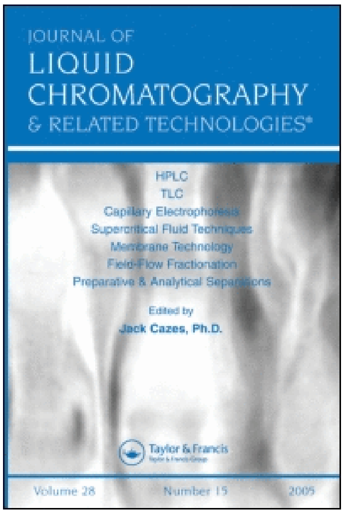


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Chromatographic Separations of Oligovinylpyridines. II. HPLC Separations of Radically and Anionically Oligomerized 2- and 4-Vinylpyridines

Franz P. Schmitz[a]; Heinz Hilgers[ab]
[a] Lehrstuhl für Makromolekulare Chemie RWTH Aachen, Worringerweg, Aachen Federal Republic of Germany [b] IBM Deutschland GmbH, Werk Mainz, Mainz, Fed. Rep. Germany

To cite this Article Schmitz, Franz P. and Hilgers, Heinz(1986) 'Chromatographic Separations of Oligovinylpyridines. II. HPLC Separations of Radically and Anionically Oligomerized 2- and 4-Vinylpyridines', Journal of Liquid Chromatography & Related Technologies, 9: 13, 2809 — 2823

To link to this Article: DOI: 10.1080/01483918608074152

URL: http://dx.doi.org/10.1080/01483918608074152

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(13), 2809-2823 (1986)

CHROMATOGRAPHIC SEPARATIONS OF OLIGOVINYLPYRIDINES. II. HPLC SEPARATIONS OF RADICALLY AND ANIONICALLY OLIGOMERIZED 2- AND 4-VINYLPYRIDINES

Franz P. Schmitz* and Heinz Hilgers+
Lehrstuhl für Makromolekulare Chemie
RWTH Aachen, Worringerweg
D-1500 Aachen
Federal Republic of Germany

ABSTRACT

HPLC-separations of oligomers obtained by radical and anionic oligomerization of 2- and 4-vinylpyridine by means of gradient elution are reported. The eluent systems used were pentane/methanol and nitrous oxide/methanol. Elution is shown to occur more rapidly with 2-vinylpyridine oligomers. Using nitrous oxide/methanol, separation with respect to degree of oligomerization was enhanced compared to pentane/methanol. Differences in the elution behavior of 2- and 4-vinylpyridine oligomers are ascribed to differences in interactions of the respective oligomer molecules with the stationary and the mobile phase, caused by the different position of the nitrogen atom in these two oligomer types.

+ Present address: IBM Deutschland GmbH, Werk Mainz, D-6500 Mainz, Fed. Rep. Germany

0148-3919/86/0913-2809$3.50/0

INTRODUCTION

Recently, chromatographic procedures have been developed allowing chromatographic studies of the oligomerization of vinylpyridines. In addition to HPLC (1-3) and TLC (2), medium pressure LC (1, 3-7) and supercritical fluid chromatography, SFC (8) have been used. The medium pressure separation technique, although lacking high resolution, was well suitable for separation on a preparative scale. Separations were reported of anionically prepared oligomers from 2-vinylpyridine, 2VPy (1, 3, 7), 4-vinylpyridine, 4VPy (6), α-methyl-2-vinylpyridine (2-isopropenylpyridine) (5), and α-methyl-4-vinylpyridine (4-isopropenylpyridine) (4, 5) as well as of radically prepared oligomers from 2-vinylpyridine (2, 8). The separations were performed on silica using gradient elution, the primary component of the mobile phase being an alkane (pentane (2, 8), hexane (1, 3-7), or isooctane (1, 3)) and the second component consisting of pure methanol (2, 8) or of mixtures of methylene chloride and methanol (1, 3-7).

