Z) and $(Z+n)$ = carbon number of the n-alkane used

n = is the difference in the carbon atoms for the n-alkanes

$t_{R(Z)}$ and $t_{R(Z+n)}$ are chosen so that they bracket the retention time of the substance, that is $t_{R(Z)} \leq t_{R(x)} \leq t_{R(Z+n)}$.

According to Kováts, the polarity of a stationary phase may be characterized by determining the retention indices of a number of test substances on the stationary phase of interest and on squalane(36). On a non-polar phase such as squalane, the solutes emerge in the order of their boiling points while the retention on a polar phase depends on interaction between the active groups in the test substance and those of the stationary phase. Thus the difference between the retention indices on the polar and non-polar phases will be characteristic of this interaction and is given by equation 2, where squalane is taken as the non-polar phase:

$$\Delta I_X = I_X^{polar} - I_X^{non\text{-}polar} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

Originally Rohrschneider[38] used benzene, ethanol, methyl ethyl ketone, nitromethane, and pyridine to characterize stationary phases. McReynolds elaborated the concept of the phase specific constants from two points:

a. For practical reasons he proposed the use of a higher homologue for three of the five test substances originally proposed by Rohrschneider; and

b. he proposed the addition of five more test substances.

The first proposal has been widely accepted; however, the additional test substances are only rarely used when characterizing new phases. Takács *et al*[39,40] have concluded that in most practical cases the following five test substances are satisfactory: benzene, n-butanol, 2-pentanone, 1-nitropropane, and pyridine.

The determination of the retention indices, using equation 1, of substances with retention times of the same order of magnitude as the dead time, may be subject to a large error. Considering that $t_R = t_R - t_M$ and the logarithmic nature of equation 1, a small inaccuracy in the determination t_M will yield a large error in the determination of the retention index when t_R is of the same order of magnitude as t_M however, if t_R is very much larger than t_M this error will be negligible. Therefore, in the calculation of the retention indices the determination of the dead time should be made with the greatest accuracy possible. For detectors not responding to air, methane has been recommended. Garcia *et al*[41] have found that methane may be retained by stationary phases at relatively high temperatures. In order to decrease the magnitude of this error, the dead-time should preferably be calculated.

Kaiser[42] has published a program for the calculation of the mathematical dead time (t_M), using a Texas TI59 calculator coupled to a printer. As a printer was not available, a simpler and more automated program was developed[43] for this calculation, using a Texas TI59 calculator. The program calculates parameters a, b and t_M of a three-parameter model which can be transformed into the following form:

$$\log (t_R - t_M) = a + bZ$$

a = intercept of the log t'_R *versus* carbon number function.
b = slope of the log t'_R *versus* carbon number function.
Z = carbon number of the n-alkane used.

The dead time is found numerically by a hill-climbing procedure applied to the correlation coefficient. The slope and the intercept are obtained by linear regression which allows normal statistical methods[44] to be applied to calculations of confidence limits of the retention indices. Statistical data treatment usually requires eleven replicate analyses. Takács and Králik[45] did five replicate analyses while Cramers *et al*[46] did six replicate measurements in their studies of the repeatability of the retention indices. In this study five replicate measurements were made on the n-alkanes and the five McReynolds probes.

2.3.6 Determination of the glass-transition temperature

At the glass transition of a polymer, physical properties change dramatically from those characteristic of a brittle, glassy material to those of a rubber-like plastic. The retention time of a solute injected onto a column coated with a stationary phase in the glassy state will be considerably shorter than when the stationary phase has become rubber-like and plastic. The partition ratio $k = t'_R/t_M$ expresses how many times longer the solute molecules spend in the stationary phase than in the mobile phase. Normally, capillary columns have k values considerably lower than packed columns. Also, in a homologous series like the n-alkanes, k increases as the carbon number increases. Therefore, as hexane has been used to determine T_g on packed columns[47], nonane appeared to be a reasonable first choice for capillary columns. The determination of the T_g has been shown by Wasik[23] to be independent of the nature of the solute. However, the solute should have a measurable retention time and the enthalpy for the solute-solvent interaction should be sensitive to changes in the structure of the stationary phase.

The specific retention volume (V_g) of a solute is related to the differential heat of evaporation (ΔH_e) and the absolute temperature (T) through the Littlewood equation:

$$\log V_g = \Delta H_e/2{,}3\ RT + \text{constant.}$$

A plot of log t'_R *vs* 1/T has been shown by Smolková *et al*[47] to be more convenient to use when determining the glass-transition temperature. The lower point of this Z-shaped curve was taken as the T_g in accordance with the work by Abushihada *et al*[48].

2.3.7 Column evaluation and test methods

The major requirements for a good column are: (1) the column should be highly inert; (2) very efficient; and (3) thermally stable. Ideally a test mixture should be able to diagnose any one of these problems.

Various test mixtures have been proposed for the testing of capillary columns with respect to their efficiency, polarity, and inertness.

High-resolution gas chromatography requires the highest performance characteristics. Cram has proposed that capillary columns be characterized in terms of their chromatographic performance by the following parameters:

1. The Trennzahl or separation number (TZ) is associated with both the selectivity and the efficiency of the column. An evaluation of the separation takes into account the interval between retention times (t_R) and peak widths at half height ($b_{0,5}$), as shown in the formula proposed by Kaiser[49]:

$$TZ = \frac{t_{R(2)} - t_{R(1)}}{b_{0,5(1)} + b_{0,5(2)}} - 1$$

   From this formula it can be seen that the greater the difference between the retention times, the higher the selectivity; and the wider the peaks, the poorer the efficiency, hence the separation as a whole.

2. The number of theoretical plates describes the efficiency of a column. The efficiency is a function of the kinetic processes occurring in the column and determines the peak widths of the analysed substances. The number of theoretical plates is calculated from the ratio of the retention time (t_R) and the peak width ($b_{0,5}$) at half height:

$$n_{theor} = 5,54 \left(\frac{t_R}{b_{0,5}}\right)^2 .$$

   The height equivalent to a theoretical plate (h) permits the comparison of the efficiency of columns of different lengths (L):

$$h = \frac{n}{L} .$$

From the Van Deemter[50] theory of velocity it follows that h is a function of the carrier gas velocity, diffusion and resistance to mass transfer between the carrier gas and the liquid phase.

3. The base-line shift, ΔI_B, during temperature programming is an indication of column bleed. A very stable or low-bleed column exhibits negligible base-line shift, even at high detector sensitivities. A high-bleed column will show a large base-line shift at a high temperature. The temperature where the base-line deviates by more than 3×10^{-12} amps from the initial base-line is called T_{max}. This definition facilitates the comparison of different columns.

4. The acid-base ratio (A:B) determines the acidity or basicity of the capillary column. A major drawback to the use of glass for capillary columns is its activity towards both acids and bases. The test for adsorption due to this activity is important as regards a decision on which column can be used for samples containing acidic and basic components. Normally a column is suitable for either acids or bases. The acid-base pair chosen was 2,6-dimethylphenol (DMP) and 2,4-dimethylanaline (DMA). The acid-base ratio is determined by measuring the relative height of the DMA and DMP peaks. When A:B is 1:0 the column is so strongly acidic that the DMA has been entirely adsorbed, while an A:B of 0:1 reflects a strongly basic column.

5. The second central moment or variance of the peak describes the peak shape sensitivity to adsorption of 1-octanol. This primary alcohol is appropriate for testing columns coated with a liquid phase without hydroxy groups in their structures. Glycol-type stationary phases normally show 100 % height with 1-octanol.

Accurate measurement of the third moment requires on-line digital data acquisition and computer calculations. As these facilities were not available, the tailing factor at 10 % of the peak height, as described by Schieke[51], was determined:

$$TF = \frac{a}{b} \times 100$$

where a and b were measured at 10 % of the peak height, as shown in Figure 1.

The efficiency parameter in the Cram test was modified because Kaiser[25] has proposed a new efficiency parameter. He proposed the real plate number (n_{real}) to replace the theoretical plate number (n_{theor}) and the effective plate number (n_{eff}). Kaiser showed that a linear relationship exists between the peak width at half height ($b_{0,5}$) and the retention time (r_R) as shown in Figure 2. From the slopes of the various lines the definition of the various efficiency parameters may be written in the following forms:

$$n_{theor} = 5,54 \left(\frac{t_R}{b_{0,5}}\right)^2$$

$$n_{real} = 5,54 \left(\frac{t_R - t_M}{b_{0,5} - b_o}\right)^2 \qquad b_0 = \text{width of peak at } t_M$$

$$n_{eff} = 5,54 \left(\frac{t_R - t_M}{b_{0,5}}\right)^2$$

From Figure 2 the definition of n_{real} is seen to be inversely related to the slope of the $b_{0,5}$ *vs* t_R curve; clearly this describes accurately what is occurring. The inverse of the definition of n_{theor} and n_{eff} leads to curves with slopes that are either too small or too large; therefore, at short retention times (i.e. at small values of the distribution coefficient $k = \frac{t_R - t_M}{t_M}$), n_{theor} will be larger than n_{real} while n_{eff} will be smaller than n_{real}. At long retention times there will be very little difference between these three efficiency parameters.

FIGURE 1

Definition of the tailing factor

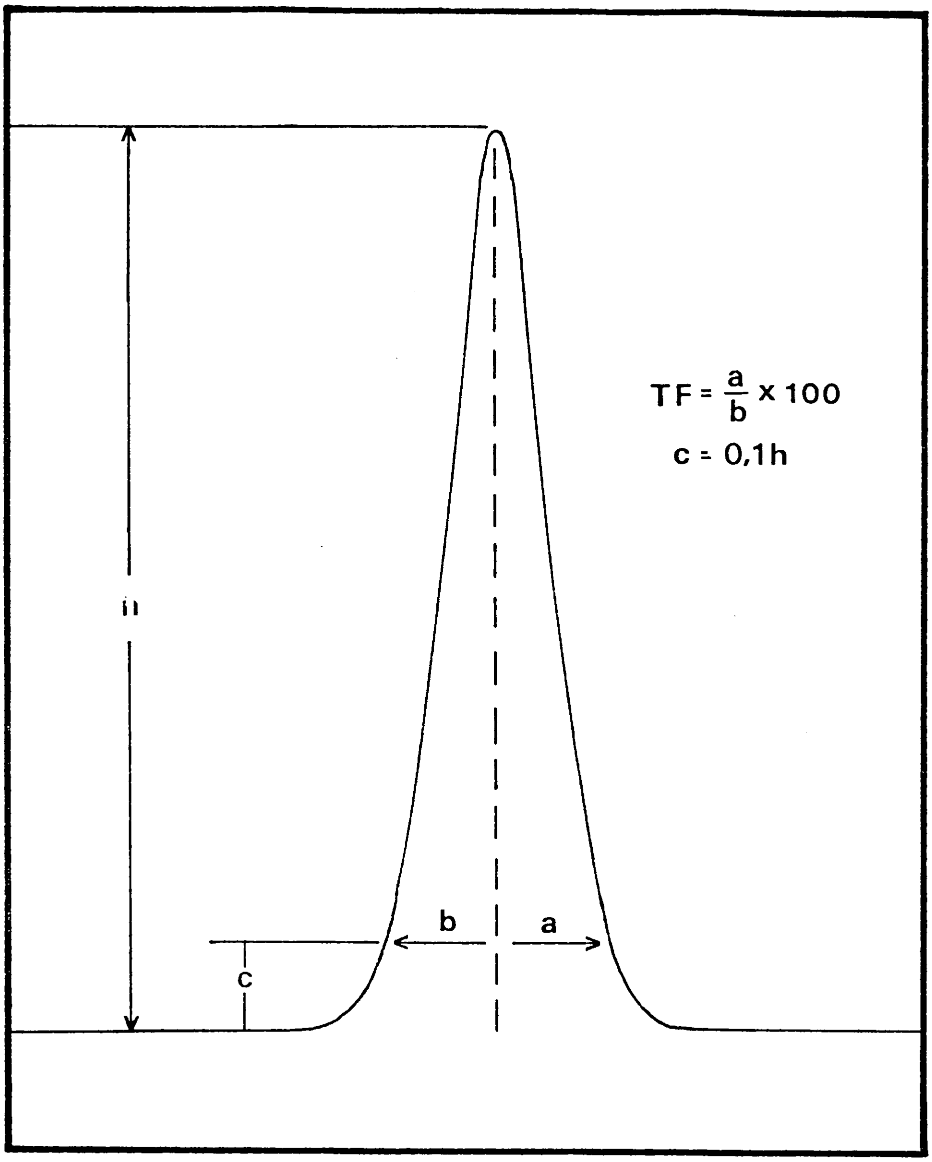
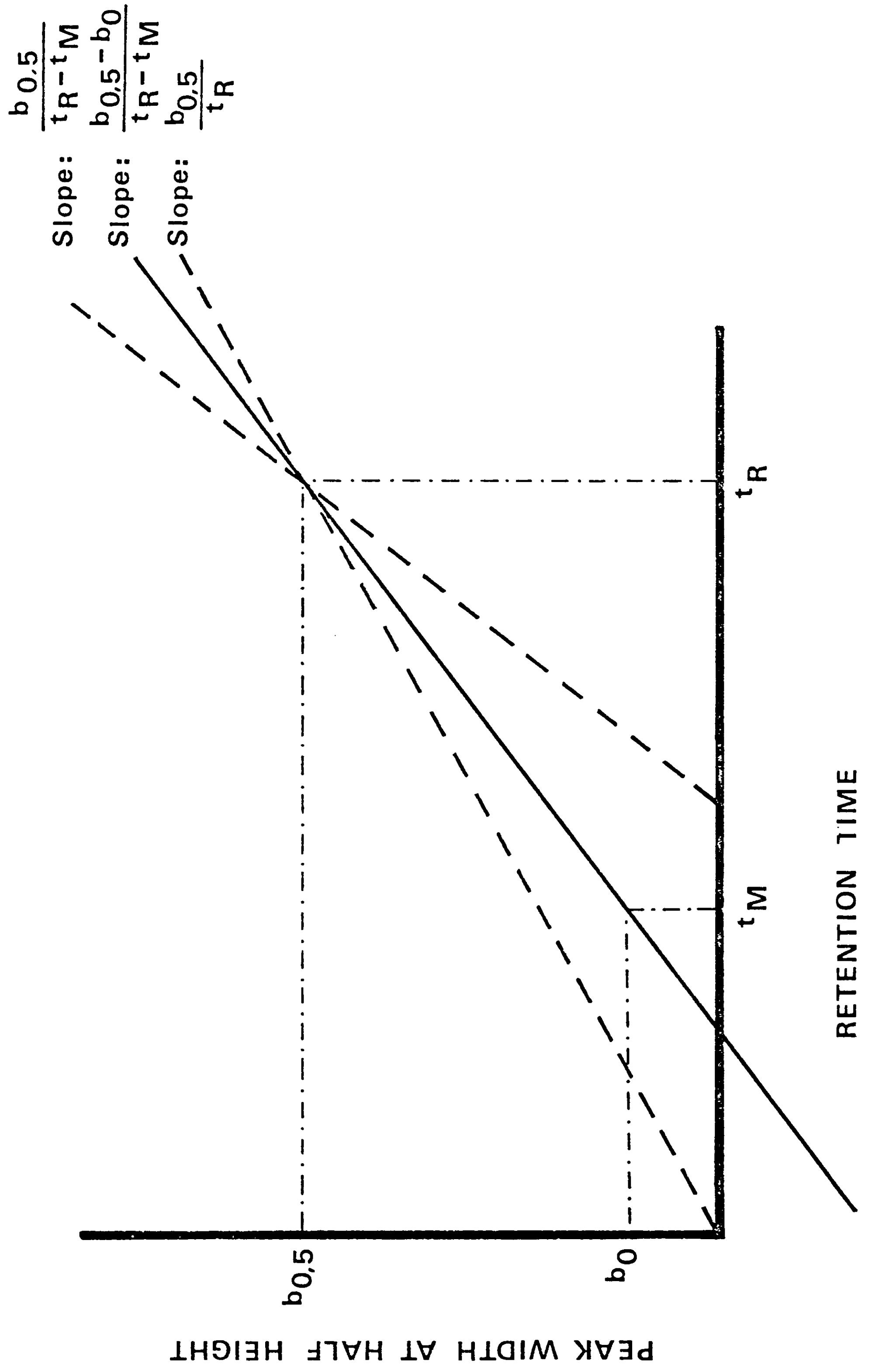


