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DETERMINATION OF THE MOLECULAR-WEIGHT DISTRIBUTION OF POLYMERS BY PAPER CHROMATOGRAPHY

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SUMMARY

A method has been developed for the determination of the polydispersity of oligomers and polymers by means of paper chromatography. This method is based on the relationship between the distribution of polymer components along the solvent front on the paper and the molecular weight of these components. The application of the method has been demonstrated for phenol–formaldehyde novolak resins (PFNR) in acetone–light petroleum (5:4) as solvent. The criteria for selecting solvent systems for the development of chromatograms, the conditions and procedures of running PFNR chromatograms and processing them, and calibration methods are described. The relationship between the number of a strip on the chromatogram and the average molecular weight of the polymer components located on it has been established.

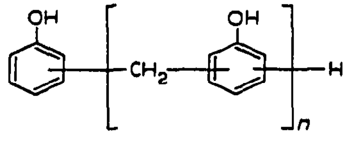
The use of paper chromatography for the determination of the molecular-weight distribution is simple, relatively rapid (2 days for PFNR) and requires only a very small amount of polymer (0.03 g for PFNR).

Low-molecular-weight volatile impurities do not interfere in the analysis as they are evaporated during the development of the chromatogram. The method is convenient for the analysis of low-molecular-weight products formed in the initial stages of polycondensation as well as for the investigation of the change in molecular-weight distribution during the synthesizing and subsequent processing of polymers.

INTRODUCTION

There is some reference in the literature[1,2] to the possibility of applying paper chromatography to the determination of the fractional composition of polymers, but so far this method has not found any extensive applications. However, for a number of polymers, and especially for oligomers, paper chromatography may be a convenient method of evaluating the polydispersity. The physical principle of this method is simple. In the process of chromatography, multiple re-distribution of the components of the mixture being analyzed occurs between the mobile and stationary phases[3]. The stationary phase is usually formed by the cellulose of the chromatographic paper and the water present in its pores. Organic solvents are usually used as the mobile phase. As the solubility of a polymer in organic solvents decreases as the molecular weight increases, the fraction of the lowest molecular weight travels the furthest distance on the chromatogram*. The distribution of the polymer on the paper along the solvent front may therefore reflect the molecular-weight distribution (MWD) of the product being investigated.

This paper describes the application of paper chromatography to the determination of the MWD of phenol–formaldehyde novolak polymers (PFNP):



The appropriate solvent system to be used in this method is selected on the following basis. The solubility of the polymer should depend substantially on its molecular weight only, and not on other factors such as, in the case of PFNP, the isomeric composition, which is determined by the ratio of *o,o'*-, *o,p'*- and *p,p'*-methylene bonds in the polymer molecule[4]. Taking this into consideration, the solvent was selected using the following two criteria: first, in the developed chromatograms of PFNP fractions, the fractions of higher molecular weight should be located closest to the starting line; and secondly, a mixture of *o,o'*-, *o,p'*- and *p,p'*-dihydroxydiphenylmethanes, which could be considered as a model PFNP of equal molecular weights and different isomeric composition, should not separate into components. The solvent system (acetone–light petroleum, b.p. 80–120°) met these requirements.

The quantitative determination of the polymer on the chromatogram can be carried out by elution of the substance from the paper and determination of the optical density of the eluate. Because in the case of PFNP it is difficult to elute all of the coloured products from the chromatogram, elution was performed from colourless chromatograms. This technique permitted conditions to be selected that enabled the polymer to be virtually completely eluted. Preliminary experiments involving colouring matter indicated that the polymer was located on the chromatogram at the greatest distance from the starting point.