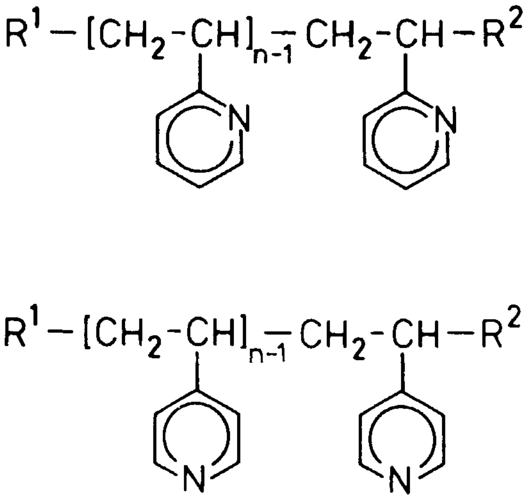
In the present paper ,HPLC-separations of oligomers from 2- and 4-vinylpyridine prepared by radical or by anionic initiation are reported. Additionally, it will be shown how the separation can be influenced by exchanging pentane as the primary component of the eluent system by nitrous oxide.

EXPERIMENTAL PART

Oligomerization Reactions

Radical Oligomerizations:

1.56 mg azo-bis(isobutyronotrile), AIBN, were added to a solution of 2 ml vinylpyridine (molar ratio 1:1) in 200 ml dry toluene at 90 °C. After stirring for 1 h under N_2 atmosphere,



O2VPy

O4VPy

FIGURE 1: Structure of oligo-2-vinylpyridines (O2VPy) and oligo-4-vinylpyridines (O4VPy).
R^1, end group caused by initiation reaction
R^2, end group caused by termination reaction

the solvent was removed by distillation. Purification of the products was obtained by passing a solution in methanol (5%, w/v) through sampling cartridges filled with silica (SEP-PAK 51900, Waters, Mass., USA).

Anionic oligomerizations:

To a solution of the monomer in tetrahydrofuran, THF, in a Schlenk tube the initiator butyl lithium, BuLi, was added as quickly as possible by means of syringes. Reaction conditions were 2 min at -20 °C under N_2 atmosphere, the reaction being stopped by addition of methyl iodide. Monomer concentrations were 20 mg/ml, molar monomer/initiator ratios being 10:1 (2VPy) and 3:1 (4VPy). Lithium iodide was removed by precipitation upon concentration of the solution; further purification of the products was achieved as with the radically prepared oligomers.

Chromatography

The separations were carried out using an HPLC instrument 1084 B from Hewlett-Packard. For working with nitrous oxide, N_2O, some modifications to this instrument were necessary. First, liquid nitrous oxide was fed to the pump directly from the transport cylinder by raising the pressure in the cylinder by means of helium gas. Second, since detection in the liquid state necessitated applying pressures of ca. 100 bar, a high pressure resistant UV detector cell as described by McManigill et al. (9) was used; the pressure level was controlled by means of a valve at the detector outlet. Third, storage of potentially hazardous mixtures of N_2O and methanol leaving the chromatograph had to be avoided. Therefore, methanol was separated from N_2O in the effluent line by lowering the pressure. Methanol was collected in a separation vessel and nitrous oxide, being now in the gaseous state, was directed to the outlet.

The separation columns of stainless steel of length 25 cm and internal diameter 4.6 mm were packed with silica (LiChrosorb Si 100, 10 µm, from Merck, Darmstadt, Fed. Rep. Germany) using the slurry method described elsewhere (10). Pentane and methanol were distilled and degassed before use; N_2O (Linde, Höllriegelskreuth, Fed. Rep. Germany) was of 99.5% purity.

The chromatograms were obtained applying a liquid flow rate of 1ml/min and a detection wavelength of 254 nm. 60 µl of methanol solutions of the oligomeric samples (concentrations 1-5%, w/v) were injected for each chromatographic run. The eluent gradients were formed by linearly increasing the ratio Q_B,

$$Q_B = \frac{P_B}{1 - P_B} \qquad (1)$$

where P_B is the volume fraction of eluent component B (methanol), measured at the pumps. Different gradients had to be applied for the two oligomer types (cf. Table 1). Pressures at

TABLE 1
Chromatographic Conditions for the Oligovinylpyridine Separations.

