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HIGH-RESOLUTION GAS CHROMATOGRAPHY WITH LIQUID CRYSTAL GLASS CAPILLARIES

IX. SEPARATION OF ISOMERIC C₉-C₁₁ *n*-ALKENES AND *n*-ALKANES

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SUMMARY

The separation of isomeric C₉-C₁₁ *n*-alkenes and *n*-alkanes was studied on high-efficiency glass capillary columns coated with nematic 4-*n*-pentylacetophenone (O-4-*n*-pentyloxybenzoyl oxime) (PBO) stationary phase. The separation was optimized with respect to the stationary phase film thickness, column temperature and carrier gas flow-rate. The use of PBO liquid crystal as the stationary phase makes it possible to prepare high-efficiency, stable glass capillary columns with improved properties in terms of resolution and speed of separation.

INTRODUCTION

In earlier work^{1,2} using liquid crystals as stationary phases in capillary gas chromatography (GC) we achieved substantially faster and more complete separations of isomeric C₁₀-C₁₇ *n*-alkenes in comparison with separations on common stationary phases. However, with decenes some isomeric pairs were only partly separated and *cis*-4- and *cis*-5-decene were not separated at all.

This problem was solved for some pairs of positional isomers, *e.g.*, *trans*-5- and *trans*-6-dodecene, by reversing their retention sequence. However, a similar solution for *cis*-4- and *cis*-5-decene lacks a more selective crystal than 4-methoxy-4'-ethoxyazoxybenzene (MEAB)¹. In the separation of similar pairs of isomers with a double bond in the centre of the carbon chain, *e.g.*, *n*-tetradecenes, the use of a less selective crystal, 4-*n*-pentylacetophenone (O-4-*n*-pentyloxybenzoyl oxime) (PBO), resulted³ in a better separation than the use of highly selective MEAB. We have therefore studied the possibilities of improved separations of isomeric C₉-C₁₁ *n*-alkenes on PBO as a stationary phase by capillary GC. The separation of isomeric

n-alkenes from the corresponding *n*-alkanes was included as they are often both present in samples.

EXPERIMENTAL

A mixture of all 25 isomeric C₉–C₁₁ *n*-alkenes and the corresponding *n*-alkanes served as a model mixture. The separations were performed on glass columns (100 m × 0.25 mm I.D.) coated by the dynamic method by 1.5–10% solutions of PBO liquid crystal in chloroform. The procedure for the preparation of capillary columns with PBO was described in a previous paper⁴. The efficiency of the column used for the optimal separation of the mixture of C₉–C₁₁ *n*-alkenes and *n*-alkanes, measured for 1-undecene at a capacity ratio $k = 10.2$ at 56°C, under a hydrogen carrier gas inlet pressure of 0.18 MPa and at a mean linear velocity of $\bar{u} = 30 \text{ cm s}^{-1}$, was 430 000 theoretical and 360 000 effective plates.

A Perkin-Elmer F-11 gas chromatograph equipped with a flame ionization detector was used to measure the retention characteristics. Retention indices of *n*-alkenes were measured with the accuracy expressed in terms of the standard deviation, S.D. = 0.15.

RESULTS AND DISCUSSION

The GC characteristics of PBO were studied by measuring the capacity ratios of *n*-nonane (Fig. 1), 1-nonyne and *p*-xylene (Fig. 2) and selectivity factors, α , for *p*- and *m*-xylenes with respect to temperature, starting the column heating from the range of the crystalline phase to the range of the isotropic liquid and by cooling to the temperature of solidification of PBO (Fig. 3). In view of the substantial influence

