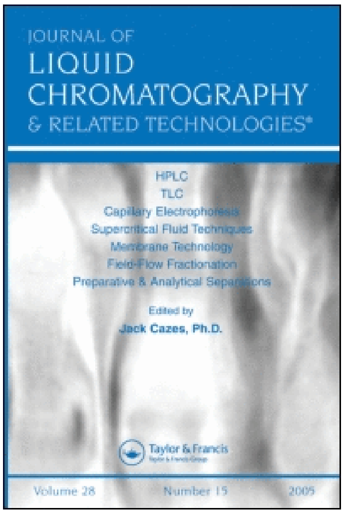

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APPLICATION OF GEL PERMEATION CHROMATOGRAPHY FOR INVESTIGATION OF 9-(2,3-EPOXYPROPYL)-CARBAZOLE OLIGOMERS

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ABSTRACT

Gel permeation chromatography on dextran gels "Sephadex LH-20" and "Sephadex LH-60" in the solution of dimethyl formamide was used for the estimation of molecular weight and molecular weight distribution of 9-(2,3-epoxypropyl)carbazole oligomers and for the investigation of the process of their obtaining as well. The simple numerical method of the instrumental dispersion correction as well as the principle of "the differential chromatograms" was used to interpret the gel permeation chromatography data. The method used permits to separate 9-(2,3-epoxypropyl)carbazole oligomers within the range of molecular weights 150-15000.

INTRODUCTION

9-(2,3-epoxypropyl)carbazole (EPC) oligomers obtained by anionic and cationic polymerization are known as perspective organic semiconductors for electrophotography (1,2).

As the value of molecular weight (MW) and molecular weight distribution (MWD) of oligomers of this type considerably affects their properties the choise of a good determination method of these parameters is an important factor in the field of

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these investigations. Gel permeation chromatography (GPC) is fit the best for the determination of the MW and MWD of poly/9-(2,3-epoxypropyl)carbazole/ (PEPC) especially as the UV-absorbtion intensity of the solution of PEPC and a comparatively high MW of the elementary unit give possibility to use a simple equipment - a single short column furnished with the hydrostatic feeding of eluant, a continuous UV-absorbtion measuring cell made of ordinary optical glass and the UV-spectrophotometer as a detector.

EXPERIMENTAL

The GPC of EPC oligomers was carried out in the solution of dimethylformamide (DMFA) using dextran gels "Sephadex LH-20" and "Sephadex LH-60". The UV-spectro-photometer "Specord UV VIS" operating as a detector at the constant wavelength 294 nm was used. Samples (0.5 ml) were injected as a solution in eluant (0.05-0.4%). The elution rate was 20 ml/h. The elution volume measurement was carried out by means of graduated glass tube with the accuracy of 0.1 ml and marked on the elution curve at 2-3 ml intervals by means of the special button on the recorder. The detector's response - optical density of the PEPC solution in DMFA at the wavelenght 294 nm does not depend on the degree of polymerization in the investigated range of MW and can be transformed directly into the concentration.

RESULTS AND DISCUSSION

The numerical method of the correction of instrument spreading for the GPC data treatment was used (3,4). The essence of the method is as follows: a chromatogram described in general by the equation of instrument spreading 1 (5) is divided into a sufficient number of little intervals. This equation

$$\int_0^\infty F(v) = \int_0^\infty A(v,y)\, W(y)\, dy \qquad (1)$$

is expressed in the matrix form with a sufficient degree of accuracy:

$$F = A \cdot W \qquad (2), \text{ where}$$

F - the matrix of the experimental chromatogram function values,

A - the matrix of the instrument spreading function values,

W - the matrix of the corrected chromatogram function values.

When the function of instrument spreading represents the Gaussian distribution, every member of the matrix A is calculated by means of the equation:

$$a_{ik} = \delta (h_k/\pi)^{1/2} \exp/-h_k(i-k)^2\delta^2/ \qquad (3), \text{ where}$$

δ - the interval of the division, ml or counts,

h_k - the coefficient of instrument spreading at the elution volume v_k, ml^{-2} or $counts^{-2}$,

i and k - numerical variables.