Chromatogram in Fig.	Substrate*	p_i** bar	Primary eluent component	gradient type+
2a	O4VPy,r	46	pentane	I
2b	O4VPy,r	149	N_2O	I
3a	O4VPy,a	47	pentane	I
3b	O4VPy,a	149	N_2O	I
4a	O4VPy,a	147	N_2O	I
4b	O4VPy,a	149	N_2O	II
5a	O2Vpy,r	41	pentane	II
5b	O2VPy,r	148	N_2O	II
6a	O2VPy,a	46	pentane	II
6b	O2VPy,a	154	N_2O	II

* r, prepared by radical initiation
a, prepared by anionic initiation

** pressure at column inlet at the start of the chromatographic run

\+ gradient I, increasing methanol content from 10 to 60% (v/v) within 100 min according to eq. 1
gradient II, increasing methanol content from 5 to 40% (v/v) within 160 min according to eq. 1 after an initial isocratic period of 10 min at 5% methanol

the inlet of the separation column were around 45 bar with pentane/methanol and approximately 150 bar with nitrous oxide/ methanol. The separation conditions are summarized in Table 1.

RESULTS AND DISCUSSION

In a previous paper (2) it was shown that gradient elution using the eluent pair pentane/methanol was well suitable for the separation of oligo-2-vinylpyridines (O2VPy) prepared by means of radical initiation. Figs. 2a, 3a, 4a, and 6a show that this combination of a nonsolvent (pentane) and a solvent (methanol) could generally be applied to the separation of 2- and 4- vinylpyridine oligomers. Additionally, it was tested whether and to what extent the exchange of the nonsolvent component of the eluent system influences these separations. For this purpose, we chose nitrous oxide (N_2O) as the primary eluent component for the following reasons: On the one hand, nitrous oxide is more polar than pentane, and on the other hand, due to its gaseous nature at ambient conditions, nitrous oxide may be of interest for preparative scale separations. It is easily removed from the collected fractions and thus prevents handling large amounts of solvent with the work-up of the collected fractions.

From the separations of the oligo-4-vinylpyridines (O4VPy) it can be seen that, applying the same gradient program, the use of N_2O produces larger retention time differences for the respective peak groups. Each of these peak groups appearing in the chromatograms corresponds to a degree of oligomerization. The additional separations within the respective peak groups are due to configurational isomerism and to structural variations; however, the nature of these species has not yet become known. To judge from the chromatograms, the radically prepared 4VPy oligomers seem to be of lesser structural inhomogeneity than those prepared anionically (cf. Figs. 2 and 3).

Whereas the separation with respect to molecular weight, i.e., with respect to degree of oligomerization, increases by replacing pentane with nitrous oxide, just the opposite is observed with the 4VPy oligomers concerning the separation within a given degree of oligomerization; at equal chromatographic conditions and sample concentration, enhanced splitting of the peak groups is obtained with pentane (cf. Figs. 2 and 3).

In Fig. 4 the influence of the gradient slope on the separation is demonstrated. The sample concentration was increased for

