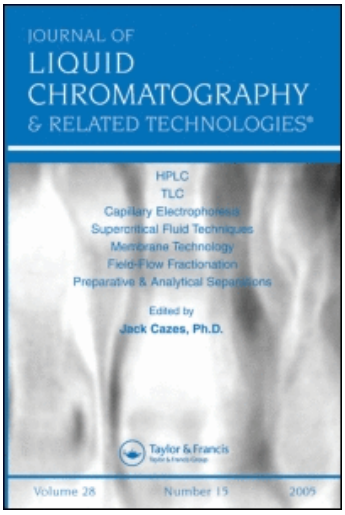

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CHROMATOGRAPHIC SEPARATIONS OF OLIGOVINYLPYRIDINES 1. ANALYTICAL-SCALE CHROMATOGRAPHY OF RADICALLY OLIGOMERIZED 2-VINYLPYRIDINE BY HPLC AND TLC

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ABSTRACT

Oligomer mixtures of 2-vinylpyridine prepared by radical oligomerization were separated by TLC and HPLC. With TLC, using diethyl ether as the eluent, good separations could be achieved up to a degree of oligomerization of n=3. TLC could therefore be used as a rapid test for the presence of oligomers in the reaction mixture. For HPLC-separations pentane and methanol were used as eluents, applying gradients in eluent composition with increasing methanol content. Corresponding to different end groups and isomerism of the oligomers, additional separations within a given degree of oligomerization were observed.

INTRODUCTION

Poly(vinylpyridine)s show interesting features: owing to their basic and nucleophilic properties they are able to catalyze

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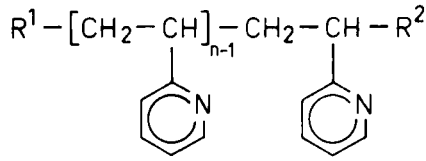

Fig. 1: Structure of oligo-2-vinylpyridines.
R_1: end group caused by initiation reaction,
R_2: end group caused by termination reaction.

a number of reactions (1-3), and they can furthermore be used as complexing agents (4-6). For detailed studies of these features, investigation of the correlation between degree of polymerization and structure on one hand and properties on the other would be of interest, employing individual, defined oligomers.

To our knowledge, only one of the numerous investigations on oligo(vinylpyridine)s included chromatographic analysis (7), using an eluent system consisting of hexane, methylene chloride and methanol and applying gradient elution. By this technique, separations of isomers (as was demonstrated for the trimer) of oligo(2-vinylpyridine)s from anionic oligomerization could be achieved.

We report here on analytical-scale chromatographic separations of oligo(vinylpyridine)s prepared by radical oligomerization. Analyses of oligomers prepared by anionic initiation and preparative-scale separations will be reported in subsequent papers.

EXPERIMENTAL PART

Radical oligomerization by means of azo-bis(isobutyronitrile), AIBN:

390 mg AIBN were added to a solution of 0,513 ml 2-vinylpyridine in 50 ml dry toluene at 60°C. After stirring for 4 h most of the solvent was removed by distillation. Products of higher molecular

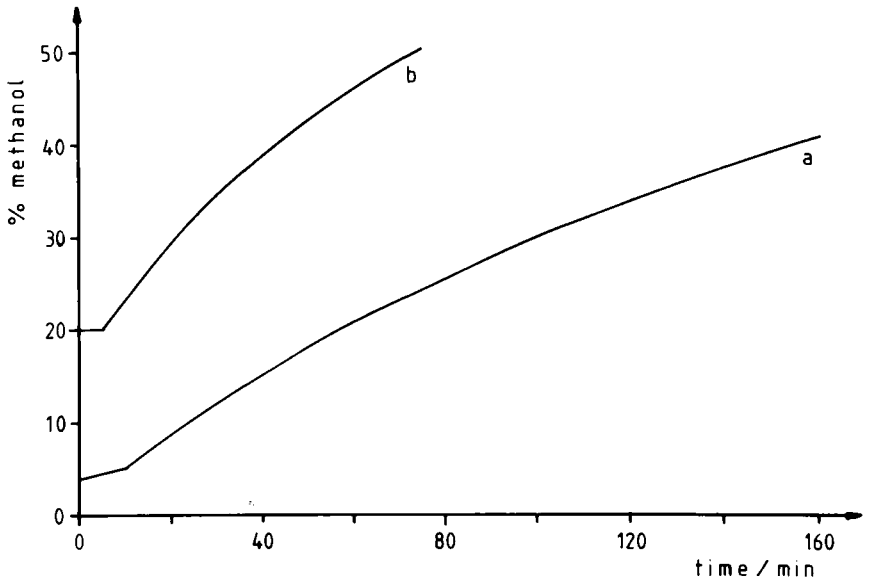

Fig. 2: Eluent composition gradients applied for the chromatograms shown in Figs. 6-9, 11 (a) and in Fig. 12 (b).