FIGURE 2

Peak width at half height versus retention time



The separation number TZ was, according to this new theory, expressed as TZ_{10}. This corresponds to the number of peaks which can be separated between k = 0 and k = 10:

$$TZ_{10} = \frac{10\ t_M}{b_{10} + b_0} - 1$$

The Grob test was not altered. Briefly, this test contains, in addition to the DMA-DMP pair, a more stringent acid-base pair, namely 2-ethylhexanoic acid (S) and dicyclohexylamine (am). The adsorption of alcohols is measured by 1-octanol (ol) (as used in many test mixtures) and 2,3-butanediol (D). The adsorption of aldehydes is measured using n-nonanal (al). The separation number TZ of Kaiser[49] was determined, using the methyl esters of C_{10}, C_{11}, and C_{12} carboxylic acids.

The test is based on temperature-programmed runs starting at 40 °C. A number of stationary phases are viscous or solid at this temperature (e.g. Carbowax 20M, FFAP, and Silar 10). In some instances, this difficulty can be overcome simply by cooling the column for the shortest possible time. This approach did not succeed with the copolymer stationary phases and the temperature program had to be started at 60-80 °C.

2.3.8 Determination of the minimum operating temperature

At temperatures below the minimum operating temperature the peaks are broad, tailing, and overlapping. In order to determine the temperature at which the columns start to function efficiently, the real plate height was determined at the following temperatures: 60 °C, 80 °C, 100 °C, 120 °C, 140 °C, 160 °C, and 180 °C. At each temperature the carrier-gas flow rate was set at a linear flow rate of 12 cm/s.

2.3.9 Determination of the upper temperature limit

On heating a glass capillary column, the stationary phase film may be disrupted in a number of different ways, for example: (1) the stationary phase may rearrange due to surface tension, and form droplets at a temperature well below the decomposition temperature of the stationary phase. Rearrangements are usually encountered when liquid stationary phases are used and this severely limits the use of these stationary phases at high temperatures. Gums rearrange only after prolonged use at high temperatures; (2) the glass surface may catalyse the decomposition at relatively low temperatures, leading to excessive column bleed; and (3) traces of oxygen in the carrier gas may be sufficient to cause oxidation even at low temperatures.

When the upper temperature limit of a stationary phase is to be determined, it is essential to specify the nature of the column wall and the treatment that these walls have received, together with the purity of the carrier gas. The loss of mass due to evaporation and/or pyrolitic destruction alone may be determined thermogravimetrically. (However, some metals also catalyse the decomposition of stationary phases.)

The upper temperature limit may be determined in the gas chromatograph by measuring the real plate height after conditioning at 120 °C for 20 h. This formed a reference against which the efficiency of the columns was compared after conditioning at 200 °C, 225 °C, 250 °C, and 275 °C for 20 h. When the efficiency of a column deteriorated markedly after one of these conditionings, this temperature was taken as the upper temperature. Any large discrepancy between this tempera=ture and the decomposition temperature determined thermogravimetrically may be ascribed to one of the three examples explained above.

2.3.10 Separation of a complex mixture

The perfume from a men's aftershave lotion contains a large variety of different compounds. The separation of these compounds on columns coated with commercial stationary phases can only be achieved by temperature programming the columns; therefore, in order to compare separations achieved on the copolymer column with a column coated with a commercial stationary phase, the perfume was injected onto the columns, using the following conditions: (1) The initial column temperature was 120 °C; (2) the temperature was programmed upwards at a rate of 2 °C/min until the stationary phase bleed became excessive; (3) a split ratio of 120:1 was used; and (4) 0,2 μℓ perfume was injected.

The initial column temperature was chosen as 120 °C as the majority of the copolymer stationary phases began to function efficiently at this temperature.

2.4 Analysis of Copolymers

2.4.1 Differential scanning calorimetry

Differential scanning calorimetry may be used to determine fundamental thermal properties of plastics, such as transition temperatures, heats of transition, and heat capacity.

The DSC-1B[52] (Perkin-Elmer) contains an average temperature circuit that measures and controls the temperature of a sample and a reference holder to conform to a predetermined time-temperature program. At the same time a temperature-difference circuit compares the temperatures of the sample and reference holders, and proportions power to the heaters in each holder so that the temperatures remain equal. When the sample undergoes a thermal transition, the power to the two heaters is adjusted to maintain their temperatures, and a signal proportional to the power difference is plotted on a recorder.

The glass-transition temperature of the copolymers was determined, using a DSC-1B. The low-temperature cover was filled with liquid nitrogen and 5-10 mg samples were cooled to -80 °C. The temperature was maintained at -80 °C for 10 min before temperature programming upwards at a rate of 16 °C/min.

2.4.2 Thermogravimetric analysis (TG)

A Perkin-Elmer TGS-2 analyser was used to show where the copolymers decompose on heating. The determination of the point on the TG curve where the maximum mass loss occurs, is facilitated by recording a differential thermogravimetric curve. The temperature was programmed upwards at a rate of 20 °C/min, using 10-20 mg samples.

2.4.3 Infrared spectra

Thin films of the copolymers and homopolymers of VA and VP were cast in petri dishes from an acetone solution of the copolymers (400 mg/10 ml acetone). In the case of the poly-CTFE homopolymer, the powdered polymer was mixed with potassium bromide (2 mg/200 mg KBr) and pressed into thin discs. The homopolymers of EVE and BVE (prepared[53] by catalysis with boron trifluoride etherate) were cast onto sodium chloride discs by first dissolving the polymers in a small amount of acetone.

The discs and films were used to record the infrared spectra on a Perkin-Elmer 467 Grating Infrared Spectrophotometer. The spectra of the homopolymers were used to show the presence of the various monomer units in the spectra of the copolymers.

2.4.4 Number-average molecular mass

The number-average molecular mass ($\bar{M}_n$) of the copolymers was determined on a Knauer membrane osmometer at 30 °C, using tetrahydrofuran as the solvent. Sartorius-regenerated cellulose membranes (cat. No 11539) were used.

Measurement is achieved by placing a dilute solution of the copolymers on the upper side of the membrane. The solvent on the underside of the membrane can diffuse through the membrane into the copolymer solution while the solute molecules are retained by the membrane. A negative pressure in the lower cell is thereby produced, which corresponds to the osmotic pressure in the upper cell. This negative pressure (Π in cm) is measured electronically.

In order to determine the molecular mass, at least four solutions of varying concentrations were measured. A plot of Π/c *vs* the concentration (c) was extrapolated to zero concentration in accordance with the van't Hoff equation of osmotic pressure:

$$\bar{M}_n = \frac{R \cdot T}{\left(\frac{\Pi}{c}\right)_{c \to o} \cdot \text{density}}$$

3. RESULTS

3.1 Deactivation of Capillary Columns

In Table III are some typical values for the tailing factors (TF %) of a number of different probes after the columns had received one deactivation treatment, using Carbowax 1000. Due to the poor injector design, the straightened end of the capillary column was adjusted until the tailing factor of hexane was approximately 100 %. The reproducibility and the degree of deactivation can be seen to be excellent for the single deactivation treatment. In view of the fact that the columns were to be coated with thick films of stationary phases, one deactivation was considered sufficient to deactivate the columns' surfaces. It must be remembered that Carbowax 1000 is an extremely polar stationary phase, therefore multiple deactivations could contribute to the polarity of a stationary phase coating such a surface.

TABLE III

The tailing factors after one deactivation with Carbowax 1000

Test substance	Column No 1	Column No 2	Column No 3	Column No 4	Column No 5
hexane	100	98	94	97	97
benzene	97	95	90	95	89
acetone	91	98	95	88	92
ethanol	82	86	83	77	83
MIBK	77	72	80	75	83
heptanol	56	51	50	49	58
pyridine	67	61	61	56	54

3.2 The Minimum Operating Temperature

In Table IV the real plate height is shown as a function of the temperature for the various columns. With increasing temperature the real plate height decreases and then becomes constant. The temperature where the real plate height became constant was taken as the minimum operating temperature. The minimum operating temperatures for the EVE/CTFE, VA/CTFE, FFAP, BVE/CTFE, and VP/CTFE columns are 130 °C, 150 °C, 90 °C, 110 °C, and 90 °C respectively. It is interesting to note that the FFAP column becomes efficient at 40 °C higher than the minimum operating temperature quoted by the tables of Analabs[54]. The melting transition of FFAP, as shown in Figure 5, occurs over the temperature range 20 to 60 °C. From this DSC curve the conclusion may erroneously be drawn that FFAP should start to function efficiently at temperatures higher than 60 °C.

The VP/CTFE copolymer column has a minimum operating temperature 40 °C lower than the VA/CTFE copolymer, while the BVE/CTFE starts to function efficiently 40 °C lower than the EVE/CTFE column. The lengthening of the side chain of the acetate and ether groups has clearly had the desired effect of lowering the minimum operating temperature.