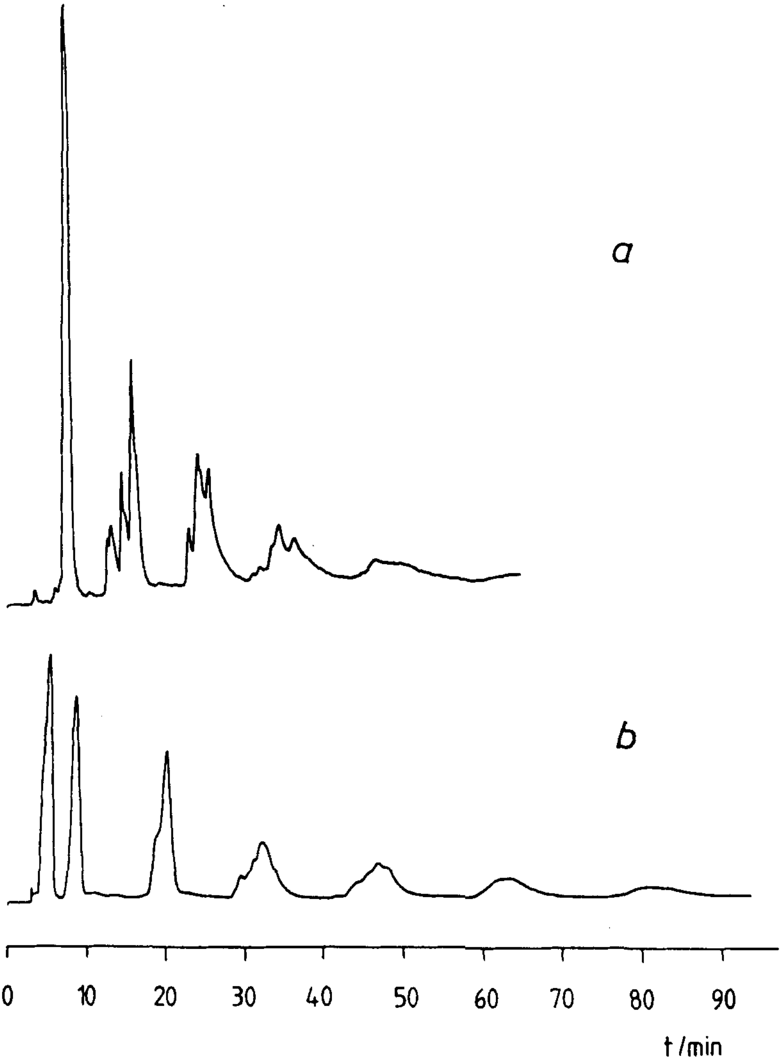


FIGURE 2: Separations of oligo-4-vinylpyridines prepared by radical initiation.

a, pentane/methanol as the eluent; b, nitrous oxide/methanol as the eluent. For chromatographic conditions see Experimental Part and Table 1.