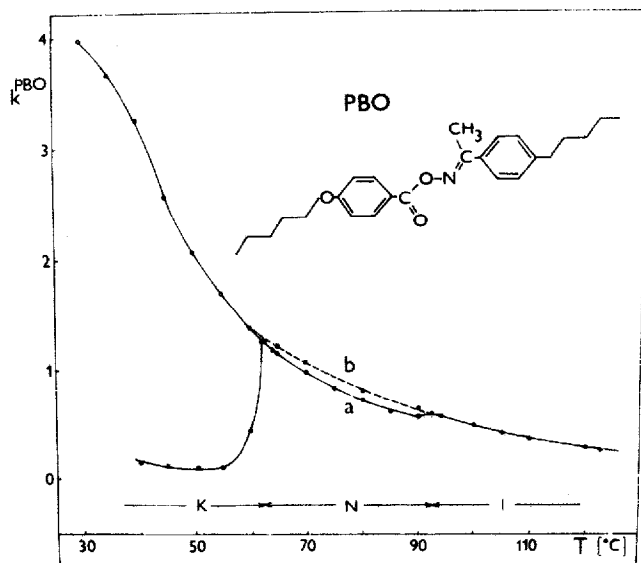


Fig. 1. Dependence of the capacity ratio on the temperature of the column coated with PBO for *n*-nonane. K = crystalline phase; N = nematic mesophase; I = isotropic phase.

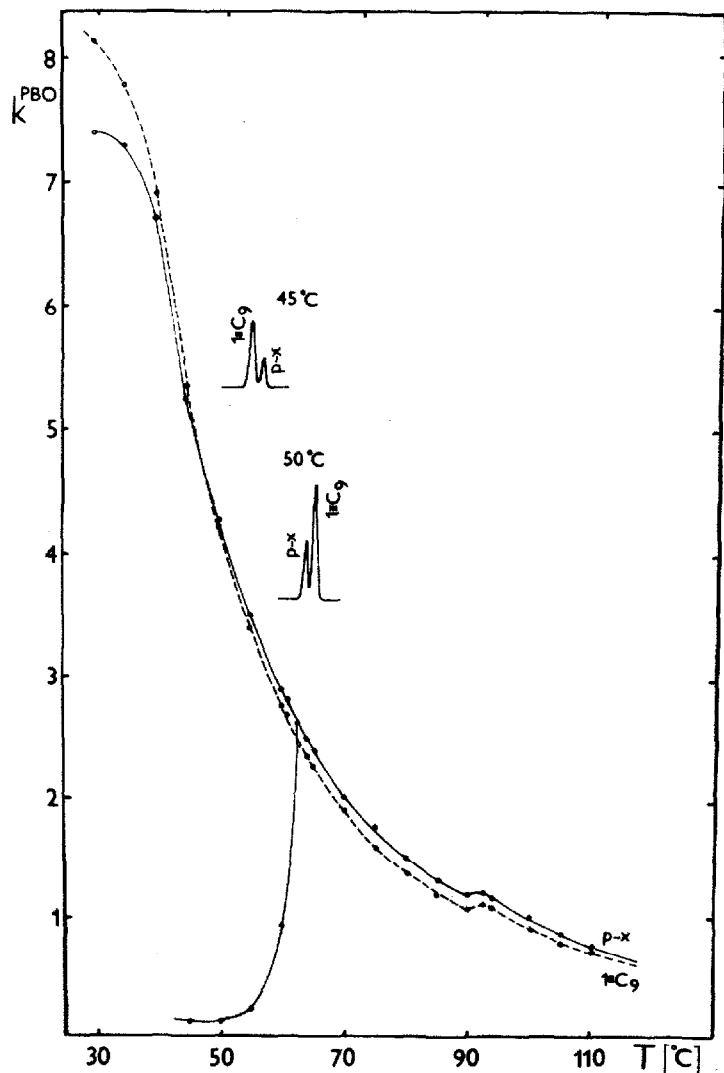


Fig. 2. Dependence of the capacity ratio on the temperature of the column coated with PBO for 1-nonyne ($I \equiv C_9$) and *p*-xylene (*p-x*).

on retention parameters⁴ of conditioning of the capillary column with PBO, we used a column prepared with a 10% solution of PBO in chloroform, conditioned at ambient temperature overnight.