TABLE IV

The real plate height as a function of the temperature

$t/^{o}C$	EVE/CTFE h_{real}/mm	VA/CTFE h_{real}/mm	FFAP h_{real}/mm	BVE/CTFE h_{real}/mm	VP/CTFE h_{real}/mm
60			0,91	1,83	1,93
80			0,81	1,12	0,86
90			0,64	0,86	0,51
100	3,13		0,53	0,54	0,46
120	0,75	2,52	0,57		
140	0,51	0,79			
160	0,46	0,60			
180	0,43	0,59			

3.3 McReynolds Constants

3.3.1 The Kováts retention indices

The average of five replicate measurements of the retention times ($\bar{t}_R$) of the C_6 - C_{12} n-alkanes, benzene, n-butanol, 2-pentanone, 1-nitropropane, and pyridine are shown in Table V, together with the standard deviation (s.d.) of these measurements. The mean retention times of the n-alkanes were used to calculate the mathematical dead time, together with the slope, intercept, and correlation coefficient of the log t'_R *vs* carbon number function, using the Texas TI59 calculator. Once these parameters were calculated, the retention times of benzene, n-butanol, 2-pentanone, 1-nitropropane, and pyridine were entered into the calculator and the retention indices of these five probes were calculated. Using standard statistical methods, the 95 % confidence limits of these retention indices were calculated, because the reproducibility of these indices depends on the deviations of the log t'_R *vs* carbon number function together with the deviations of the retention times of the five McReynolds probes.

The confidence limits for the five McReynolds probes on the non-polar columns (squalane, BVE/CTFE, and EVE/CTFE) are seen in Table V to be of the order of 0,5 index units, while on the polar columns (OV-17, VP/CTFE, and VA/CTFE) the confidence limits are generally less than 3 index units. The SE-52 and OV-225 showed confidence limits of the order of 10 index units. These poor confidence limits could be expected in view of the poor correlation coefficient found for the log t'_R *vs* carbon number function.

The reproducibility of these indices, however, gives no indication of their accuracy. Fortunately McReynolds[24] has published values for the retention indices of the five probes on squalane. In Table VI the values that McReynolds determined for the five probes are seen to be generally higher than the values determined in this investigation, as shown in Table V.

TABLE V

Retention times and Kováts retention indices of the five basic McReynolds probes

	Squalane		BVE/CTFE		SE 52		EVE/CTFE		OV 17		VP/CTFE		OV 225		VA/CTFE	
n-alkane	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.
C6	207,3	0,24	169,4	0,21	161,9	0,28	156,3	0,16	159,2	0,46	166,8	0,15	156,6	0,32	153,7	0,30
C7	254,1	0,63	177,3	0,19	173,7	0,30	161,8	0,16	167,3	0,30	174,2	0,33	161,7	0,32	155,7	0,34
C8	353,7	0,67	191,7	0,54	190,8	0,14	171,7	0,16	181,3	0,20	186,0	0,32	168,1	0,30	159,1	0,37
C9	561,3	2,43	218,2	0,47	221,2	0,20	189,6	0,23	206,8	0,47	207,2	0,41	178,7	0,10	164,7	0,36
C10	1 001,7	5,17	266,4	0,56	275,1	0,28	221,8	0,29	250,8	0,94	244,9	0,58	196,9	0,41	174,0	0,42
C11			354,6	0,59	370,7	0,38	279,3	0,40	329,6	0,76	311,8	0,85	227,6	0,24	189,5	0,41
C12			514,8	2,14	539,9				469,8	1,14	430,9	1,65	279,4	0,50	214,4	0,51
r	0,999 999		0,999 996		0,999 8		0,999 999		0,999 999		0,999 95		0,999 6		0,999 993	
t_M	164,9		159,9		147,6		149,4		148,8		157,7		149,8		150,6	
Slope	0,323 7		0,261 6		0,237 5		0,255 2		0,248 0		0,244 9		0,210 3		0,219 3	
Intercept	-0,315 0		-0,589 1		-0,264 2		-0,692 9		-0,470 2		-0,505 7		-0,420 9		-0,824 2	
Probes	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.	$\bar{t}_{R/s}$	s.d.
Benzene	216,7	0,16	176,8	0,12	170,0	0,20	166,7	0,53	176,4	0,14	183,5	0,15	173,4	0,14	165,4	0,05
Butanol	204,4	0,17	175,1	0,20	168,4	0,14	165,1	0,11	175,0	0,20	189,2	0,38	185,4	0,25	174,7	0,46
2-Pentanone	210,7	0,19	180,4	0,16	170,4	0,14	171,9	0,84	179,4	0,14	191,4	0,26	186,2	0,24	174,6	0,17
Nitropropane	211,5	0,24	188,6	0,58	174,6	0,24	181,4	0,13	192,0	0,28	207,4	0,19	216,0	0,14	197,0	0,65
Pyridine	234,2	0,18	197,6	0,37	184,6	0,65	186,9	0,59	207,0	0,66	220,6	0,43	217,2	0,44	198,4	0,38
Probes	I	C.L.	I	C.L.	I	C.L.	I	C.L.	I	C.L.	I	C.L.	I	C.L.	I	C.L.
Benzene	626,9	0,3	756,6	0,2	679,2	7,7	756,6	0,4	770,6	1,0	782,9	3,3	852,6	10,0	909,7	1,3
Butanol	590,5	0,3	740,1	0,1	665,6	7,9	740,1	0,4	761,5	1,0	818,4	3,3	937,6	9,9	1 006,2	1,4
2-Pentanone	610,4	0,3	801,3	0,2	682,4	7,7	801,3	0,4	788,7	0,9	830,3	3,4	942,2	9,9	1 005,4	1,4
Nitropropane	612,7	0,3	861,3	0,3	713,4	7,4	861,3	0,4	849,1	0,9	899,2	3,4	1 065,8	11,3	1 135,9	1,6
Pyridine	665,9	0,2	888,3	0,4	771,0	7,1	888,3	0,4	901,3	0,9	940,9	3,2	1 069,5	11,3	1 141,8	1,6

TABLE VI

Comparison of the Kováts retention indices

Stationary Phase	I Benzene	I Butanol	I 2-Pentanone	I Nitropropane	I Pyridine
Squalane	627	591	610	612	665
$\text{Squalane}_{\text{McR}}$	653	590	627	652	699

3.3.2 McReynolds constants

In Table VII the four copolymer columns are shown in order of increasing polarity, together with columns coated with commercial stationary phases of similar polarity. The average polarity was determined from the sum of the ΔI values for the five McReynolds probes. The lengthening of the side chain of the acetate and ether decreased the polarity of the stationary phases, e.g. VP/CTFE is less polar than VA/CTFE while BVE/CTFE is less polar than EVE/CTFE.

The McReynolds constants are derived from the difference between two Kováts indices. In most cases the reproducibility of these indices has been shown to be better than 3 index units, therefore, the reproducibility of the McReynolds constants should be better than 5 index units. In Table VIII the McReynolds constants found on SE-52, OV-17, and OV-225 are compared with the values shown in McReynolds tables[24]. The SE-52 and OV-17 columns are more polar while OV-225 is less polar than McReynolds values. The Carbowax 1000 deactivation, together with the very low values for the Kováts indices for squalane, are probably responsible for the high McReynolds constants found on the apolar columns.

TABLE VII

Summary of the McReynolds constants

Stationary Phase	Δ I Benzene	Δ I Butanol	Δ I 2-Pentanone	Δ I Nitropropane	Δ I Pyridine
BVE/CTFE	68	87	117	170	162
SE-52	52	75	72	101	105
EVE/CTFE	130	150	191	249	222
OV-17	143	171	179	237	236
VP/CTFE	156	228	220	287	278
OV-225	226	347	332	454	405
VA/CTFE	283	416	395	523	475

TABLE VIII

Comparison of the McReynolds constants

	Δ I Benzene	Δ I Butanol	Δ I 2-Pentanone	Δ I Nitropropane	Δ I Pyridine	ΣΔI
SE-52	52	75	72	101	105	405
$\text{SE-52}_{\text{McR}}$	32	72	65	98	67	334
OV-17	143	171	179	237	236	1 300
$\text{OV-17}_{\text{McR}}$	119	158	162	243	202	884
OV-225	226	347	332	454	405	1 765
$\text{OV-225}_{\text{McR}}$	228	369	338	492	386	1 813

3.4 The Upper Temperature Limit

The bleed from a freshly coated column is usually so large that it is impossible to measure the efficiency of a column, therefore the first conditioning treatment that the columns received on installation in the gas chromatograph was to program the temperature to 120 $^{\circ}$C. After this short conditioning the real plate height and the acid-base ratio were measured, as shown in Table IX. Included in this table are the real plate height and acid:base ratio measured at 120 ^{o}C, after conditioning the columns at 120 ^{o}C, 200 ^{o}C, 225 ^{o}C, 250 ^{o}C, and 275 ^{o}C for 20 h. The acidity of the columns is seen to increase progressively with con= ditioning. The upper temperature limit for the BVE/CTFE and VP/CTFE copolymers is seen to be 275 ^{o}C, and 250 ^{o}C for the EVE/CTFE and VA/CTFE copolymers. This is surprising in view of the fact that with an increase in the length of the side chain, the stability of the BVE/CTFE and VP/CTFE copolymers would be expected to be less than the EVE/CTFE and VA/CTFE copolymers. The BVE/CTFE and VP/CTFE copolymers are soft and rubbery while the VA/CTFE and EVE/CTFE copolymers are hard and glassy at room temperature.

The effect of conditioning on the McReynolds constants of the VA/CTFE and VP/CTFE is shown in Table X. In this table the McReynolds constants on the VA/CTFE column remained fairly constant while on the VP/CTFE column they decreased significantly after conditioning at 200 ^{o}C.

The effect of conditioning on the lower temperature limit of the VP/CTFE column was briefly investigated, as shown in Table XI. The lower temperature limit can be seen not to be affected by conditioning until the conditioning temperature exceeded 200 ^{o}C.

TABLE IX

The effect of conditioning on the real plate height and the A:B ratio

Temperature of condi= tioning	BVE/CTFE		EVE/CTFE		VP/CTFE		VA/CTFE	
	h_{real}/mm	A:B	h_{real}/mm	A:B	h_{real}/mm	A:B	h_{real}/mm	A:B
After temp. programming	0,70	1:0,40	1,07	1:0,78	1,59	1:0,8	2,63	1:0,98
120	0,70	1:0,33	0,59	1:0,58	0,46	1:0,79	2,52	1:0,97
200	0,55	1:0	0,98	1:0	0,47	1:0,67	3,64	1:0,80
225	0,51	1:0	0,78	1:0	0,46	1:0,37	3,84	1:0,30
250	0,61	1:0	column destroyed		0,59	1:0	column destroyed	
275	column destroyed				column destroyed			

TABLE X

Comparison of the McReynolds numbers of the VA/CTFE and VP/CTFE stationary phases after conditioning at 120 °C and 200 °C for 20 h

Stationary Phase	Δ I Benzene	Δ I 1-Butanol	Δ I 2-Pentanone	Δ I 1-Nitropropane	Δ I Pyridine
VA/CTFE 120 °C	283	416	395	523	475
VA/CTFE 200 °C	284	417	408	526	488
VP/CTFE 120 °C	156	228	220	287	278
VP/CTFE 200 °C	112	213	187	258	243

TABLE XI

The effect of conditioning on the lower temperature limit of the VP/CTFE column

$t/^{\circ}C$	h_{real}/mm	h_{real}/mm	h_{real}/mm	h_{real}/mm
	After conditioning at 120 °C for 20 h	After conditioning at 200 °C for 20 h	After conditioning at 225 °C for 20 h	After conditioning at 250 °C for 20 h
60	1,98	2,12	6,95	7,36
80	0,86	0,99	2,05	2,85
100	0,51	0,52	1,05	1,02
120	0,46	0,47	0,46	0,59
140	0,47	0,56	0,44	0,56

3.5 Column Tests

3.5.1 The modified Cram test

The results of the five basic tests on the various columns are shown in Table XII. To simplify comparisons in this table, the copolymer columns are grouped together with columns coated with commercial stationary phases of similar polarity. All the columns were preconditioned at 120 °C and 200 °C for 20 h prior to testing at 120 °C.

The efficiency parameter shows that the VP/CTFE column is slightly more efficient than OV-17 while the BVE/CTFE column is less efficient than the SE-52 column. The EVE/CTFE and the VA/CTFE columns, on the other hand, did not compare favourably with the commercial columns. It must, however, be remembered that at 120 °C these columns had not reached their minimum operating temperature. In Table IV these two columns can be seen to operate more efficiently at higher temperatures. The separating power of the columns showed the same trends found for the efficiency parameter with the exception of the VP/CTFE column.

The separating power of this column is smaller than the OV-17 column, although the efficiency is marginally greater.

The bleed, as measured by T_{max}, shows that the EVE/CTFE, VP/CTFE, and VA/CTFE stationary phases bleed less than the commercial stationary phases, while the BVE/CTFE stationary phase bleeds more than the SE-52 stationary phase.

The acid-base ratio shows that all copolymer columns are more acidic than the columns coated with commercial stationary phases. Octanol shows greater tailing on the copolymer columns than on the columns coated with commercial stationary phases.