weights were obtained by precipitation from diethyl ether. The degree of oligomerization was controlled by varying the monomer/ initiator ratio.

Chromatography

TLC: Aluminum foils, coated with Kieselgel 60/Kieselgur F 259, layer thickness 0,2 mm (Merck, West Germany), with fluorescence indicator, were used. Eluents were diethyl ether and methanol, both dried and distilled before use.

LC: Glass columns of length 50 cm and internal diameter 2,8 cm were packed with silicagel (LiChroprep Si 100, 40-63 µm) or aluminum oxide (150 basic, 63-200 µm) (both from Merck); the eluent was methanol. UV-detectors, recorders and fraction collectors from LKB were used.

HPLC: The separations were carried out with an instrument 1084B from Hewlett Packard. Columns of stainless steel of lengh 25 cm and internal diameter 4,6 mm were packed with silicagel (LiChrosorb Si 100, 10 µm, Merck) using a slurry method. Eluents were pentane and methanol; the chromatographic runs were carried out by rising the methanol content (Fig. 2); the total flow rate was 1,5 ml/min. Eluents were distilled from sodium and degassed before use.

RESULTS AND DISCUSSION

By properly chosing the monomer/initiator ratio, oligomeric 2-vinylpyridine samples could easily be obtained by radical oligomerization. Both the ^{1}H- and the ^{13}C-NMR spectra of the products thus obtained showed no indications for branched or even crosslinked products, whereas such side reactions can often be observed with oligo-(2-vinylpyridine)s obtained by anionic oligomerization (8).

For a rapid determination if - and to what extent - oligomers have been formed thin-layer chromatography was found to be suitable. Using diethyl ether as the eluent, only oligomers up to a degree of oligomerization of n=3 are able to migrate along the TLC-plate, whereas products of higher molecular weight remain at the starting point (Fig. 3). Separations within the regions for the respective degrees of oligomerizations are due to products with different end groups and/or isomerism. Adding methanol to the eluent results in improved transport properties of the eluent mixture, as is shown in Fig. 4.

However, the quality of the separation decreases with increasing methanol content; finally, with pure methanol as the eluent, resolution is almost completely lost in the thin-layer chromatograms of the radically oligomerized samples.

The eluent system pentane/methanol turned out to be most suitable for separating oligo-2-vinylpyridines by HPLC. As is usu-

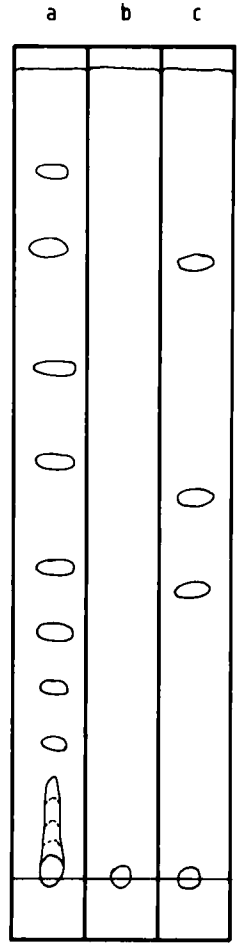

Fig. 3: Thin-layer chromatograms,
a: from radical oligomerization,
b: from radical polymerization,
c: from a mixture of test substances (cf. Fig. 6).

