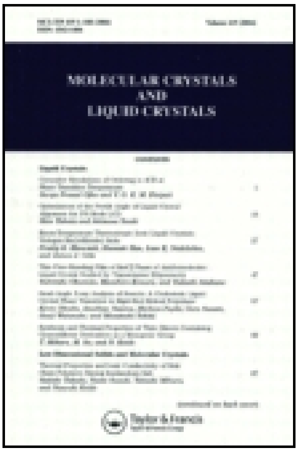

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GAS CHROMATOGRAPHY ANALYSIS OF DIPHENYL-DIACETYLENE LIQUID CRYSTALS

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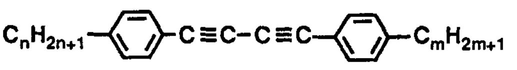
Abstract A gas chromatography method is used to investigate the purity of dialkyl-diphenyl-diacetylene liquid crystal components and at the same time identify the structure and concentration of the major impurities.

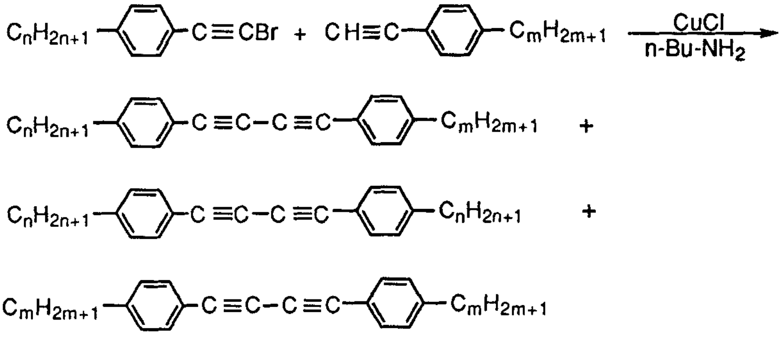
INTRODUCTION

The diphenyl-diacetylene liquid crystals (LCs) exhibit high birefringence, and at the same time low rotational viscosity, thereby they are very useful as LC mixtures for infrared, millimeter wave and nonlinear optics applications[1-3]. Several alkyl-diphenyl-diacetylene LC structures have been reported in the literature with non-polar[4-6] and polar[7-9] terminal groups in the *para* position of the phenyl ring. The polar terminal substitutions included cyano, fluoro, chloro, trifluoromethyl groups resulted in extremely high melting temperatures. The non-polar alkyl or alkoxy end groups exhibited moderately high melting temperatures dependent on the alkyl chain length. The synthesis of unsymmetrical alkyl substituted diphenyl-diacetylene homologs[5] (PTTP-nm, with structure shown below) resulted in high birefringence, relatively low viscosity, wide temperature range and low heat of fusion enthalpy LC components. The PTTP-nm LCs posses very low dielectric anisotropy, however they are excellent candidates for high birefringence host mixtures.



(PTTP-nm)

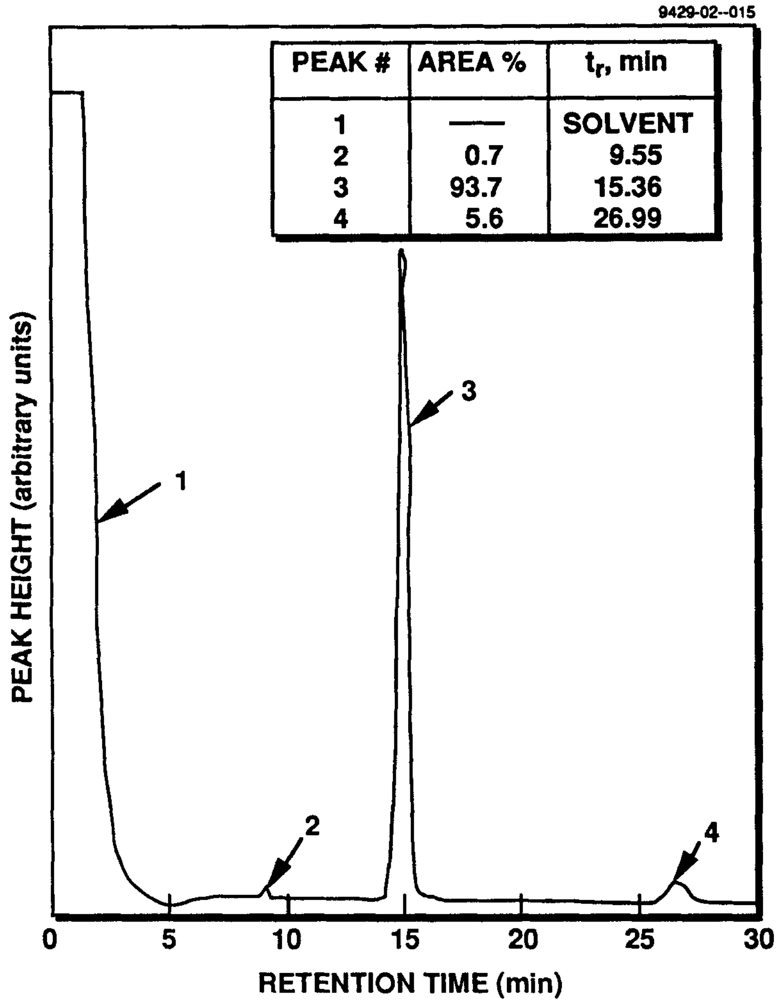
The synthesis[10] of unsymmetrical alkyl substituted diphenyl-diacetylene homologs are based on the coupling reaction of acetylenes to form diacetylenes. The general procedure for the preparation of 4-*n*-alkylphenylacetylenes followed the Corey and Fuchs[11] procedure using the appropriate para-substituted benzaldehyde as the starting materials. The intermediate β,β'-dibromostyryl derivative was treated with *n*-butyllithium at -78°C to be converted into the 4-*n*-alkylphenylacetylene, or reacted with potassium t-butoxide in refluxing toluene to form the bromoacetylide. The resulting asymmetrical diphenyl-diacetylenes were obtained by the Cadiot-Chodkiewicz coupling of 4-*n*-alkylphenylacetylene and 1-bromoacetylene intermediates. In the final coupling reaction of these two acetylenes with different terminal alkyl substitution it is difficult to obtain very high yield of the unsymmetrical diacetylenes totally free of the symmetrical components (PTTP-nn and PTTP-mm).