TABLE XII

The modified Cram test

Stationary Phase	n_{real}/m^{-1}	TZ_{10}	T_{max}	A:B	TF % Octanol
BVE/CTFE	1 400	69	220	1:0,33	63
SE-52	2 200	89	230	1:0,69	85
EVE/CTFE	1 000	55	246	1:0	69
OV-17	2 000	83	206	1:0,72	83
VP/CTFE	2 100	71	218	1:0,67	71
VA/CTFE	300	24	228	1:0,67	69
OV-225	1 900	78	188	1:0,77	92

3.5.2 The Grob test

The separation numbers TZ_1 and TZ_2 show that the copolymer columns and the commercial stationary phases have comparable separation efficiencies. The BVE/CTFE column completely adsorbed aldehydes while the VP/CTFE column adsorbed aldehydes more strongly than OV-17. The octanol test shows that the copolymer and the commercial stationary phases adsorb alcohols to a similar degree. The diol test shows VP/CTFE to be the least adsorbing, while the other three adsorbed practically all of the diol. The acid-base ratio shows that VP/CTFE and OV-17 are very similar while BVE/CTFE is better than SE-52. All the columns were totally adsorbing when it came to the more stringent acid/base test, using dicyclohexylamine and 2-ethylhexanoic acid.

The thickness of the film of the copolymer stationary phases could not be obtained by the Grob method. This method is based on the elution of the methyl ester of the C_{12} carboxylic acid. Quantification of the film thickness requires calibration of a stationary phase of interest. This method is ideal for columns coated by the dynamic coating technique. When columns are coated by the static method, the film thickness may easily be calculated, using the formula given by Rutten and Rijks[55]:

$$d_f = \frac{d\ c}{4}$$

d_f = the film thickness in μm
d = column inside diameter in μm
c = volume ratio of the stationary phase to solvent used to prepare a solution.

For the VP/CTFE, OV-17, BVE/CTFE, and SE-52 coated columns the film thickness was found to be 0,41 μm, 0,45 μm, 0,41 μm, and 0,40 μm respectively. The values found for the OV-17 and SE-52 coated columns compare favourably with the values found by the Grob technique.

TABLE XIII

The Grob test

al = Nonanal, ol = 1-Octanol, D = 2,3-Butanediol,

A = 2,6-Dimethylanaline, P = 2,6-Dimethylphenol,

am = Dicyclohexylamine, S = 2-Ethylhexanoic acid,

d_f = film thickness in µm

Stationary Phase	TZ_1	TZ_2	al	ol	D	A	P	am	S	d_f/µm
VP/CTFE	25	26	46	69	35	94	98	0	0	
OV-17	21	20	100	58	5	100	91	0	0	0,42
BVE/CTFE	22	23	0	53	0	83	100	0	0	
SE-52	22	19	100	38	5	59	57	0	0	0,40

3.6 Separation of a Complex Mixture

The separation of the perfume on the copolymers and commercial stationary phases of similar polarity is shown in Figures 3a-g. A split ratio 120:1 was used, 0,2 µℓ was injected, the initial tem= perature was 120 °C, the rate of temperature programming was 2 °C/min, and the attenuation was set on 64x10^{-12}.

1. BVE/CTFE Figure 3a *vs* SE-52 Figure 3b

   The BVE/CTFE column separates fewer peaks than the SE-52 column.

2. EVE/CTFE Figure 3c *vs* OV-17 Figure 3d

   The EVE/CTFE column separates fewer peaks than OV-17. The bleed of the OV-17 is higher than the copolymer column.

3. VP/CTFE Figure 3e *vs* OV-225 Figure 3f

   The VP/CTFE column initially separates more peaks than OV-225 but at higher temperatures the OV-225 separates more peaks than the VP/CTFE column.