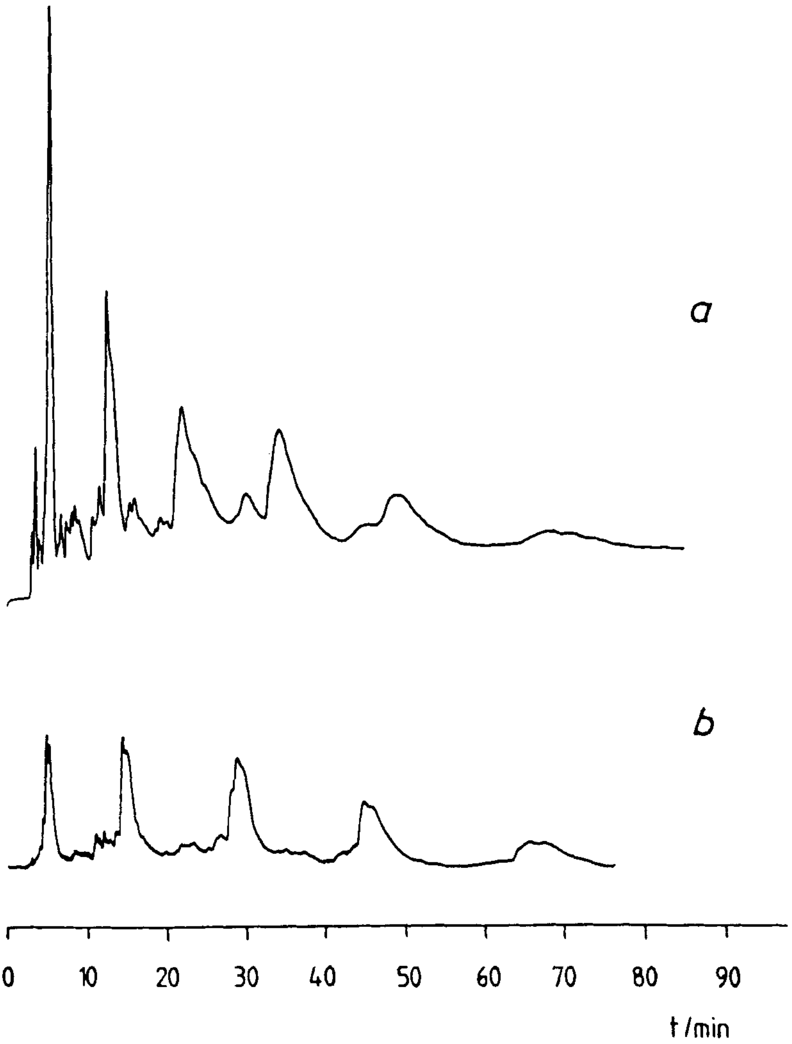


FIGURE 3: Separations of oligo-4-vinylpyridines prepared by anionic initiation.
a, pentane/methanol as the eluent; b, nitrous oxide/methanol as the eluent. For chromatographic conditions see Experimental Part and Table 1.

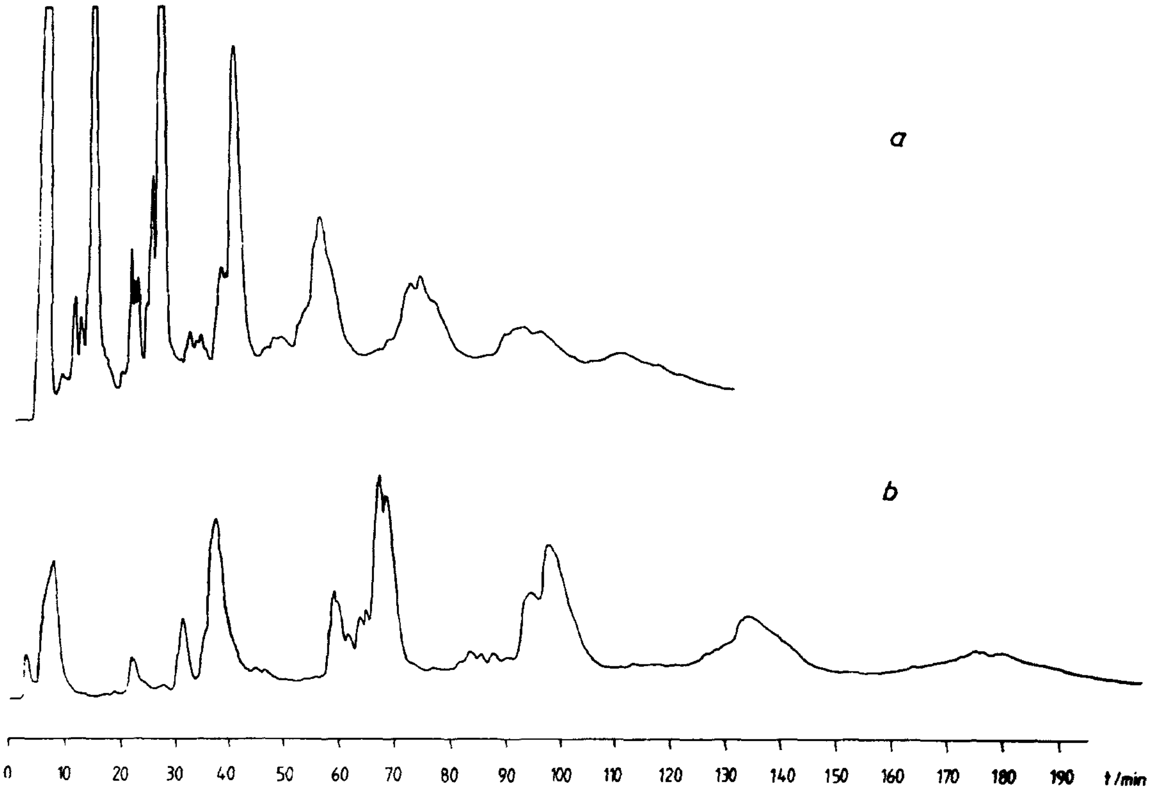


FIGURE 4: Separations of oligo-4-vinylpyridines prepared by anionic initiation.
Comparison of separations using different gradient slopes. See text and Table 1.

these two chromatograms in order to better see the effects. As expected, retention times increase distinctly with decreasing gradient slope, causing resolution between the peak groups to increase. Contrary to this, within the respective peak groups, the number of individual peaks remains constant, and the efficiency remains essentially unchanged. Retention time differences which can be observed comparing the chromatograms shown in Figs. 3b and 4a are due to the fact that the columns which were used for the separations had been in use for different times. The effect of decreasing separation efficiency as a consequence of column "ageing" has been generally observed with columns used for oligomer separations although the columns were flushed with solvent subsequent to each run.