In the heating mode of the capillary column coated with PBO, the k value for *n*-nonane changed according to curve a in Fig. 1. The temperatures of the PBO transformation from the crystalline phase to the mesophase (63°C) and from the mesophase to the isotropic liquid (93°C) were in good agreement with the data obtained by the calorimetric method (63 or 94°C)³. When the column was cooled from the isotropic liquid temperature (above 94°C), an increase in the solute retention was

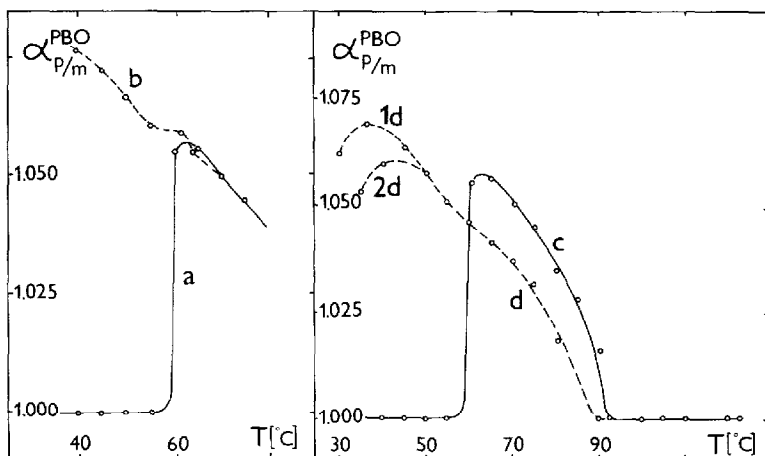


Fig. 3. Dependence of the selectivity factor for *p*- and *m*-xylene on PBO on column heating (conditioned at ambient temperature) up to 75°C (a), column cooling to 40°C (b), column heating to the temperature of the isotropic region (c) and subsequent cooling to 30°C (d). (1d) Course of $\alpha_{p/m}^{PBO}$ on cooling from the isotropic region (122.5°C); (2d) the course of $\alpha_{p/m}^{PBO}$ on cooling from the mesophase region (70°C).

observed in the range of the mesophase (curve b) in comparison with the heating mode. In the range of the PBO melting temperature, the solute retention reached a value close to that measured in the heating mode. On further cooling the column below the melting temperature, the k value for *n*-nonane increased more steeply up to about 30°C, after which the retention decreased as a consequence of the start of PBO solidification. When the column was heated to the temperature of the isotropic range, the retention values always followed curve b in Fig. 1, regardless of whether the mesophase temperature had been adjusted by column heating or cooling.

A similar dependence of k versus temperature (T) for 1-nonyne and *p*-xylene is illustrated in Fig. 2. In the range of undercooling of the PBO mesophase, the steepness of the above dependence differs for 1-nonyne and *p*-xylene. It is steeper for the more linear 1-nonyne molecule and shows a reversed retention sequence for these hydrocarbons in a narrow temperature range of 5°C. The course of the dependence of k versus T is also different at temperatures close to the point of PBO solidification. It is steeper for 1-nonyne, probably owing to the easier penetration of the more linear molecules of 1-nonyne in the crystal lamellae at the beginning of solidification of the liquid crystal.

The dependences of the selectivity factors for *p*- and *m*-xylenes, obtained under conditions identical with those in Fig. 1 by heating the PBO column to 75°C (a), cooling it to 40°C (b) and heating it from 40 to 122°C (c) and subsequent cooling to 30°C (d), are illustrated in Fig. 3. On cooling the PBO column that had been heated to the temperature of the isotropic range, the values of α were substantially lower in the mesophase than those obtained during the first column heating to the mesophase only. This indicates a decrease in the selectivity of the liquid crystal after such column heating. Similarly in the range of column undercooling (below 63°C), α increased as the temperature decreased, but the values α were lower. Curve 2d in Fig. 3 suggests PBO solidification at a higher temperature and hence lower α values obtainable in

the range of the liquid crystal undercooling by cooling the column from the mesophase range (from 70°C) compared with cooling from the isotropic range. In the PBO isotropic region the *p*- and *m*-xylene pair was not separated. The separation with the reversed elution sequence, *i.e.*, *p*- and *m*-xylene, in which these isomers are eluted on common stationary phases, was not obtained in the PBO isotropic region (up to 122°C) even with an effective column efficiency of 150 000 theoretical plates. This indicates that the liquid crystal retains a certain arrangement of the molecules⁵ even in the isotropic range 30°C above the temperature of clarification.