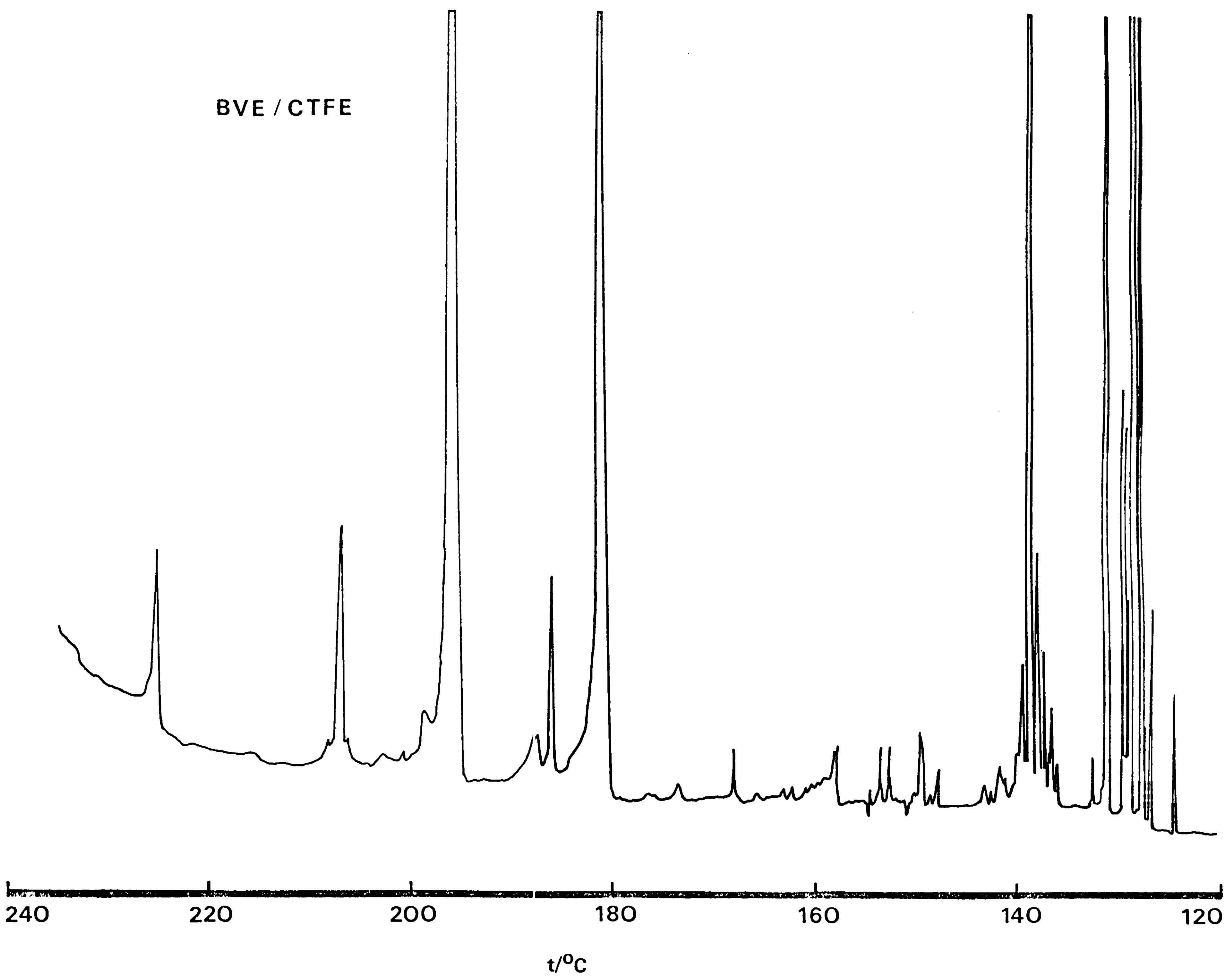


FIGURE 3a

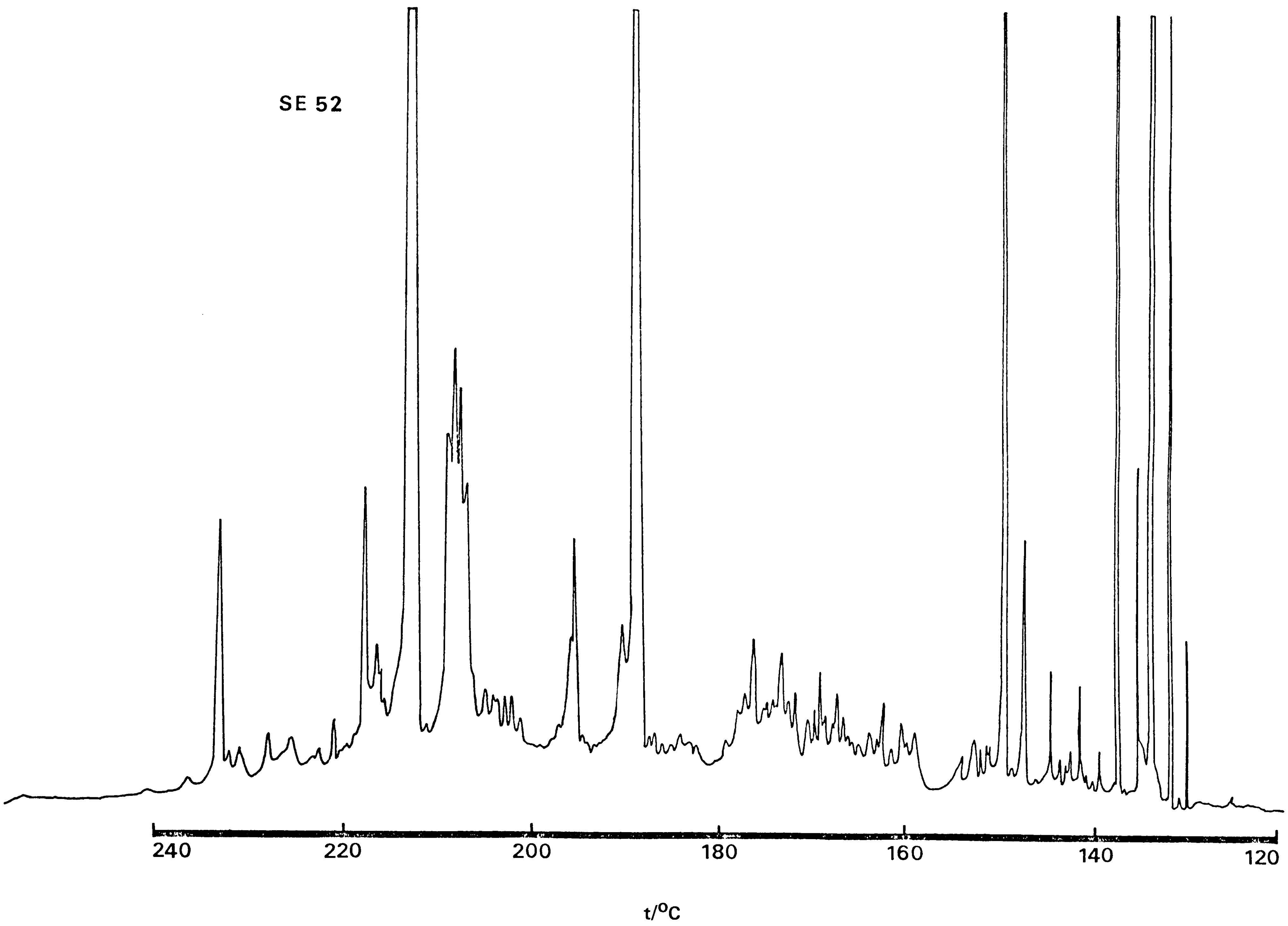


FIGURE 3b

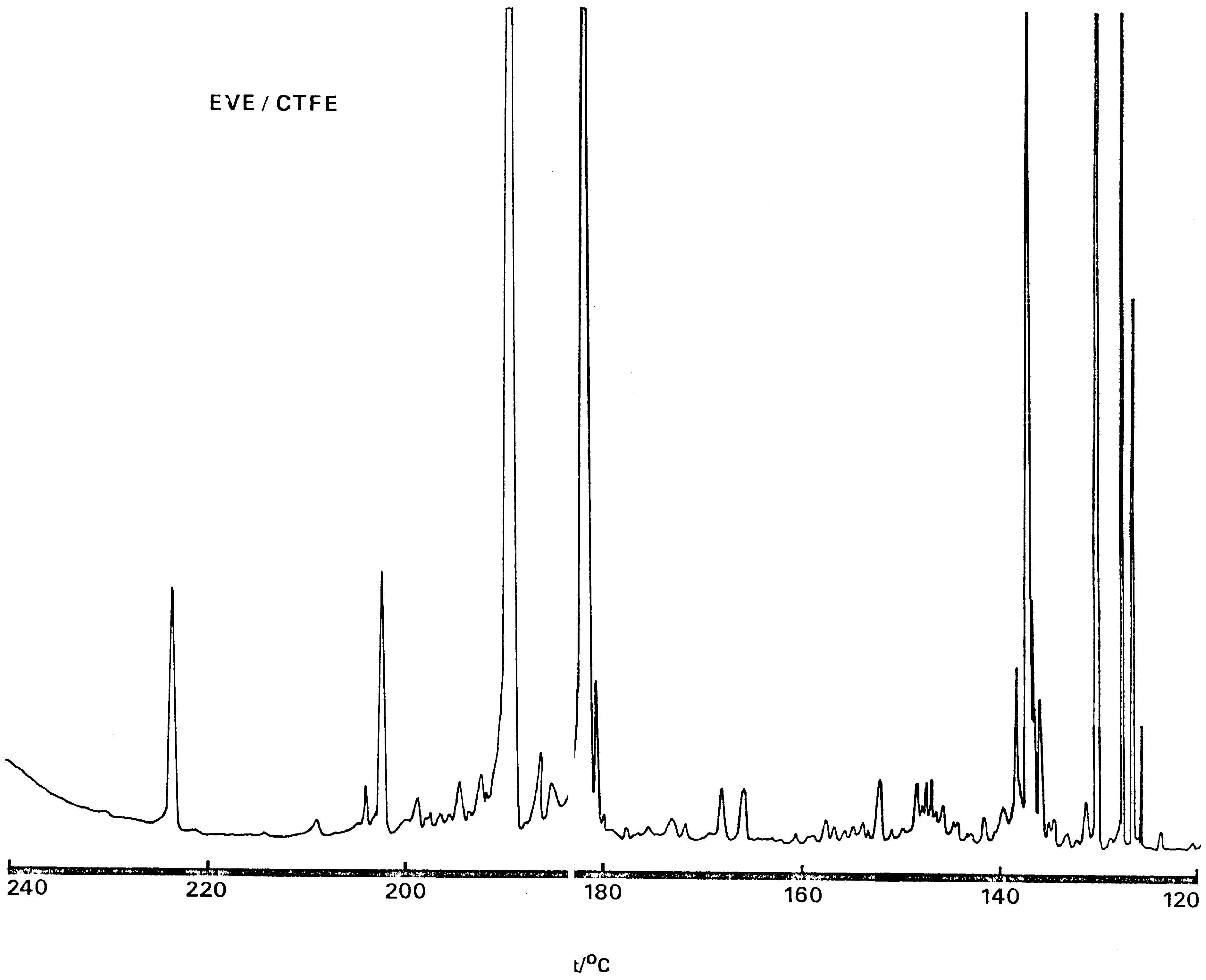


FIGURE 3c

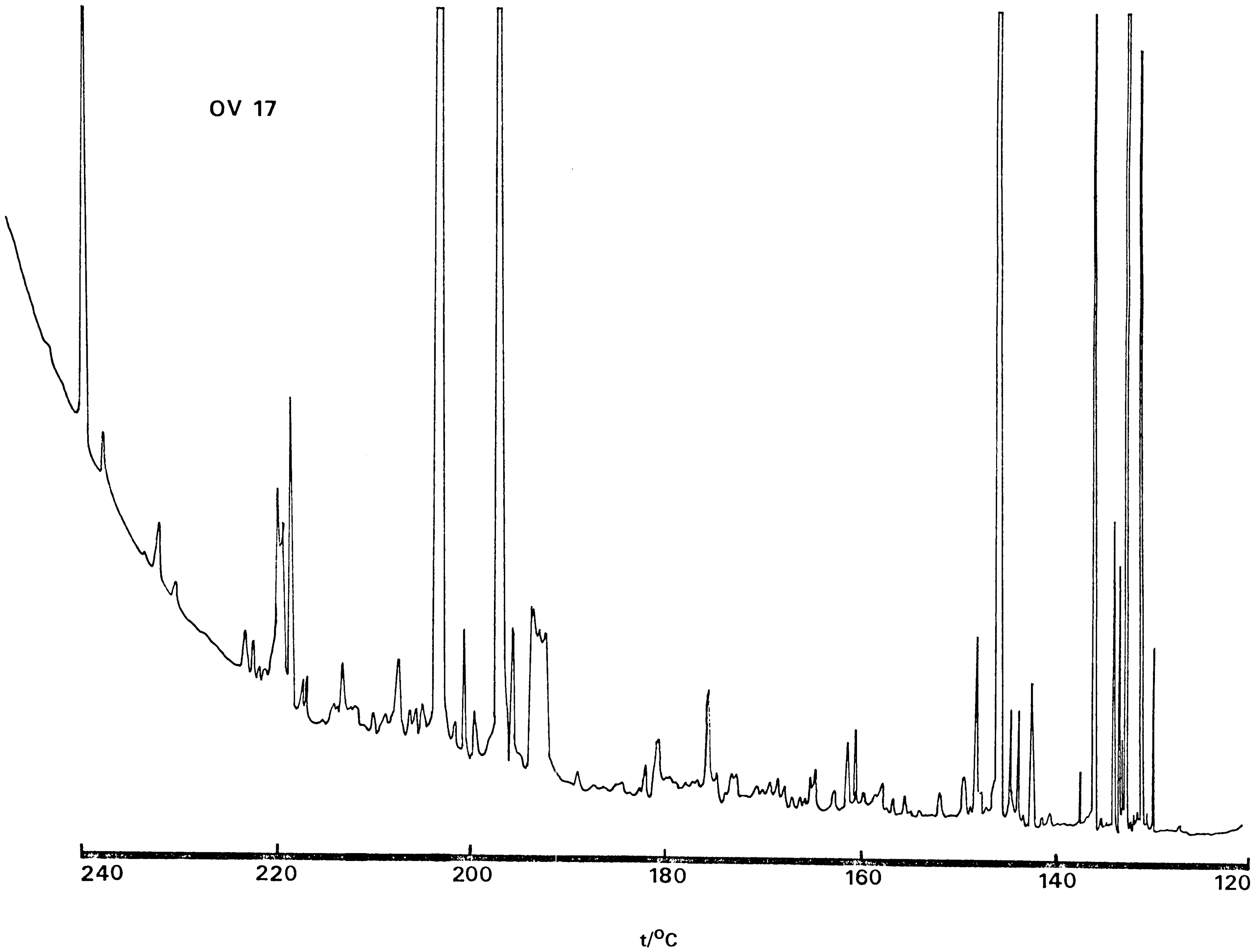


FIGURE 3d

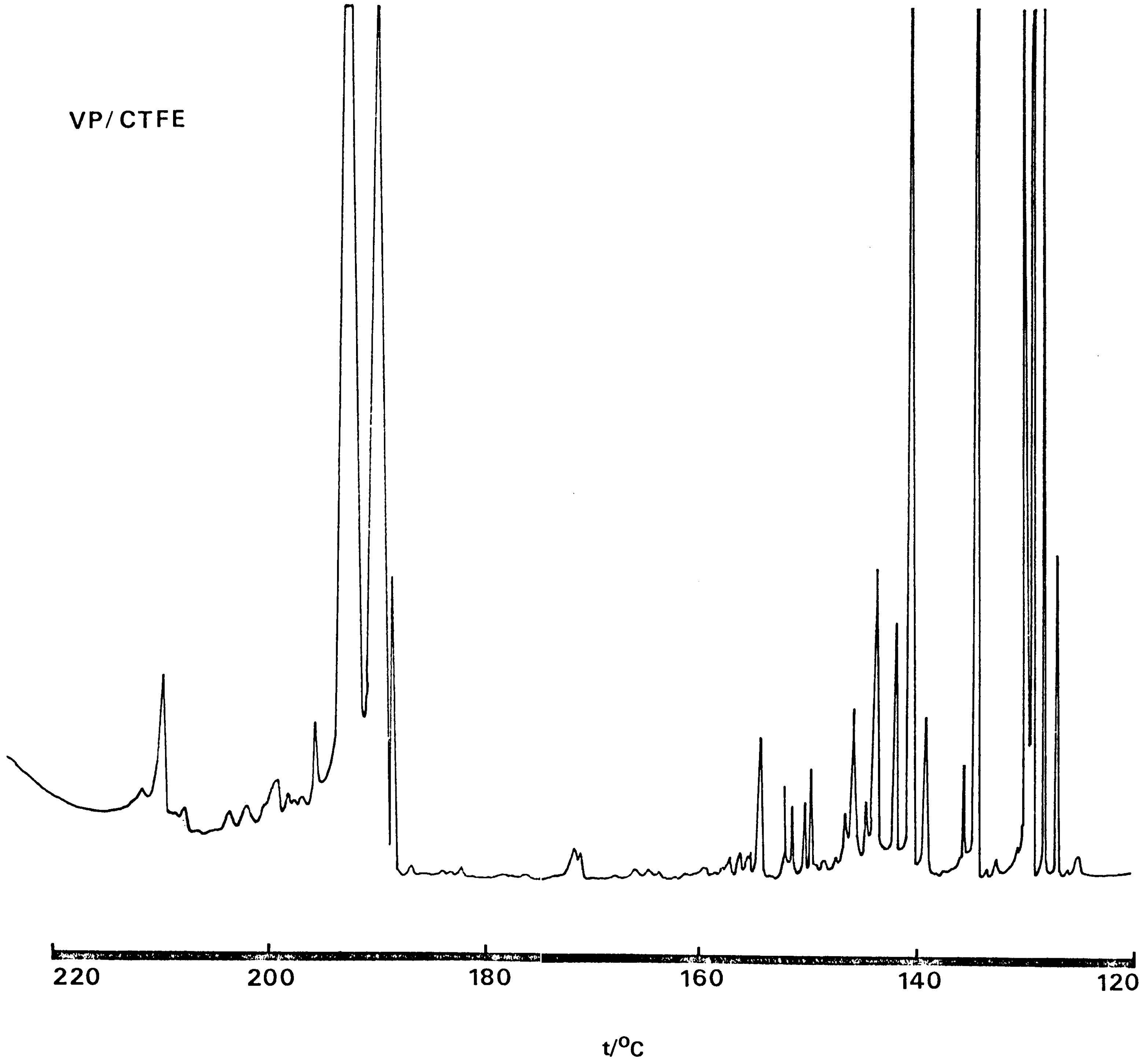
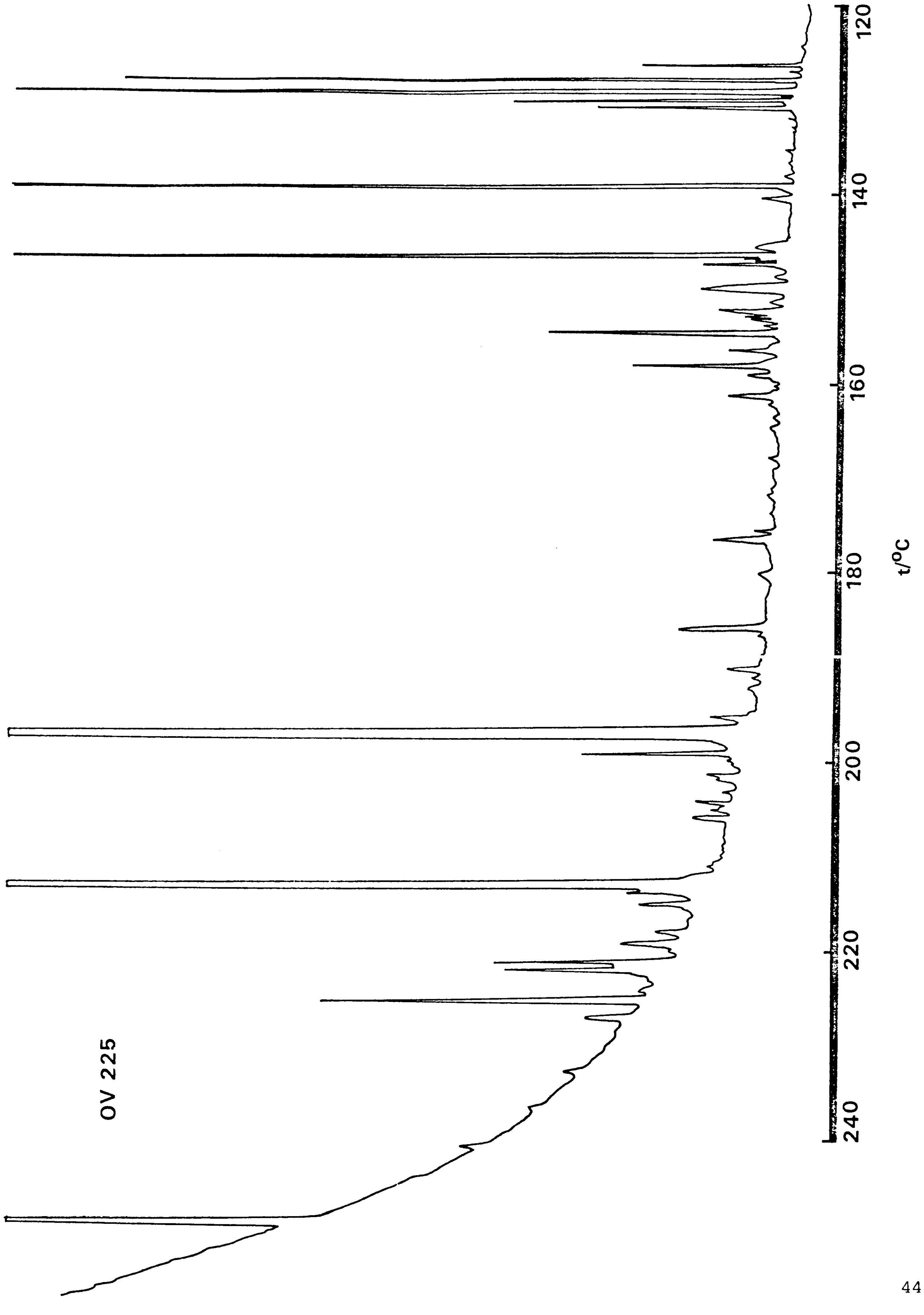


FIGURE 3e

FIGURE 3f



4. VA/CTFE Figure 3g *vs* OV-225 Figure 3f

The VA/CTFE column shows broad overlapping peaks and obviously does not have the separating power that the OV-225 column possesses.