EXPERIMENTAL

Gas chromatography (GC) is a well-known analytical technique for qualitative and quantitative identification of synthesis products. The theoretical retention time (t_r) and retention index of a component depends on the column temperature, structure and purity of the stationary phase. In practice, however the temperature programmed t_r also depends on the initial temperature, the programming rate, the temperature dependence of the distribution coefficient, the carrier gas and its velocity.

A temperature programmed GC method was developed for the analysis of the dialkyl substituted diphenyl-diacetylene liquid crystal homologs. The purity of these materials was determined by using a Hewlett Packard Model 5780A GC equipped with 6 ft long x 1/8" i.d. dual columns. The column support, Gas Chrom Q, is a white diatomaceous earth of 100/200 mesh size, with maximum inertness and optimized for trace analysis. The liquid phase coating of 3% OV-17, a phenylmethyl silicone structure, is well suited for high temperature GC analysis with an operating temperature limit of 350-375°C. The column temperature was programmed from 200°C to 290°C at rate of 16°C/min. The nitrogen carrier gas flow rate was set at 30 ml/min. The injection port was maintained at 300°C and flame ionization detector at 350°C. Injected sample size was 1 μl in methylene chloride. The relative areas of components were measured on a Spectra-Physics SP4270 Integrator, excluding the solvent peak. A typical chromatograph of the 4-n-propyl-4'-n-hexyl-diphenyldiacetylene (PTTP-36), obtained with the above experimental conditions, is shown in Figure 1.



PEAK #	AREA %	t_r, min
1	—	SOLVENT
2	0.7	9.55
3	93.7	15.36
4	5.6	26.99

FIGURE 1 Gas chromatogram of PTTP-36 major component with PTTP-33 and PTTP-66 by-products.

DISCUSSION

We have found a very simple GC analysis method for simultaneous determination of the major LC components' and the symmetric LC impurities' concentration, based on their relative retention time. The gas chromatographic separation of components are affected by their molecular structure, molecular weight, vapor pressure, and their affinity for the liquid phase of the GC column. The elution order of LC homologs, with the same diphenyl-diacetylene core structure, depends on the size of their end-group. Under well-controlled, temperature programmed analysis conditions, the GC retention time is a function of the total dialkyl chain length, n+m. In our studies of numerous unsymmetrical diphenyl-diacetylene components, good peak separation was obtained at optimized GC conditions with column temperature programmed between 200 and 290°C. Fourteen unsymmetrical alkyl substituted diphenyl-diacetylene homologs were analyzed by GC with combined number of carbon atom (n + m) variation, in the terminal alkyl groups, between 6 and 14, corresponding to PTTP-24 and PTTP-68 respectively. GC retention time vs. total dialkyl chain length, n+m shown in Figure 2.

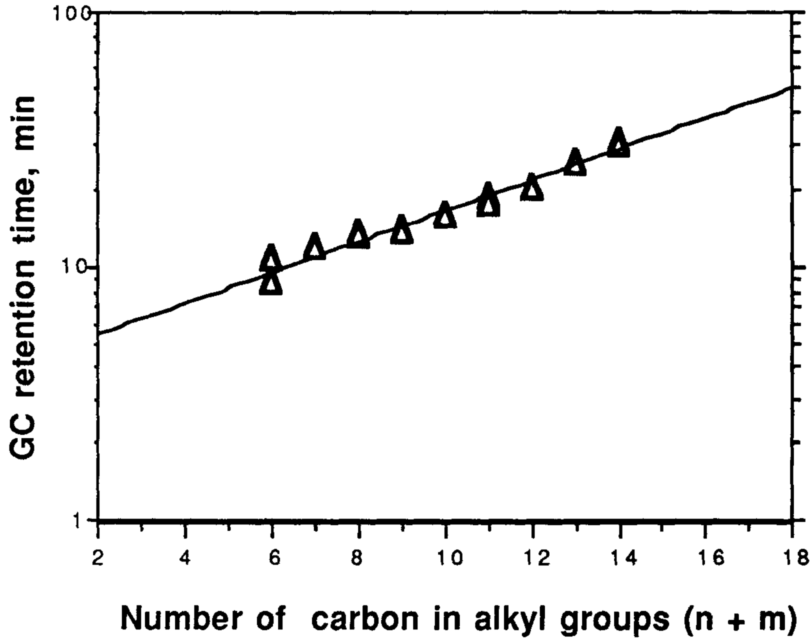


FIGURE 2 Retention time of PTTP-nm homologs.