The column coated with PBO shows the highest selectivity or the greatest changes in selectivity with temperature at lower temperatures of undercooling of the mesophase (up to 30°C). There is a constraint that is important in practice. In view of the molecular weight of the hydrocarbons studied (up to C₁₁) and the very similar properties of some isomers, lower separation temperatures can only be used with thin films of the stationary phase and with long capillary columns. The dependence of the selectivity factor on the PBO film thickness (expressed in terms of *k*) for critical pairs of decenes and undecenes is illustrated in Fig. 4. (The dependence of α on *k* is illustrated in Fig. 4 for *cis*-2- and *trans*-2- and for *cis*-4- and *cis*-5-decenes by the dashed line, as the separation was not obtained using columns with thinner PBO films.) However, α -values for critical pairs of *n*-alkenes increase with increasing film thickness, *i.e.*, the separation of *n*-alkene pairs becomes easier as the film thickness increases.

The changes in the retention values of isomeric alkenes depending on the film thickness can occur as a result of changes in the orientation of molecules of the liquid crystal caused by the surface of the glass capillary, or of the changes in the

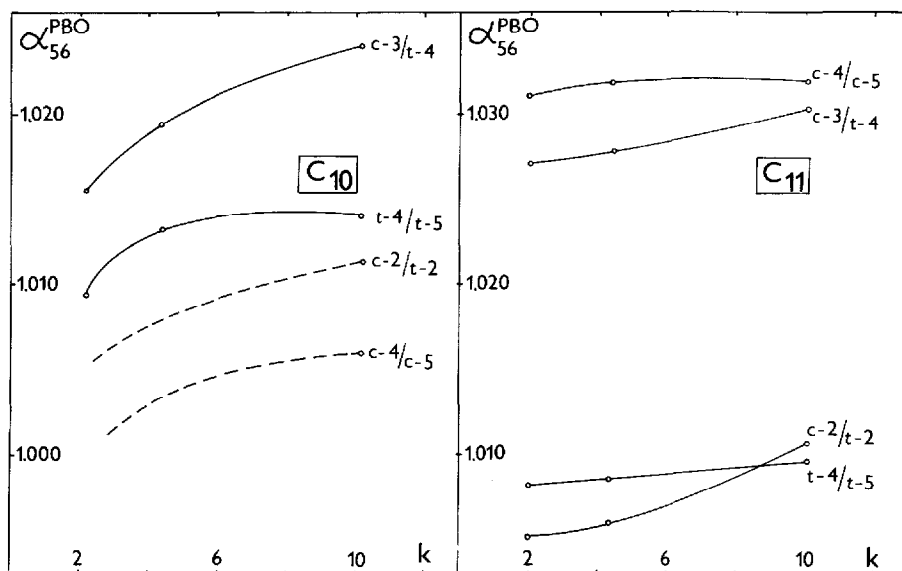


Fig. 4. Dependence of the selectivity factor, α , for critical pairs of *n*-decenes and *n*-undecenes on PBO on their capacity ratios at 56°C. *c* = *cis*; *t* = *trans*.

solution-adsorption ratio of solutes. With all the mentioned pairs of isomeric alkenes, the values of α increase with increasing film thickness and more markedly for geometric than for positional isomers. The isomer that has the lower retention is always less polar and hence also more sorbed on the gas-polar stationary phase interface. Because the relative contribution of solute adsorption on the carrier gas-polar stationary phase interface decreases as the film thickness increases, changes occur in α for pairs of isomeric alkenes. For instance, *trans*-2-decene is more linear than *cis*-2-decene but with increasing film thickness *cis*-2-decene is retained relatively more strongly, *i.e.*, in this instance the liquid crystal selectivity increases with decrease in the film thickness. However, it is generally⁶ thought that the liquid crystal selectivity increases with increase in film thickness. In accordance with this idea, even α values for *n*-alkanes increase slightly as the film thickness of PBO increase. This indicates clearly that, with change in the film thickness, the α values for *n*-alkenes result more from the changes in the adsorption of the solutes than from the changes in the orientation of the stationary phase.