3.7 The Glass Transition

The plot of log t'_R *vs* $^1/T$ for EVE/CTFE, VA/CTFE, and styrene columns is shown in Figure 4. In accordance with the work of Abushihada *et al*,[48] the glass-transition temperature (T_g) was determined at the lower point of the Z-shaped curve, as shown in Figure 4. A column coated with styrene was included as styrene has a T_g ranging from 75-100 °C and Abushihada *et al*[48] have determined the T_g for styrene, using the GC method. Some of the copolymers had T_g's at subambient temperatures, and cooling was effected by lifting the lid of the gas chromatograph and placing a metal tray containing ice over this opening.

As the measurement of T_g's using the DSC was quicker and easier at subambient temperatures, it was decided to determine the T_g's of the remaining copolymers by this method. The DSC curves showing the transitions of the various stationary phases are shown in Figure 5. All DSC curves initially increase rapidly and then become constant because all samples have a finite heat capacity. A melting transition, as shown by the FFAP curve, shows a definite peak, while a glass transition shows a small increase in heat capacity. The glass-transition temperature is recorded at the temperature where the increase in heat capacity is at a maximum.

There is excellent correlation between the T_g's for styrene, EVE/CTFE, and VA/CTFE when determined by these two methods. Abushihada *et al*[48] determined the T_g of styrene on a packed column and found it to be 94 °C.

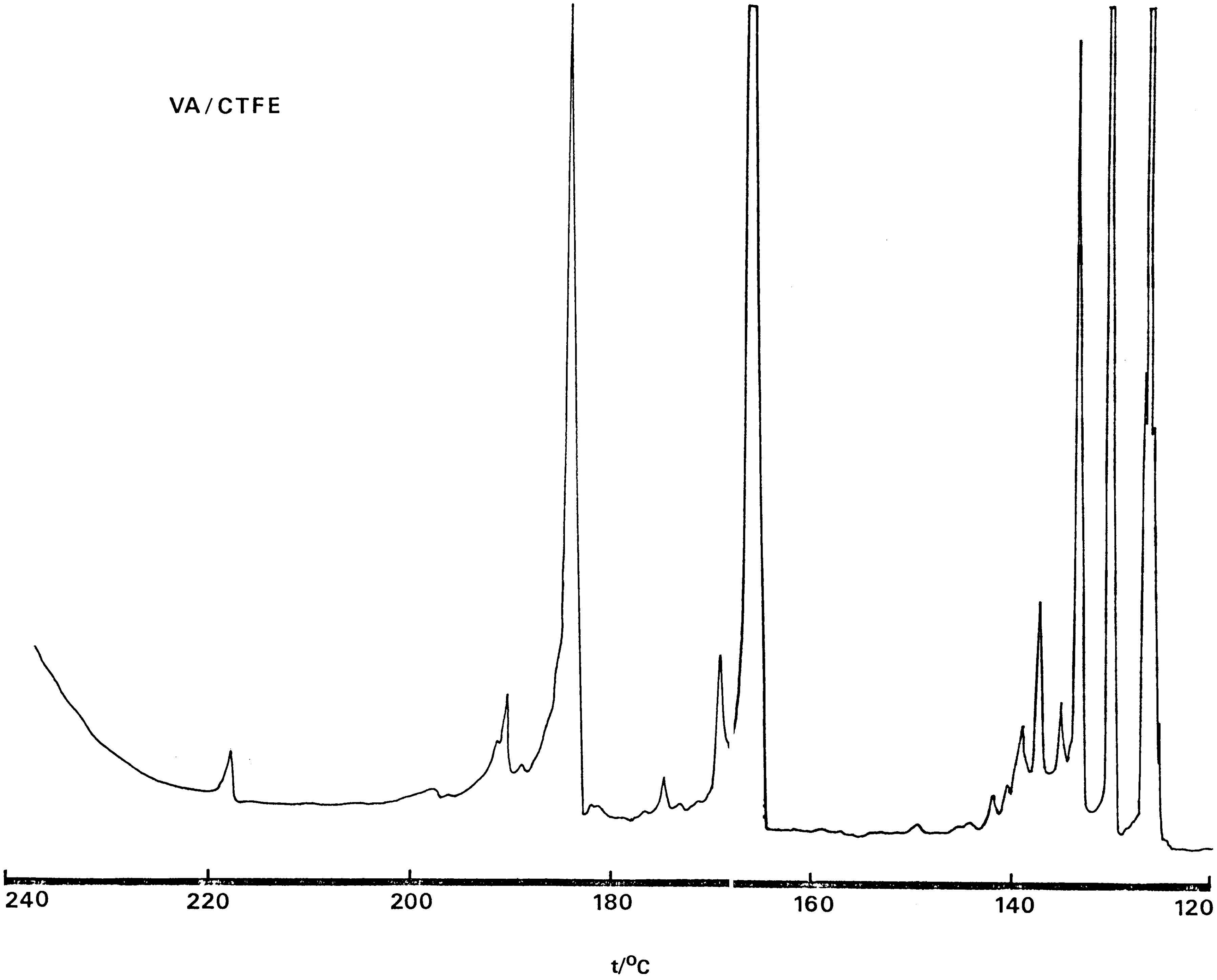


FIGURE 3g

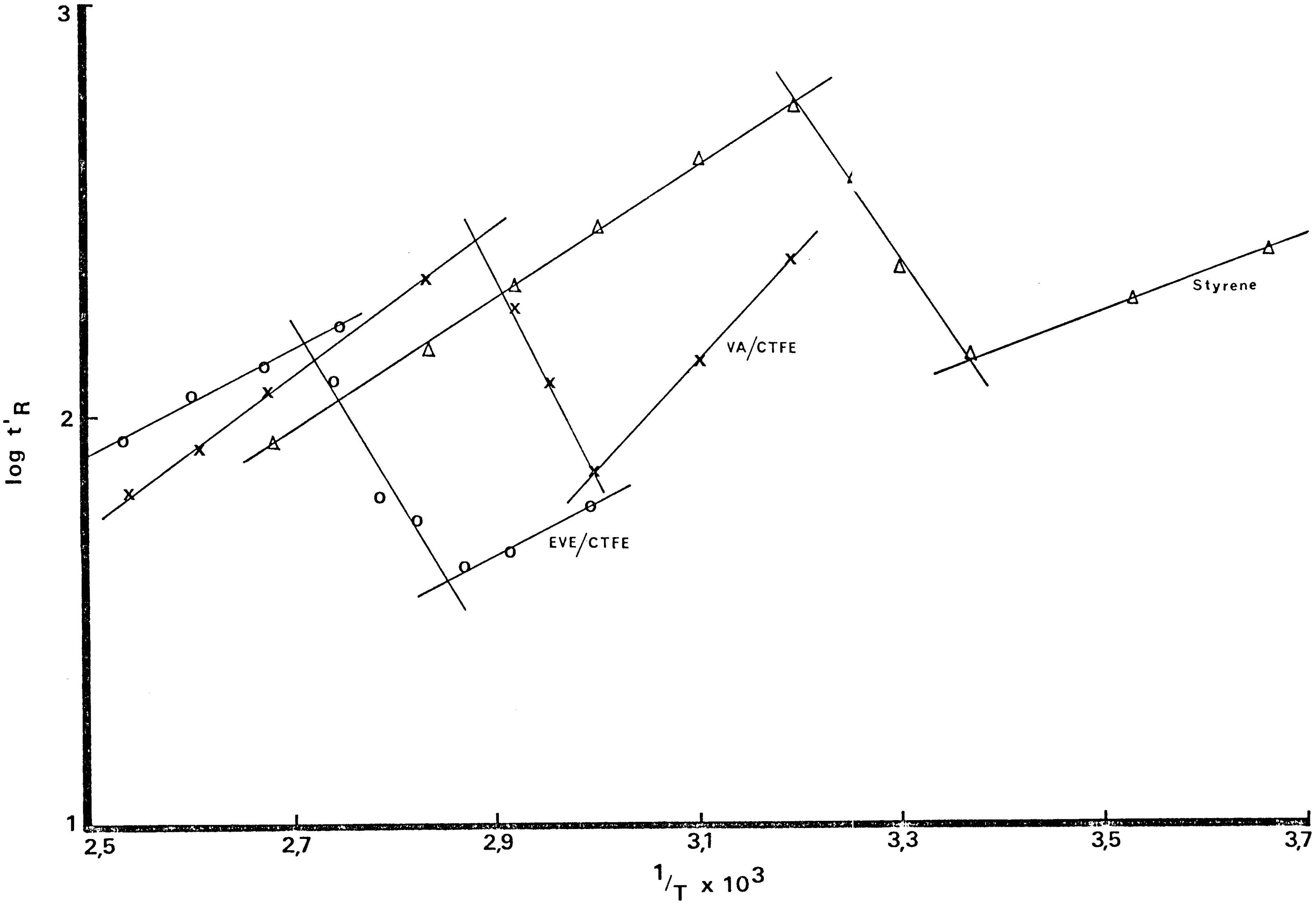
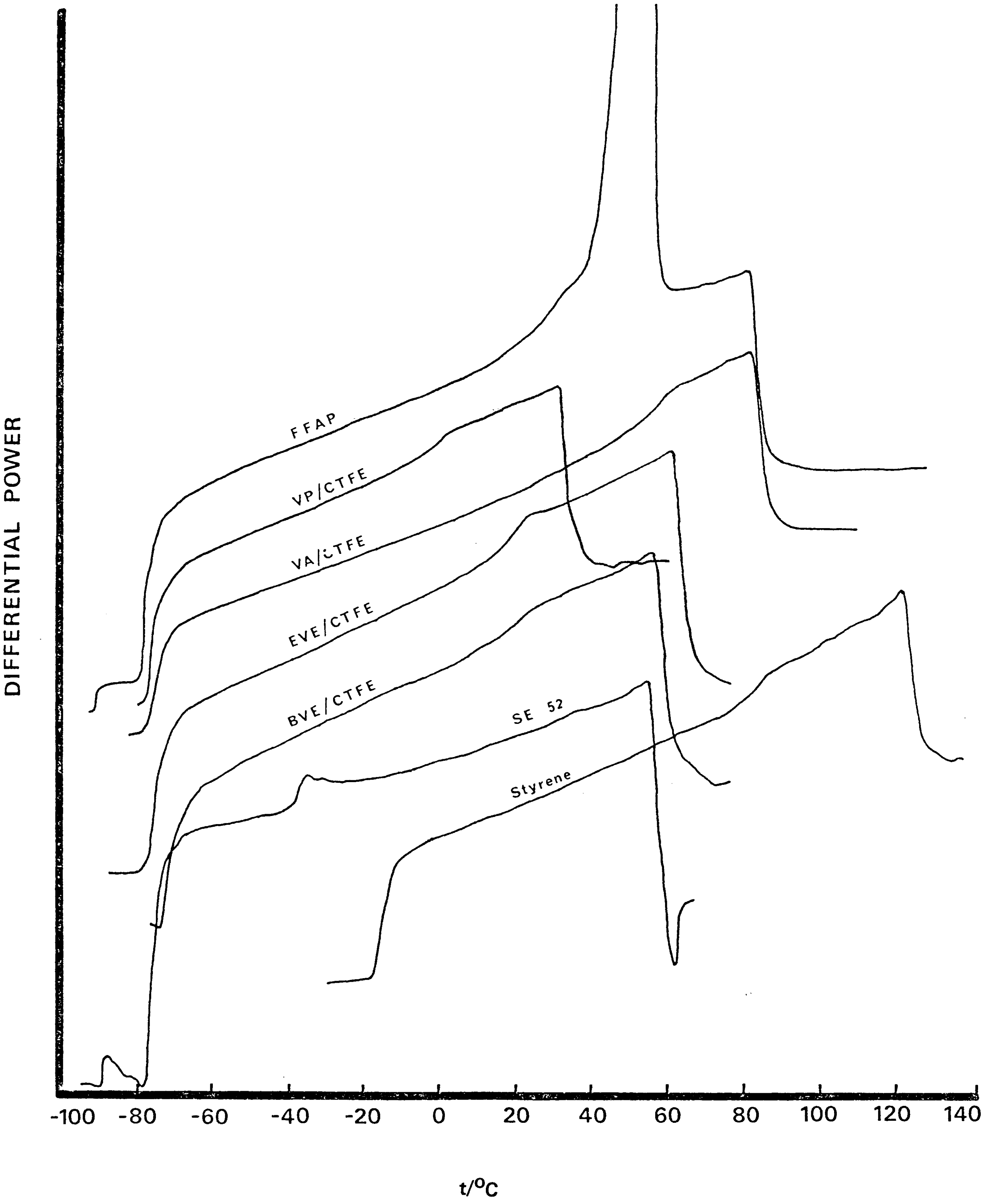


FIGURE 4

FIGURE 5


DIFFERENTIAL POWER
FFAP
VP/CTFE
VA/CTFE
EVE/CTFE
BVE/CTFE
SE 52
Styrene
-100
-80
-60
-40
-20
0
20
40
60
80
100
120
140
t/°C

The T_g of a given polymer depends on several factors such as the degree of cross-linking of the polymer, the chain flexibility, the configuration of the polymer, and the stereostructure. Since these vary with mode of preparation, it is not surprising that there is a difference between the value in the literature and the value for the T_g of styrene determined during this investigation. The minimum operating temperature was included in Table XIV so that a comparison between it and the glass-transition temperature could be made. The minimum operating temperature can be seen to be roughly 100 °C above the glass-transition temperature of the copolymers.