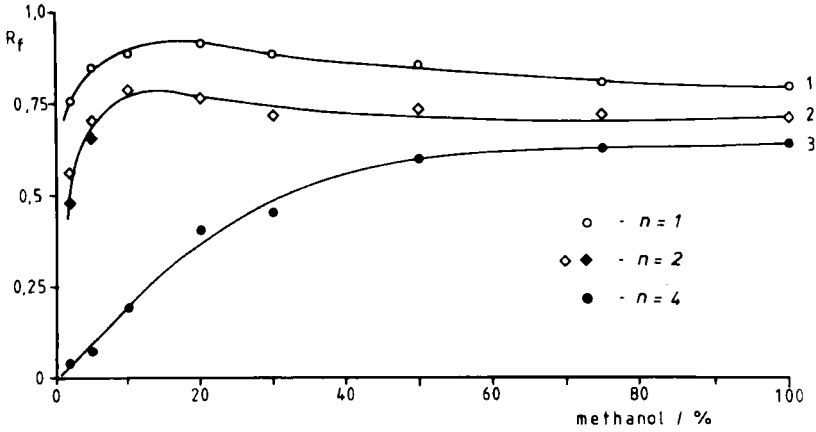

Fig. 4: Dependence of R_f-values on eluent composition, determined by means of a mixture of test substances (cf. Fig. 6). Left: 100% diethyl ether; right: 100% methanol.

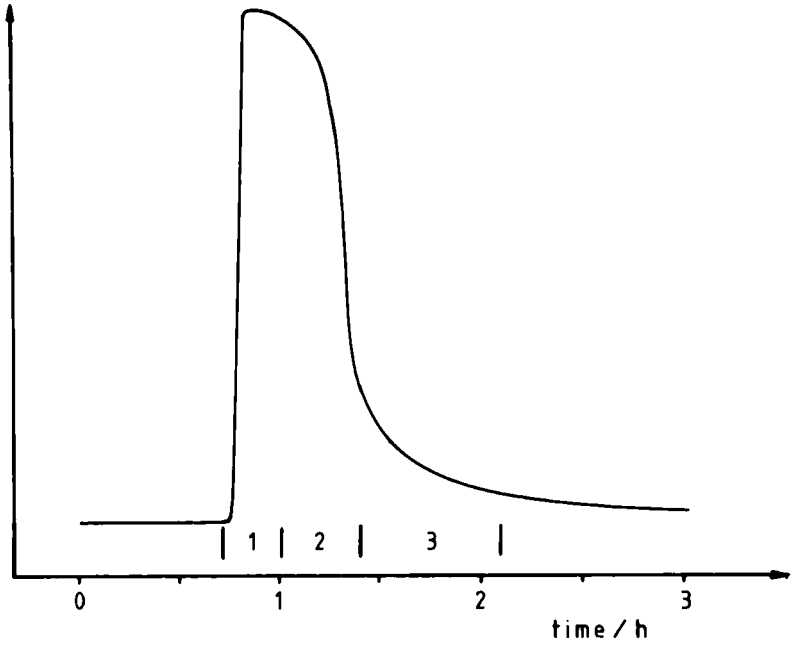

Fig. 5: Typical liquid chromatogram of an oligo(2-vinylpyridine) sample. Stationary phase: silica gel; mobile phase: methanol. The numerals correspond to the fractions collected for HPLC-separation.

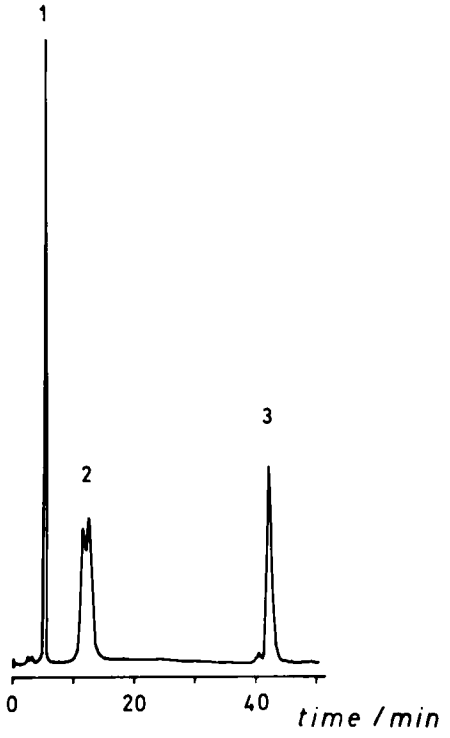

Fig. 6: HPLC-chromatograms of test substances. Conditions see text. 1: Ethylpyridine (n=1, R_1=H, R_2=H); 2: Dimer (n=2, R_1=H, R_2=CH_3); 4: Tetramer (n=4, R_1=H, R_2=CH_3).