The results of the O4VPy separations cannot be transferred to O2VPy separations without change. Although retention times are again higher using nitrous oxide/methanol compared to pentane/methanol (cf. Figs. 5 and 6), with nitrous oxide the separation within the respective peak groups each corresponding to one degree of oligomerization is enhanced. Contrary to 4VPy oligomerizations, with the 2VPy oligomers large numbers of peaks are observed per degree of oligomerization.

Comparing O2VPy and O4VPy separations, 2VPy oligomers are much more rapidly eluted than 4VPy oligomers applying the same gradient. This behavior may be explained by the nitrogen atom of the pyridine ring being closer to the polymer backbone for the 2VPy oligomers. Thus, interactions between oligomers and the stationary phase are rendered more difficult than for 4VPy oligomers with their nitrogen atoms being farther removed from the backbone (cf. Fig. 1). Consequently, higher methanol contents are needed with 4VPy oligomers for eluting equal degrees of oligomerization.

Recently, some results have been reported indicating that with different eluent compositions oligomers may be separated predominantly according to molecular weight or else rather according

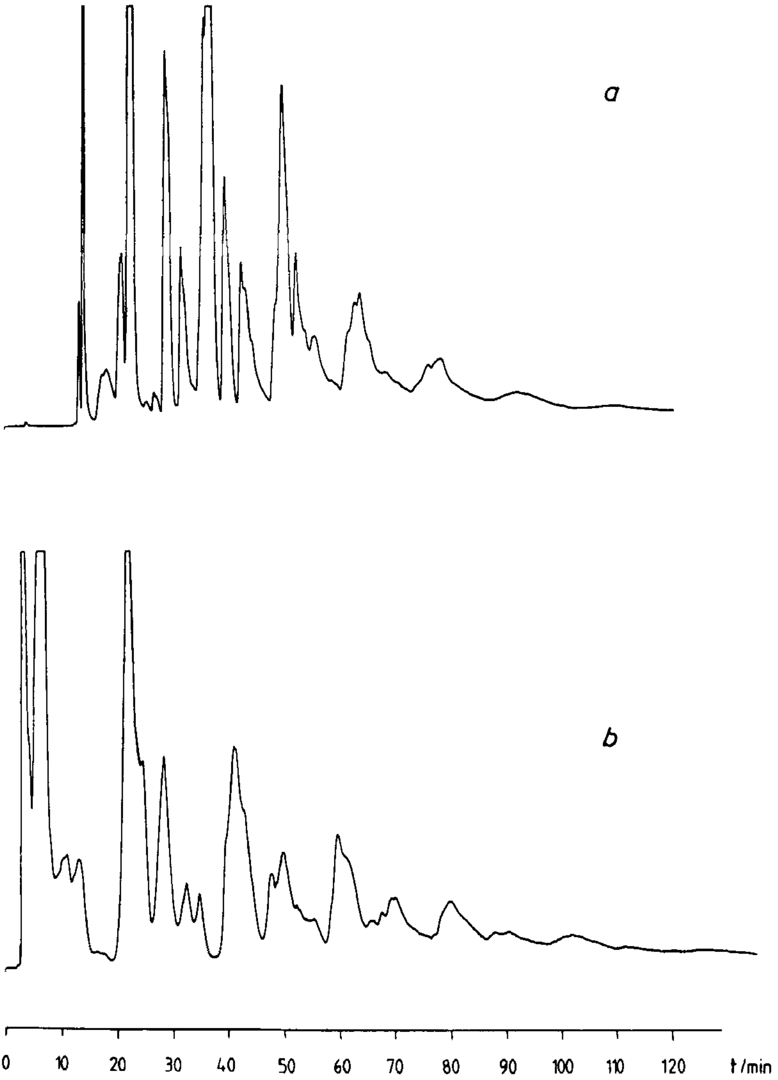


FIGURE 5: Separations of oligo-2-vinylpyridines prepared by radical initiation.

a, pentane/methanol as the eluent; b, nitrous oxide/methanol as the eluent. For chromatographic conditions see Experimental Part and Table 1.