TABLE XIV

The T_g's determined by DSC and GC together with the minimum operating temperature

Stationary Phase	DSC	GC	Minimum operating temperature
	t/°C	t/°C	t/°C
Styrene	80	80	
EVE/CTFE	20	24	130
BVE/CTFE	10		110
VP/CTFE	- 4		90
VA/CTFE	56	60	150
SE-52	-38		
FFAP	41*		85
*melting point			

3.8 The Decomposition Temperature

The TG and the DTG curves are shown in Figure 6. The temperature at which the copolymers first start to show mass losses is shown in Table XV, together with T_{max}. (The bleed of the columns is shown in Table XII.) Except for VP/CTFE, there was good correlation between the bleed found on the GC and the mass loss determined by TG.

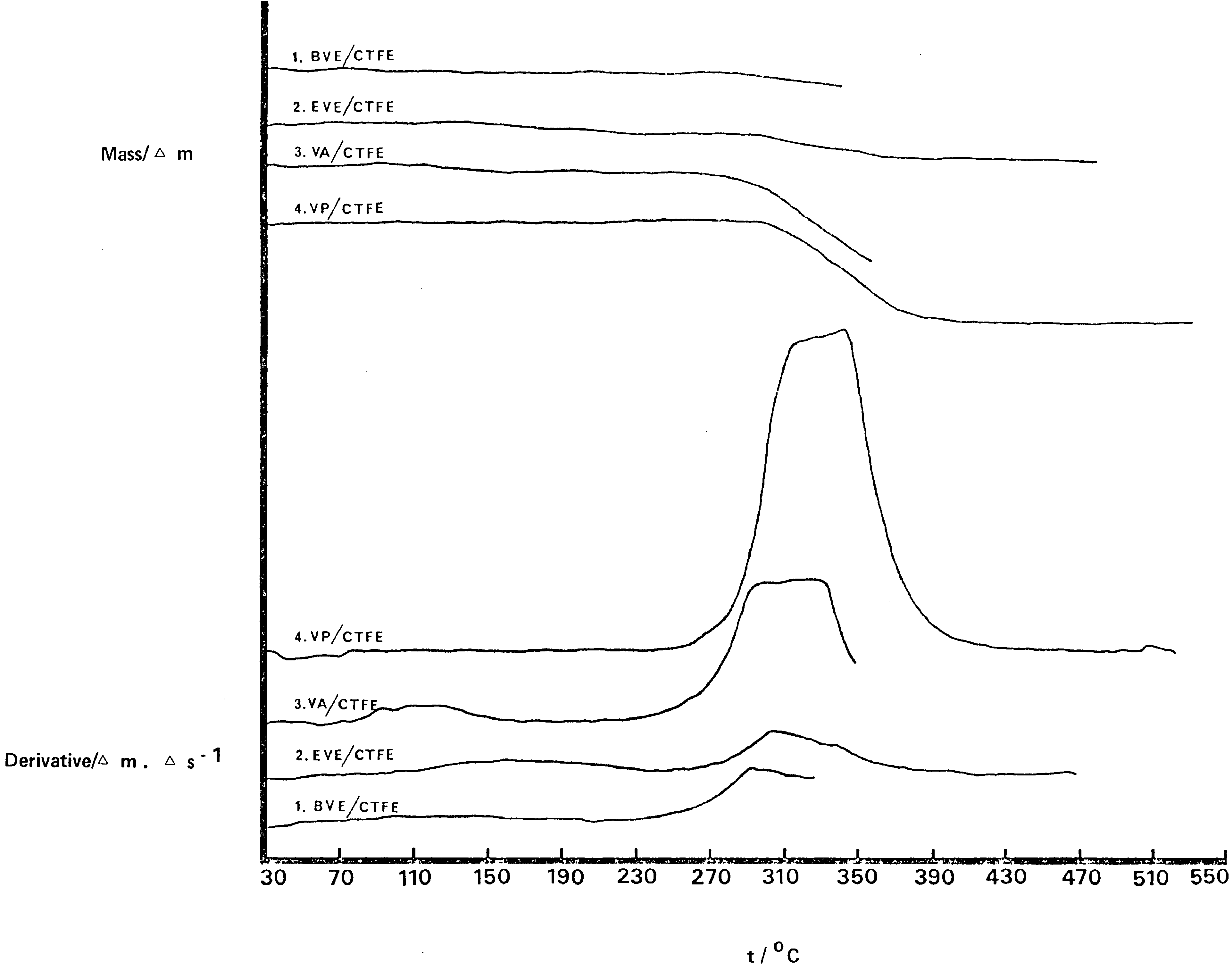

1. BVE/CTFE
2. EVE/CTFE
3. VA/CTFE
4. VP/CTFE
Mass/△ m
4. VP/CTFE
3. VA/CTFE
2. EVE/CTFE
1. BVE/CTFE
Derivative/△ m . △ s - 1
30
70
110
150
190
230
270
310
350
390
430
470
510
550
t / °C

FIGURE 6

TABLE XV

Comparison of the column bleed and mass loss determined by TG

Copolymer	T_{max}/°C	$T_{first\ mass\ loss}$/°C
BVE/CTFE	220	230
EVE/CTFE	246	260
VA/CTFE	228	230
VP/CTFE	218	260

3.9 The Number-Average Molecular Mass

The $\bar{M}_n$ for the four copolymers is shown in Table XVI. Miller and Hawkes[4] gave the $\bar{M}_n$ for SE-30 as 4×10^5. The difference between the value in the literature and the value determined in this investigation, can be accounted for by the batch-to-batch variation that occurs in any production situation. All the copolymers, as shown in Table XVI, have a molecular mass of the order of 3×10^5.

TABLE XVI

The number-average molecular mass for the various copolymers determined on a Knauer membrane osmometer at 30 °C, using tetrahydrofuran as the solvent

Copolymer	$\bar{M}_n$
BVE/CTFE	$2{,}7 \times 10^5$
EVE/CTFE	$2{,}8 \times 10^5$
VP/CTFE	$2{,}5 \times 10^5$
VA/CTFE	$2{,}9 \times 10^5$
SE-30	$2{,}5 \times 10^5$

3.10 Infrared Spectra

The infrared spectra of the copolymers should contain characteristic peaks which are also found in the spectra of the homopolymers of the two monomers that combine to form the copolymer. The spectra of BVE/CTFE and EVE/CTFE copolymers, as shown in Figures 7a and 7b, exhibit characteristic absorption peaks at 1 100 cm^{-1} due to the ether group and at 1 190 cm^{-1} due to the CF_2 group. In the spectra of the VP polymer and the VP/CTFE copolymer Figure 7c, the only difference is to be found at 1 100 cm^{-1} where the CF_2 group shows an absorption band. There is no difference to be seen in the spectra of the VA homopolymer and the VA/CTFE copolymer, as shown in Figure 7d.

4. CONCLUSIONS

The radiation-induced copolymerization of different comonomers with chloro=trifluoroethylene resulted in the production of four new gum stationary phases suitable for coating glass capillary columns. The technique of copolymerization confers on this method considerable flexibility and allows the possibility of tailor-making stationary phases for a given analytical problem. A wide range of stationary phases with controlled polarity was obtained according to the polarity classification of McReynolds. The copolymer BVE/CTFE was similar in polarity to SE-52, while VA/CTFE was more polar than OV-225. Furthermore, it was demonstrated that the polarity may be altered by -

a. changing the functional group on the side chain of the comonomer, e.g. an ether group is less polar than an acetate group; and

b. changing the number of carbon atoms on the side chain of the functional group, in other words increasing the number of carbon atoms in the side chain decreased the polarity.

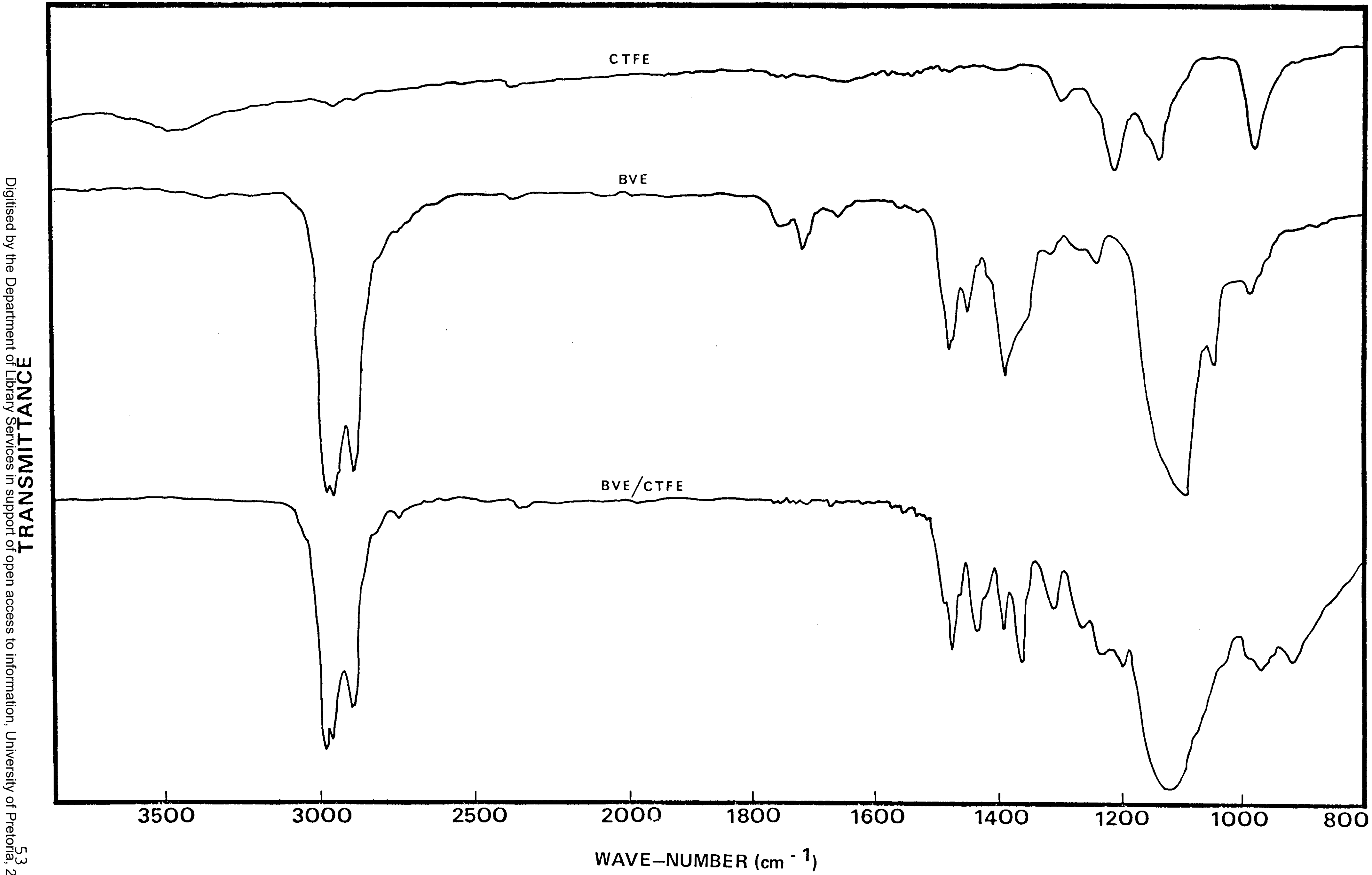

CTFE
BVE
BVE/CTFE
TRANSMITTANCE
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVE–NUMBER (cm - 1)