Individual isomers of *n*-alkenes show different retention dependences on temperature and their retention sequence does not correspond to the sequence of their dI/dT values (where I = retention index). Therefore, even the lowest temperature of the column coated with PBO need not be the most suitable for the separation of all isomers. The dependence of α for critical pairs of *n*-decenes and *n*-undecenes on the temperature of the column coated with PBO is shown in Fig. 5. The α values for the pairs of positional alkene isomers decrease as the column temperature increases, which is in accord with published data⁷; however, for the pairs of geometric isomers they increase so much that the *cis*-isomer has a greater retention and a greater dI/dT

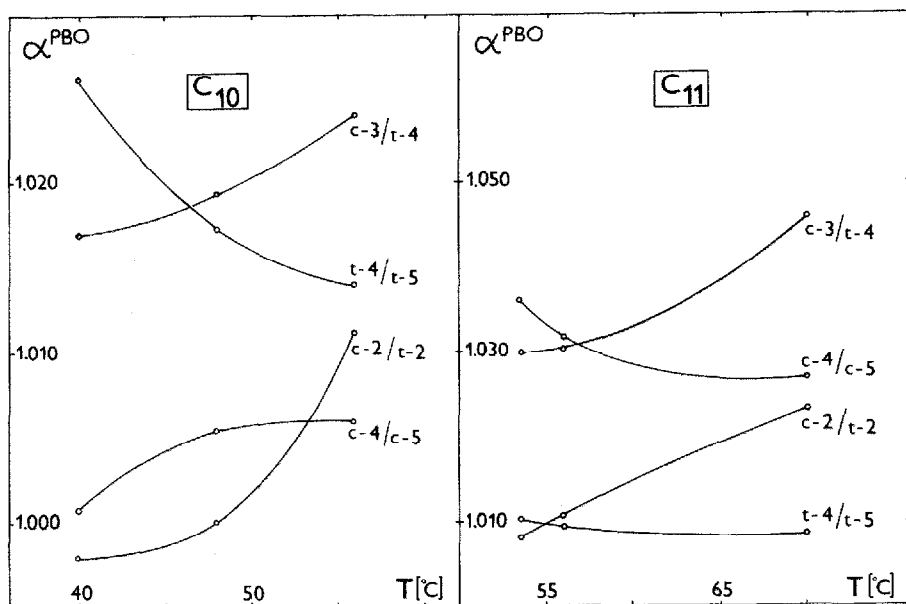


Fig. 5. Dependence of the selectivity factor, α , for the critical pairs of *n*-decenes and *n*-undecenes on the temperature of the column coated with PBO. *c* = *cis*; *t* = *trans*.

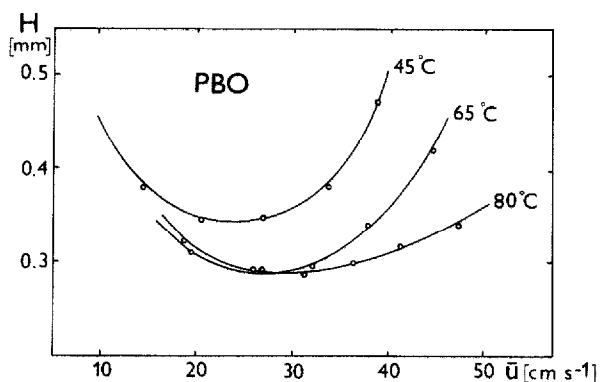


Fig. 6. Dependence of H on \bar{u}_{H_2} in a capillary column coated with PBO (100 m \times 0.25 mm I.D.) at 45, 65 and 80°C.

for the considered pairs than has the *trans*-isomer. Similar trends occur even with common stationary phases, but on liquid crystals the temperature dependence of retention is more distinctive for various isomers and may therefore be better used to optimize the separations.