The log of retention time is proportional to the number of carbon (including -CH_2 and -CH_3 groups), resulting in a good fit of all experimental points to a straight line. It is well known in gas chromatography[12] that if the logarithm of the adjusted retention time is plotted versus the carbon number of a homologous series, a linear fit is often obtained. Using the straight line relation for the major PTTP-nm components and examining the impurity peaks' retention for a typical sample of PTTP-36 is shown in Figure 3.

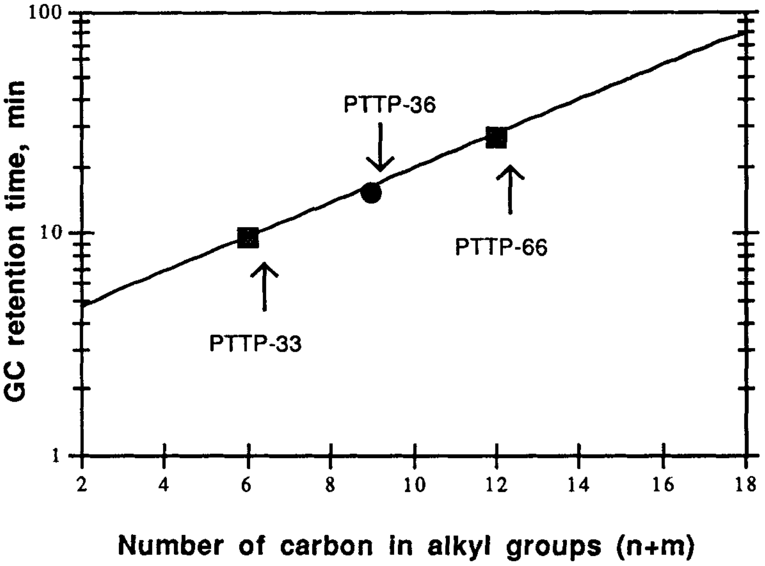


FIGURE 3 Retention time of PTTP-36 major component with PTTP-33 and PTTP-66 by-products.

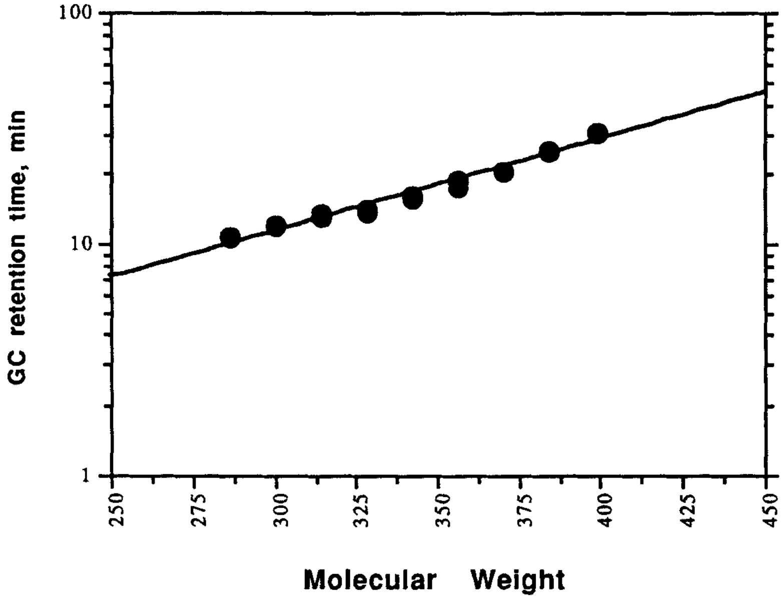


FIGURE 4 Retention time vs. molecular weight of PTTP LC components.

The small peaks before and after the major component have t_r of 9.55 and 27.02 minutes, corresponding to 6 and 12 total carbon, easily identified as PTTP-33 and PTTP-66 by-products from the synthesis. A comparison of the PTTP-nm components experimental retention times vs. their molecular weight resulted in a good straight line fit (see Figure 4), that can also be used for unknown gas chromatographic peak identification of the symmetrical PTTP components.

CONCLUSION

In studies of numerous unsymmetrical diphenyl-diacetylene components, good peak separation is obtained at optimized GC conditions with column temperature programmed between 200 and 290°C. The major unsymmetrical dialkyl diphenyl-diacetylene LCs retention time is in close agreement with a predicted logarithmic dependence on molecular size, while the impurity peaks retention time are similarly well correlated with the symmetrical PTTP-nn and PTTP-mm synthesis by-products.

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