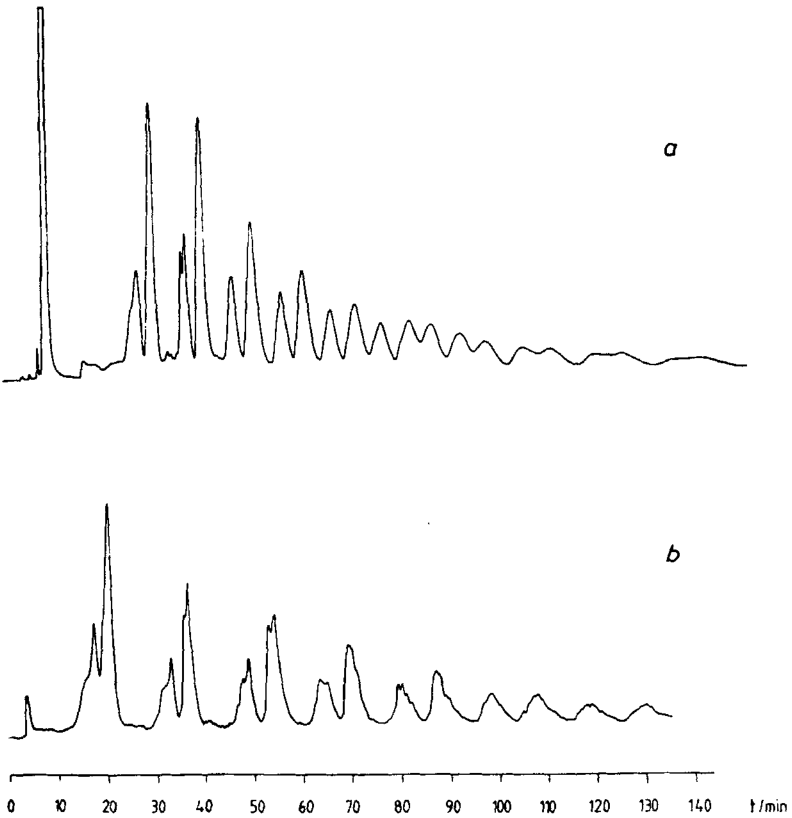


FIGURE 6: Separations of oligo-2-vinylpyridines prepared by anionic initiation.
a, pentane/methanol as the eluent; b, nitrous oxide/methanol as the eluent. For chromatographic conditions see Experimental Part and Table 1.

to chemical differences. Studies which were performed with oligostyrenes (11) or "epoxy novolac resin" oligomers (12) using C_{18}-silica showed that the extent to which separations occurred within the respective degrees of oligomerization increased with decreasing polarity of the eluent. This general statement was modified and defined more clearly by Men and Rogers (13) in that specific interactions, as e.g. induced dipoles in the side groups of the oligomer molecules, should be responsible for the order of elution of configurational isomers. Thus, the elution behavior of the vinylpyridine oligomers with pentane/methanol or nitrous oxide/methanol is also due to the competing interactions of the substrate molecules with the stationary and the mobile phase. However, to fully understand the observed elution behavior, further studies will be necessary.

The separation quality of the O2VPy separation, as shown in Fig. 6a, could be transferred to semipreparative separations without any substantial loss in resolution using pentane/methanol. In these experiments, a column was used having an internal diameter of 18 mm and a length of 25 cm, packed with the same stationary phase as used for the analytical scale separations (LiChrosorb Si 100, 10 µm), the flow rate being 10 ml/min. The results of these studies will be reported separately.