FIGURE 7a

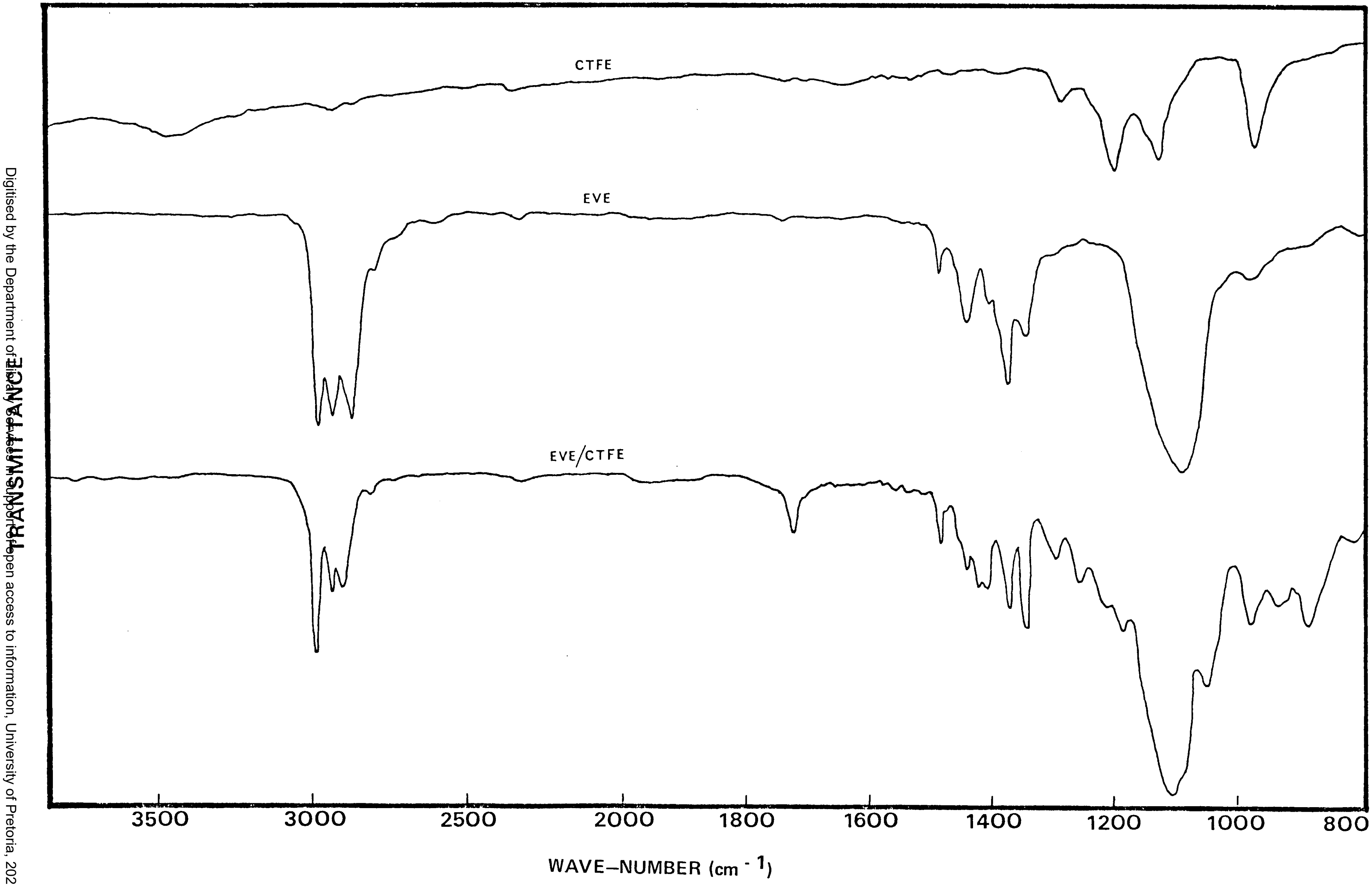

CTFE
EVE
EVE/CTFE
TRANSMITTANCE
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVE–NUMBER (cm - 1)

FIGURE 7b

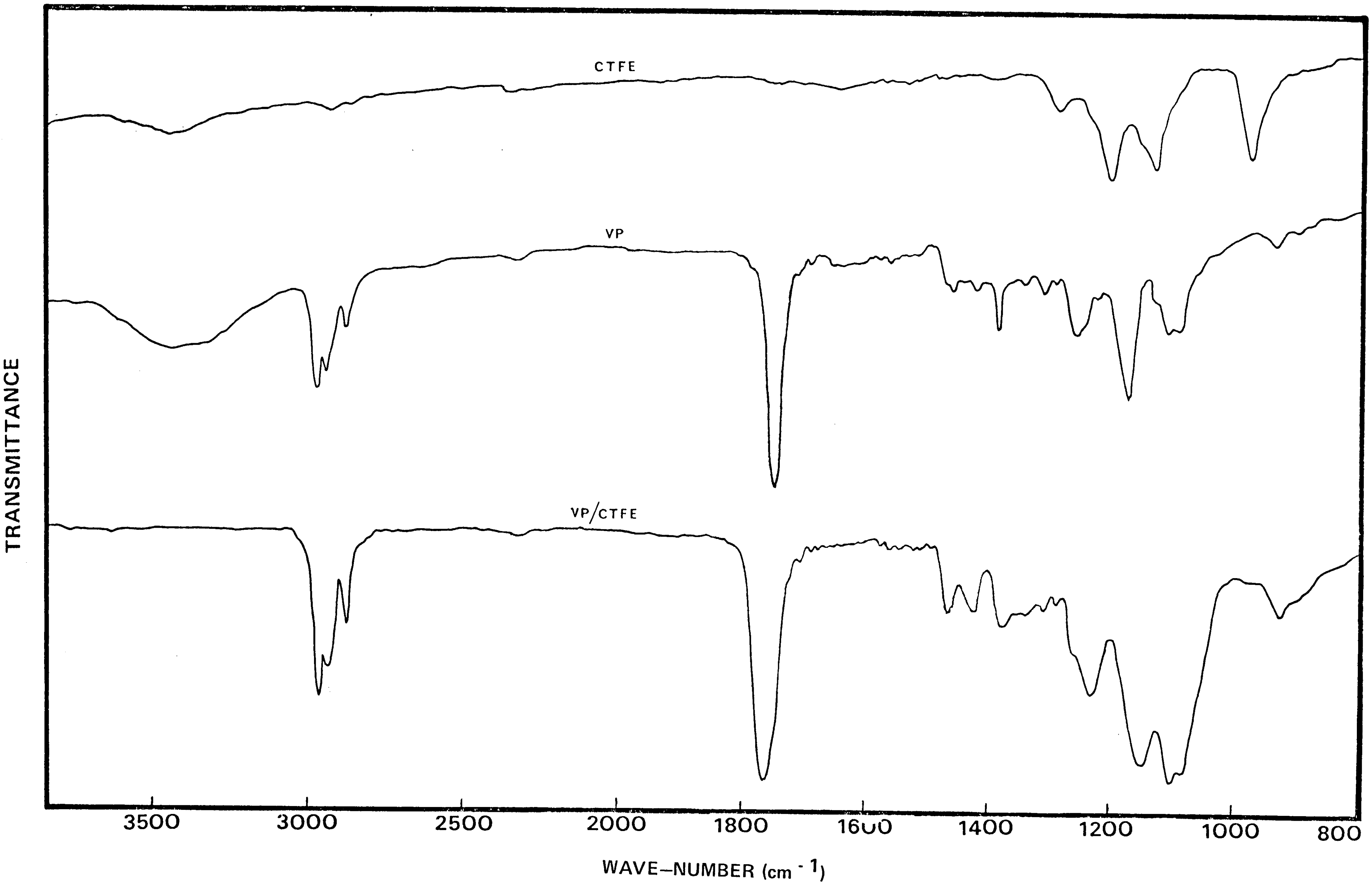

CTFE
VP
VP/CTFE
TRANSMITTANCE
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVE–NUMBER (cm^{-1})

FIGURE 7c

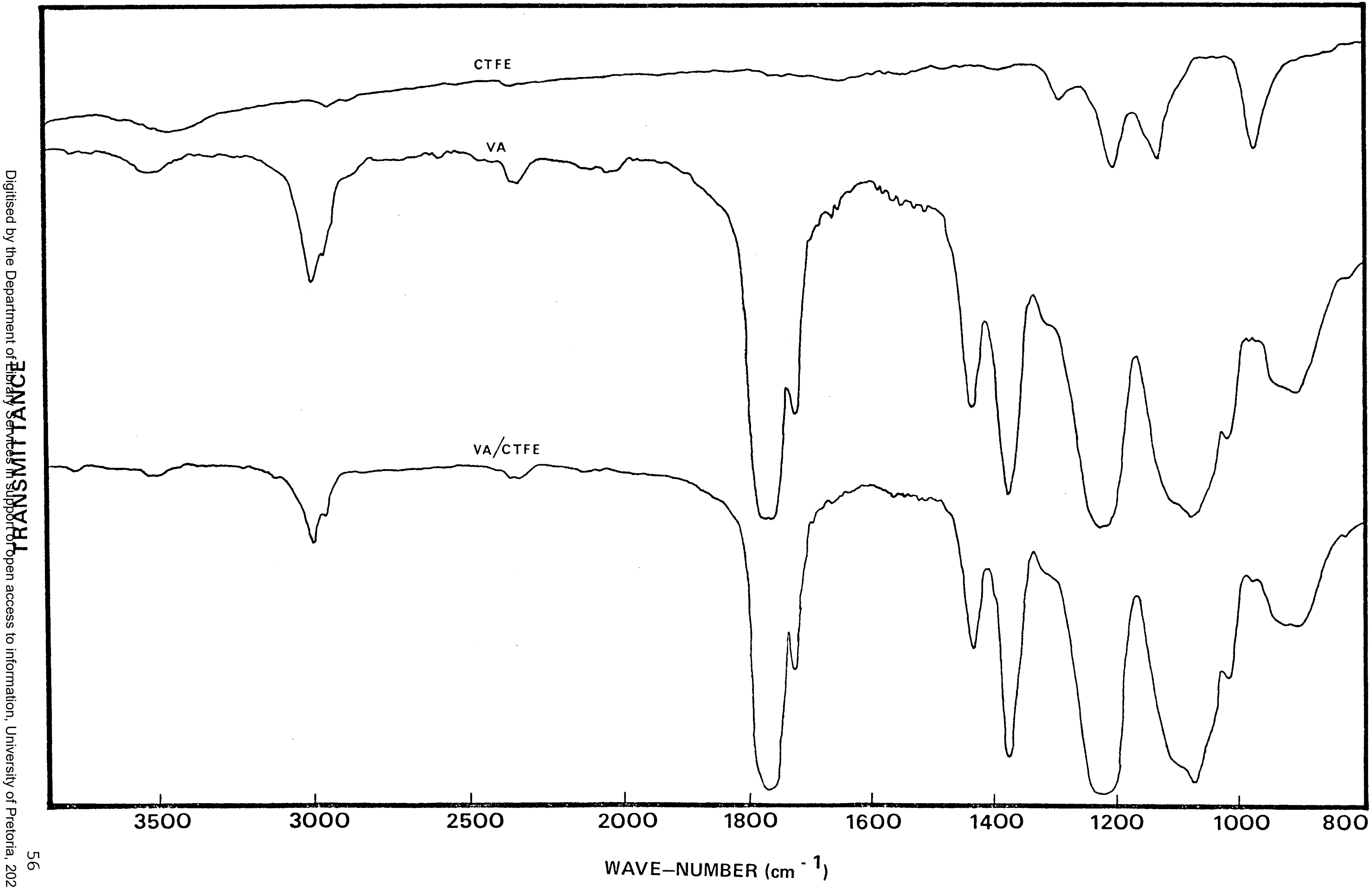

CTFE
VA
VA/CTFE
TRANSMITTANCE
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVE–NUMBER (cm^{-1})

FIGURE 7d

A factor that appears to have been ignored in the literature until now is that polymeric stationary phases with high molecular masses, $\bar{M}_n \geq 10^5$, usually do not have crystalline melting points, but exhibit glass tran=sitions characteristic of amorphous polymers. The glass-transition temperature may be determined quickly and easily, using differential scanning calorimetery. Once the glass transition has been determined, the minimum operating temperature has been shown to be approximately 100 °C higher.

There appears to be a lack of suitable parameters to describe the minimum operating temperature of gum stationary phases. For example the RSL[55] Company describe their new superox gum phase as having an "undefined melting point". What exactly is meant by "undefined melting point" is not made clear, nor do they give the temperature where it occurs. Therefore, the minimum operating temperature was determined at the temperature where the stationary phase started to function efficiently. This definition may be considered to be too severe in view of the fact that the minimum operating temperature of FFAP was found to be 30 °C higher than the value usually found in tables. The minimum operating temperature was lowered by lenghtening the side chain of the comonomer, that is BVE/CTFE exhibited a lower minimum operating temperature than EVE/CTFE, and VP/CTFE showed a lower operating temperature than VA/CTFE.

The working range for each of the copolymer stationary phases, bounded by the minimum operating temperature and 80 % of the upper operating tempera=ture, is shown below:

BVE/CTFE	110 - 220 °C
EVE/CTFE	130 - 200 °C
VP/CTFE	90 - 220 °C
VA/CTFE	150 - 200 °C.

Finally, the acidic nature of these stationary phases may be ascribed to the generation of hydrogen chloride. However, there does exist the possibility that copolymers with greatly improved thermal stability might be available through the use of tetrafluoroethylene in place of CTFE.

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