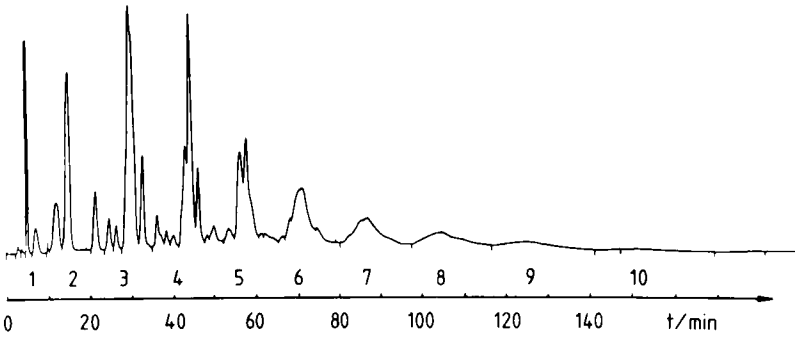

Fig. 7: HPLC-chromatogram of the first LC-fraction of an oligomer sample with monomer/initiator ratio of 1:1. Conditions see text. The numerals below the detector trace correspond to the degrees of oligomerization n.

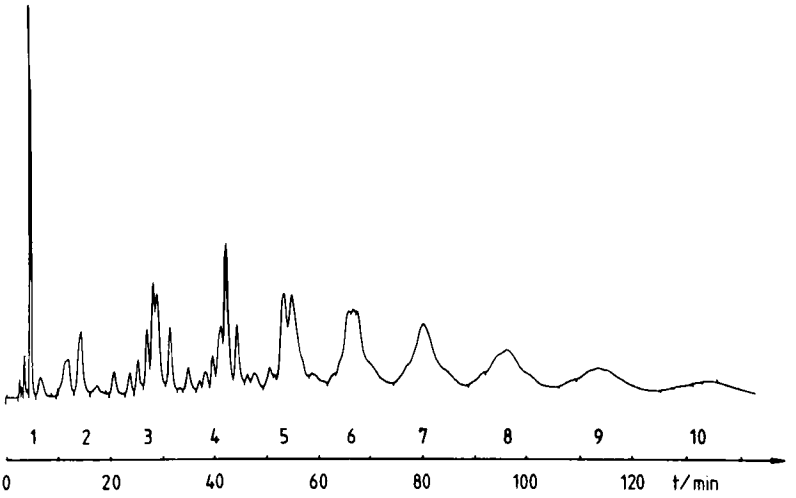

Fig. 8: HPLC-chromatogram of the first LC-fraction of an oligomer sample with monomer/initiator ratio of 1:2. For explanations see Fig. 7.

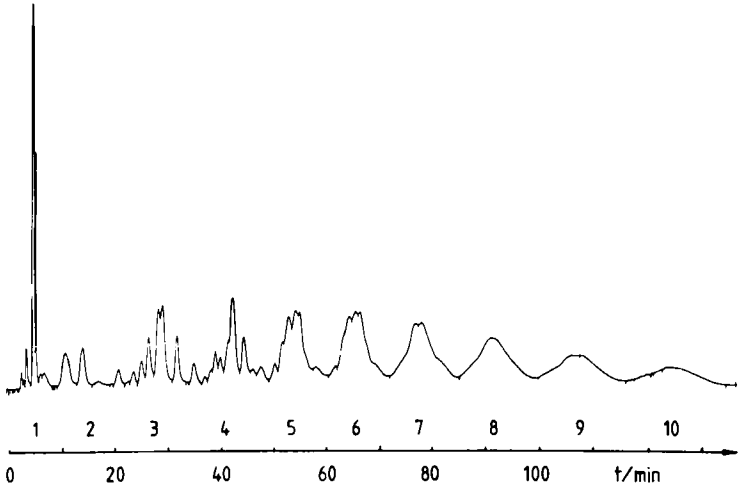

Fig. 9: HPLC-chromatogram of the first LC-fraction of an oligomer sample with monomer/initiator ratio of 1:4. For explanations see Fig. 7.