As it can be seen from Table 1, using N_2O as the primary eluent, higher pressures had to be applied compared to the pentane chromatograms in order to keep the mobile phase in the liquid state. Yet, with chromatography using liquid eluents, such differences in column pressure essentially do not cause any changes in the separations. Accordingly, chromatograms which were taken at 150 bar using pentane/methanol differred only to a minor extent from those obtained at 45 bar.

ACKNOWLEDGEMENTS

Thanks are expressed to Prof. E. Klesper for advice and encouragement, to Mr. B. Lorenschat and Mr. G. Grünheidt for experimental aid and to the Deutsche Forschungsgemeinschaft (DFG) for financial support.

REFERENCES

1 Huang, S.S., Mathis, C., and Hogen-Esch, T.E., Oligomerization of Vinyl Monomers. 9. ^{13}C NMR and Chromatographic Studies of Oligomers of 2-Vinylpyridine, Macromolecules 14, 1802 (1981)

2 Hilgers, H. and Schmitz, F.P., Chromatographic Separations of Oligovinylpyridines. 1. Analytical-Scale Chromatography of Radically Oligomerized 2-Vinylpyridine by HPLC and TLC, J. Liq. Chromatogr. 7, 2513 (1984)

3 Huang, S.S. and Hogen-Esch, T.E., Oligomerization of Vinyl Monomers. 20. Carbon-13 NMR of Oligomers of 2-Vinylpyridine. Studies of Labelled End Groups, J. Polym. Sci., Polym. Chem. Ed. 23, 1203 (1985)

4 Hashimoto, K. and Hogen-Esch, T.E., Oligomerization of Vinyl Monomers. 12. Anionic Oligomerization of 4-Isopropenylpyridine. Preparation and ^{1}H-NMR Spectroscopic Analysis of Stereoisomeric Oligomers, Macromolecules 16, 1805 (1983)

5 Hashimoto, K. and Hogen-Esch, T.E., Oligomerization of Vinyl Monomers. 13. Anionic Oligomerization of 2- and 4-Isopropenylpyridine. Stereoselectivity on Monomer Addition and Methylation Determined by End Group ^{13}C Labels, Macromolecules 16, 1809 (1983)

6 Meverden, C.C. and Hogen-Esch, T.E., Oligomerization of Vinyl Monomers. 18. Stereochemistry of Anionic Oligomerization of 4-Vinylpyridine, J. Polym. Sci., Polym. Chem. Ed. 23, 159 (1985)

7 Meverden, C.C. and Hogen-Esch, T.E., Oligomerization of vinyl monomers. 19. Studies of side reactions occurring in oligomeric models of "living" poly(2-vinylpyridine), Makromol. Chem., Rapid Commun. 5, 749 (1984)

8 Schmitz, F.P., Hilgers, H., and Klesper, E., Gradient Elution in Supercritical Fluid Chromatography, J. Chromatogr. 267, 267 (1983)

9 McManigill, D., Board, R., and Gere, D.R., Hardware Adaptations to HPLC Apparatus to Enable Operation as a Supercritical Fluid Chromatograph, Publication No. 43-5953-1647, Hewlett-Packard Co., Avondale, PA, 1982, p.21

10 Schmitz, F.P., Hilgers, H., Lorenschat, B., and Klesper, E., Separation of Oligomers with UV-Absorbing Side Groups by Supercritical Fluid Chromatography Using Eluent Gradients, J. Chromatogr. 346, 69 (1985)

11 Mourey, T.H., Smith, G.A., and Snyder, L.R., Solvent Selectivity in the Liquid Chromatographic Separation of Polystyrene Oligomers on Silica, Anal. Chem. 56, 1773 (1984)

12 Lai, S.-T. and Sangermano, L., Characterization of Epoxy Novolac Resins Using Phenyl-Bonded Phase High Performance Liquid Chromatography, J. Chromatogr. 321, 325 (1985)

13 Men, L.-C. and Rogers, L.B., Role of Polar Groups in Fractionating Isomeric Polystyrene Oligomers, J. Chromatogr. 347, 39 (1985)