The corrected chromatogram in the matrix form was calculated by means of the equation:

$$W = A^{-1} F \qquad (4).$$

For this purpose by the use of a standard computer program the inverse matrix A^{-1} is calculated and multiplied by the matrix F or by multiplying the matrixes $A \cdot W$ according to the equation 1 and obtaining the system of equations:

$$\begin{array}{l} a_{11}w_1 + a_{12}w_2 + \dots + a_{1k}w_k = f_1 \\ a_{21}w_1 + a_{22}w_2 + \dots + a_{2k}w_k = f_2 \\ \vdots \qquad\quad \vdots \qquad\qquad\quad \vdots \qquad\quad \vdots \\ a_{i1}w_1 + a_{i2}w_2 + \dots + a_{ik}w_k = f_i \end{array} \qquad (5).$$

After designing $f_1 = a_{1,k+1}$; $f_2 = a_{2,k+1}$; ... $f_i = a_{i,k+1}$ the system 5 is solved by means of a standard computer program. The solution of this system represents the desired matrix W - the corrected chromatogram.

The division interval of a chromatogram was so chosen that the determinant value of the matrix A was no less than $4\cdot10^{-9}$ as the inversion of such "singular" matrixes as well as the solution of the systems of equations based on them is impossible . Thus the interval value for the caculations was 1 and 2 ml for "Sephadex LH-20" and 3 ml for "Sephadex LH-60". In order to decrease the division interval to 1 ml the first point was transferred by 1 ml and the calculations were carried out twice or three times respectively. The results were arranged to corresponding points at 1 ml intervals. The values h_k were determined by method mentioned (4) and were assumed equal throughout the interval of elution volume as their changes were negligible.

In order to demonstrate the possibilities of the method used the experimental and corrected (h_k=0.352) elution curves of the typical product of anionic polymerization of EPC under the action of KOH having the number-average MW (M_n) 1030 and weight-average MW (M_w) 1100 are shown in Figure 1. It is evident the method permits to separate the lower PEPC oligomer homologues to the polymerization degree of n=4. For this experiment the "Sephadex LH-20" gel column was used. The MW range of oligomers separated by this column was 150-2000.

For the investigation of EPC oligomers having a higher MW, for example, the polymerization products of EPC under the action of the alluminium isopropoxide - zinc chloride catalytic system the "Sephadex LH-60" gel was used. The corresponding elution curves of the PEPC sample (M_w=4270, M_n=3020) are shown in Figure 2 (h_k= 0.091). It is obvious that this product differs in the considerably higher polydispersity than PEPC obtained by using KOH. The process itself is more complicated by

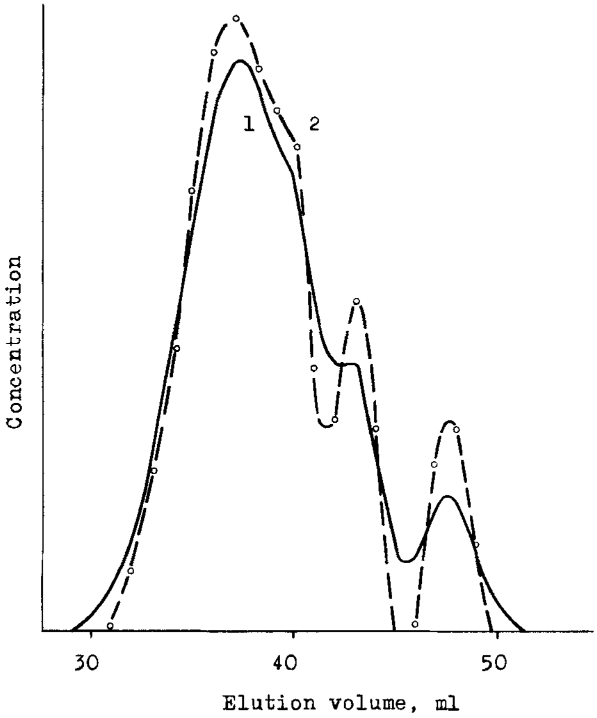

Figure 1

Experimental (1) and corrected (2) elution curves of the EPC anionic polymerization product.

instrument spreading as the low h_k value indicates. It should be noted that low h_k value results the considerable oscilation in the corrected chromatogram what is characteristic for most other methods of the instrument spreading correction (6). The PEPC MW range that is separated by this column was 200-15000. The data (see Figures 1 and 2) show that the application of both GPC variants allows to obtain the information about MW and MWD of PEPC in the range of MW 150-15000.