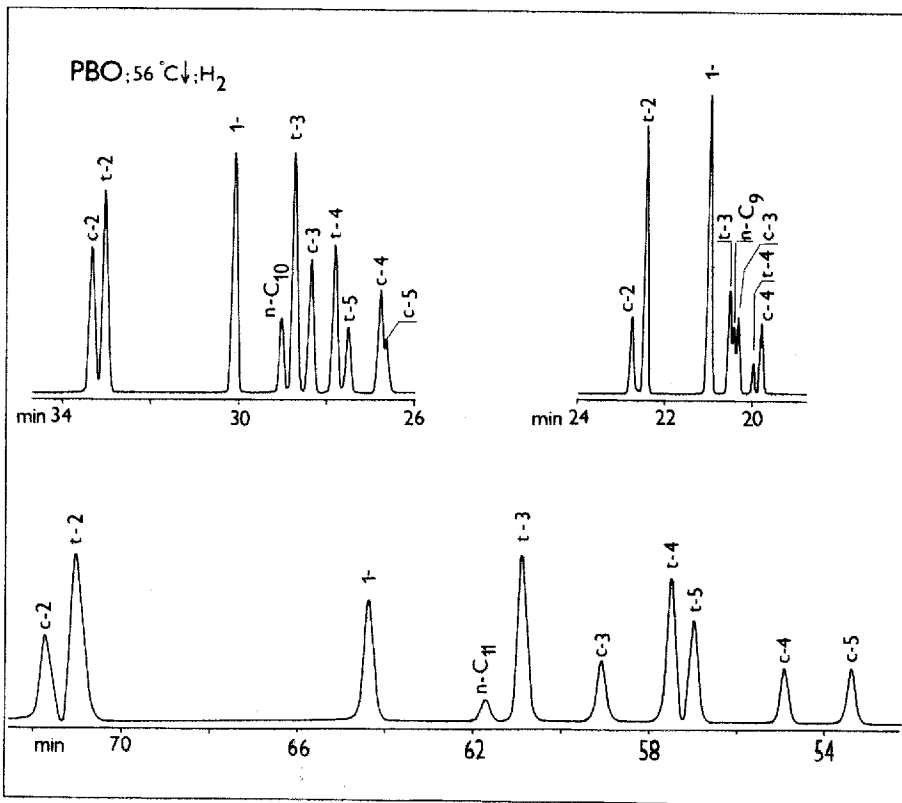


Fig. 7. Chromatogram of a mixture of C_9 - C_{11} *n*-alkenes and *n*-alkanes obtained by separation on a column coated with PBO (100 \times 0.25 mm I.D.) at 56°C at an inlet pressure of 0.16 MPa and a mean linear velocity of H_2 of 30 cm s^{-1} . *c* = *cis*-; *t* = *trans*-; 1- = 1-alkene; *n*-C = *n*-alkane.

Fig. 6 illustrates the dependence of the plate height, H , on the mean linear velocity, \bar{u} , of hydrogen carrier gas for separation on a glass capillary column (100 m \times 0.25 mm I.D.) coated with PBO. The values of \bar{u}_{\min} are lower on capillary columns coated with the liquid crystal than on columns with common stationary phases, as a consequence of the greater order of liquid crystals and hence the slower establishment of sorption equilibrium⁸. In agreement with this, a decrease in the temperature of the column coated with PBO in the mesophase region also shifts \bar{u}_{\min} to lower values.

Fig. 7 illustrates the chromatogram of the separation of a mixture of C₉–C₁₁ *n*-alkenes and *n*-alkanes, obtained under the optimal separation conditions. The separation of isomeric *n*-nonenes and *n*-nonane at 40°C is illustrated in Fig. 8. Except for the *cis*-4- and *cis*-5-decene pair, the separation of such mixtures was quicker and more complete on the PBO liquid crystal than the best separation obtained on common stationary phases⁹.