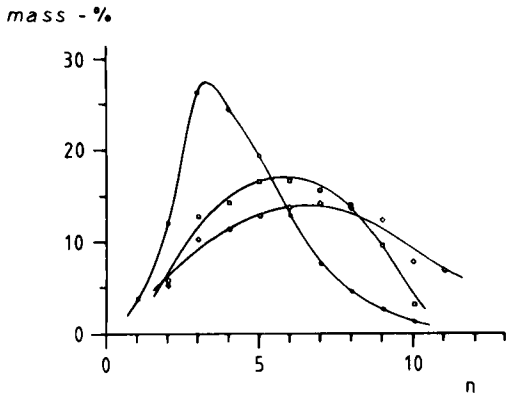

Fig. 10: Mass distribution plots for the three oligomer samples shown in Fig. 7 to 9. Monomer/initiator ratio: 1:1=(o), 1:2=(□) and 1:4=(◇).

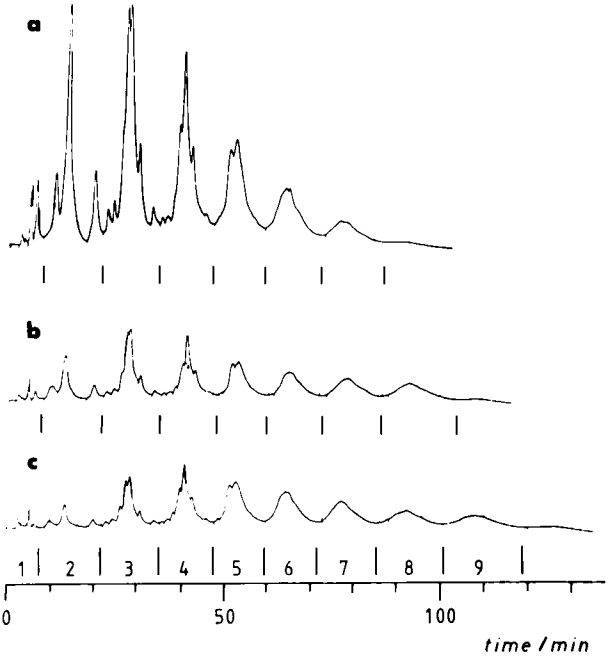

Fig. 11: HPLC-chromatograms of three subsequent fractions of an LC-separation of an oligo(2-vinylpyridine) sample with monomer/initiator ratio 1:1. For explanations see Fig. 7.

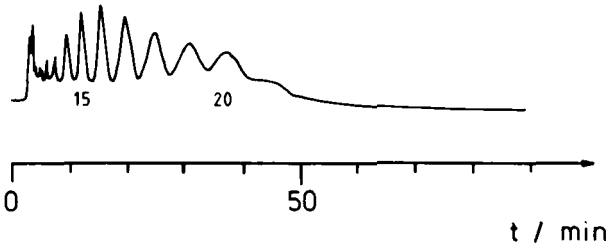

Fig. 12: HPLC-chromatogram of a lately eluting LC-fraction. For explanations see Fig. 7.

ally neccessary for the separation of oligomers, an eluent composition gradient had to be applied, in this case with a methanol content increasing from 4 to 40 % for oligomer samples of lower molecular weight. Figs. 7 to 9 show the HPLC analysis of the first of three LC-fractions (cf. Fig. 5) of a series of samples possessing increasing average degrees of oligomerization $\bar{n}$. The tentative assignments of the peaks to degrees of oligomerization are based on chromatograms of well-defined oligomers (Fig. 6).

Especially for the lower oligomers a remarkable separation within the oligomer regions of a given n was achieved. The individual peaks within these regions are due to configurational isomers and possibly different end groups. In accordance with the increasing number of possible isomers with increasing degree of oligomerization n, for n=1 to n=2 two peaks each, for n=3 at least 6 peaks and for n=4 at least 9 peaks can be observed. With increasing n and increasing peak numbers the peaks overlap, which finally results in only one broad signal for the respective degree of oligomerization. At present, the configurational and structural assignments of the oligomer peaks are not known.

Fig. 10 shows the correlation between monomer/initiator ratio and molecular weight distribution calculated from the HPLC-chromatograms: As to be expected, the distribution curves are shifted to higher $\bar{n}$-values with increasing monomer/initiator ratio. An analogous trend can be derived from the HPLC-chromatograms of three

successive LC-fractions (Fig. 11), where the relative increase of the peak areas for the higher oligomers is clearly visible.

Starting with higher methanol contents and applying steeper gradients results in rapid elution of higher oligomers (Fig. 12). The conditions for the chromatogram shown in Fig. 12 were chosen such that for each degree of oligomerization only one peak is observed.

ACKNOWLEDGEMENT

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