GPC was used not only for the analysis of the EPC polymerization products, but for the investigation of

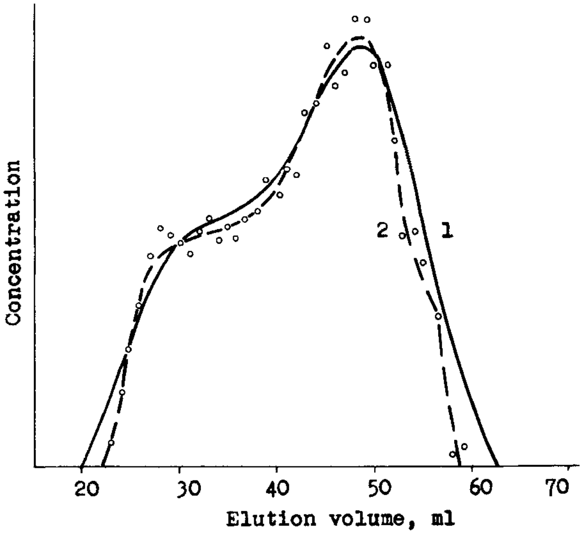

Figure 2

Experimental (1) and corrected (2) elution curves of the EPC polymerization product under the action of catalytic system aluminium isopropoxide - zinc chloride.

this process mechanism by observation on the changes of the MWD at the different monomer conversion as well. For this purpose the "differential chromatogram" principle (7) was used giving possibility to estimate the MWD of the product formed in the definite interval of time as well as the substances from which this product was formed. The investigation of this type was demonstrated by an example of the EPC polymerization in the dioxane solution under the action of sodium phenoxide in the presence of dibenzo-18-crown-6 (8). The differential MWD curves of the product formed at the different stages of monomer conversion are shown in Figure 3 a, b ("Sephadex LH-20" GPC, h_K=0.488). Each Figure has two MWD curves corresponding to different

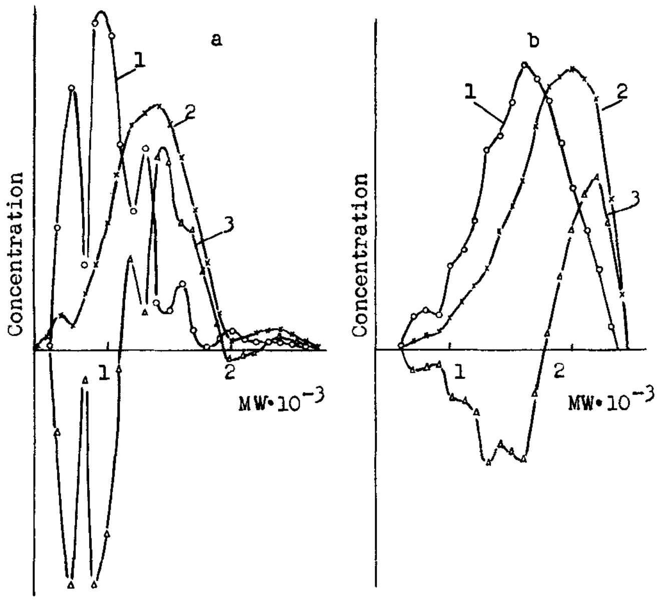

Figure 3

MWD curves of EPC polymerization products at different degrees of monomer conversion: a - 3.2% (1), 8.8% (2), MWD difference curve (3); b - 15.8% (1), 32.0% (2), MWD difference curve (3).

degrees of a monomer conversion as well as a "MWD difference curve" obtained on their basis. The monomer conversion vas 3.2 and 8.8% (Figure 3 a), and 15.8 and 32.0% (Figure 3 b). A part of the MWD difference curve below the base line corresponds to fractions of the EPC oligomer having reacted in the given time interval whereas the upper part of this curve corresponds to the reaction products. Thus it is evident that in the initial polymerization period (the change of the EPC conversion from 3.2 to 8.8%) the lower PEPC homologues (MW 700 and 900) add a monomer to form products having MW 1200, 1400, 1500 and higher. At more considerable polymerization degree (see Figure 3 b) the decrease of the content of low-molecular fractions with MW 600-1800 and the formation of much higher MW products is obvious too. Thus the investigation proved the stepping chain growth mechanism in the process.

Hence, the application of GPC by using the instrument spreading correction for the data treatment in the investigation of the synthesis and properties of EPC oligomers allows to estimate the MW and MWD of the products obtained as well as to get the definite information about the mechanism of the process.

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