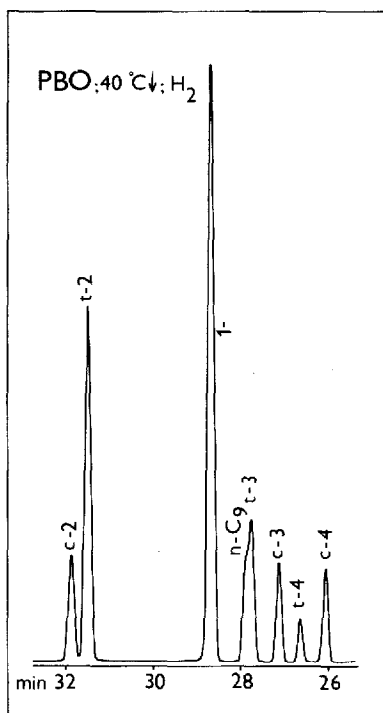


Fig. 8. Separation of isomeric *n*-nonenes and *n*-nonane at 40°C. Conditions and abbreviations as in Fig. 7.

Critical pairs of *n*-alkene isomers are retained differently on the liquid crystal and on common stationary phases. Mesogenic selectivity is related to the contribution of changes in the linearity of molecules of neighbouring alkene isomers caused by the shift of the double bond along the carbon chain. Pairs of isomers with the double bond situated in the centre of the carbon chain are the most difficult to separate on common stationary phases. A shift of the double bond changes the orientation, caus-

ing a lengthening of the carbon zig-zag chain in the direction of the molecular axis and increases the linearity of the alkene molecule and thereby also its retention on the liquid crystal. These changes appear as alternations in retentions of isomers and homologues¹. Being more linear from this viewpoint, *cis*-5-decene is more retained on the liquid crystal than on common stationary phases, and therefore is eluted with a retention close to that of *cis*-4-decene. Under the optimal conditions the selectivity factor on PBO for *cis*-4- and *cis*-5-decenes is $\alpha = 1.006$ with the required efficiency, n_{req} , being $6 \cdot 10^5$ plates for a resolution $R_{1,2} = 1$ and a capacity ratio $k = 5$. The less selective the liquid crystal used is the easier the separation of this pair will be, but the separation of other pairs of alkene isomers will be more difficult.

The glass capillary column coated with PBO employed in this study served with occasional use for 19 months. At the beginning and end of this period the measured retention indices were 989.2 and 990.0 for *p*-xylene and 980.8 and 980.3 for 1-nonyne, respectively, also the column efficiency was practically unchanged. These results suggest a high stability of the separation system with PBO liquid crystal as the stationary phase in capillary GC. The retention indices for C_9 - C_{11} *n*-alkenes on the column coated with a 10% solution of PBO in chloroform are presented in Table I.

TABLE I

RETENTION INDICES AND THEIR TEMPERATURE COEFFICIENTS FOR C_9 - C_{11} *n*-ALKENE ON PBO AS THE STATIONARY PHASE

<i>n</i> -Alkene	I_{56}^{PBO}	dI/dT (40-56°C)
<i>cis</i> -4-Nonene	893.7	0.17
<i>cis</i> -3-Nonene	899.2	0.18
<i>cis</i> -2-Nonene	920.7	0.20
<i>trans</i> -4-Nonene	895.6	0.10
<i>trans</i> -3-Nonene	901.1	0.09
<i>trans</i> -2-Nonene	917.9	0.11
1-Nonene	905.4	0.10
<i>cis</i> -5-Decene	988.0	0.32
<i>cis</i> -4-Decene	988.6	0.32
<i>cis</i> -3-Decene	996.7	0.29
<i>cis</i> -2-Decene	1019.4	0.28
<i>trans</i> -5-Decene	992.4	0.26
<i>trans</i> -4-Decene	994.0	0.23
<i>trans</i> -3-Decene	998.6	0.23
<i>trans</i> -2-Decene	1018.1	0.19
1-Decene	1005.1	0.19
<i>cis</i> -5-Undecene	1081.6	0.31*
<i>cis</i> -4-Undecene	1085.2	0.29*
<i>cis</i> -3-Undecene	1094.4	0.24*
<i>cis</i> -2-Undecene	1118.8	0.17*
<i>trans</i> -5-Undecene	1089.9	0.18*
<i>trans</i> -4-Undecene	1091.0	0.16*
<i>trans</i> -3-Undecene	1098.4	0.11*
<i>trans</i> -2-Undecene	1117.6	0.07*
1-Undecene	1105.2	0.09*

* 56-71°C.

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