In the UV spectrum of PFNP there is an absorption band at 270–280 nm attributed to the presence of aromatic rings in the polymer molecule. The proportion of the non-aromatic portion (methylene cross-links) in PFNP is not great and does not depend on the molecular weight of the polymer. Therefore, the optical density of PFNP solutions can be assumed to be proportional to the concentration of these solutions (this assumption has been confirmed by other workers[5,6]). This suggests that, after separation of PFNP by paper chromatography into n fractions, the proportion by weight of fraction i (w_i) can be calculated by the following equation:

$$w_i = \frac{D_i}{\sum\limits_{i=1}^{i=n} D_i}, \text{ where } D_i \text{ is optical density of eluate } i. \qquad (1)$$

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[*] The transport of solutes according to their molecular weights may be due not only to solubility but also partially to the molecular sieving effect of the porous stationary phase and to the adsorption effects, which act in opposition to each other and at least partially cancel out.

EXPERIMENTAL AND RESULTS

Commercial samples of PFNP and its fractions were used, the latter being obtained by the method of Yershov and Mosina[7]. The molecular weights of PFNP and its fractions were determined by ebullioscopy[8]. The correction for the free phenol content of PFNP was calculated using the conventional equation[9].

The solvents used were acetone (chemically pure), light petroleum (b.p. 80–120°) and dioxane for UV spectrophotometry, and were purified by distillation; in the case of light petroleum, a narrow cut boiling in the range of 88–96° was recovered.

The chromatograms were developed by the ascending technique on a sheet of paper (40 × 22 cm) of grade M using an acetone–light petroleum (5:4) mixture. By means of a microsyringe, $7\cdot10^{-3}$ ml of a solution of the polymer in ethanol (concentration 0.03 g/ml) was applied to each of three points on the starting line with a distance of 4 cm between the points. The distance between the starting line and the front was 22 cm, and the time for the development of the chromatogram was 4–6 h.

On the dried chromatogram, a straight line was drawn parallel to the front line at a distance of 23 cm from it. The isolated section was divided into 16 equal strips, each of which was pulverized and put into a weighing bottle, followed by 5 ml of dioxane. After 20 h, the eluates were filtered through an N1 glass filter and the optical densities were determined at a wavelength of 279 nm. The measurements were performed on a SPh-4 spectrophotometer in quartz cuvettes (light path, 10 mm). The proportion of polymer by weight in each eluate was calculated by using eqn. 1. On the basis of the results obtained, integral and differential distribution curves of the samples investigated according to the number of the strips were plotted. Such curves can be used directly for the qualitative characterization of the polymer polydispersity.

The MWD of one of the PFNP samples was determined on a Waters Ass. (Framingham, Mass., U.S.A.) gel chromatograph using columns of pore sizes $2\cdot10^4$, $2\cdot10^3$–$3\cdot10^3$, 10^3 and 2–500 Å and Styragel as the support at a temperature of 22°; 0.25% tetrahydrofuran was used as the solvent at an elution rate of 1.0 ml/min. The calibration of the gel chromatogram was performed using the linear relationship between the logarithm of the molecular weight and the yield volume[10]. Using the method suggested earlier[11], the calibration was carried out by comparing the integral distribution curve according to the number of the strip with the integral MWD curve, plotted on the basis of gel chromatographic data. The calibration results are presented in Table I.

The data in Table I were used to plot MWD curves of the samples under investigation. Fig. 1 shows integral curves for two PFNP samples as an example.

In order to check the method, the number-average molecular weights ($\bar{M}_n$), of PFNP and its fractions, calculated on the basis of the paper chromatographic results, were compared with those determined by ebullioscopy. The results obtained (Table II) indicate that the discrepancy between the $\bar{M}_n$ values determined by this method ($\Delta\bar{M}_n$) is not greater than 10%. The calculated $\bar{M}_w/\bar{M}_n$ ratios for various PFNP samples are in the range 2.0–2.4, which is in good agreement with results published elsewhere[12,13].

The proposed method of determining the MWD has the following advantages:

(1) The use of complex and expensive equipment is not necessary.

(2) Only a small amount of polymer is required for the analysis. In the case of PFNP, 0.03 g is sufficient.

(3) Low-molecular-weight volatile impurities do not interfere in the determina-

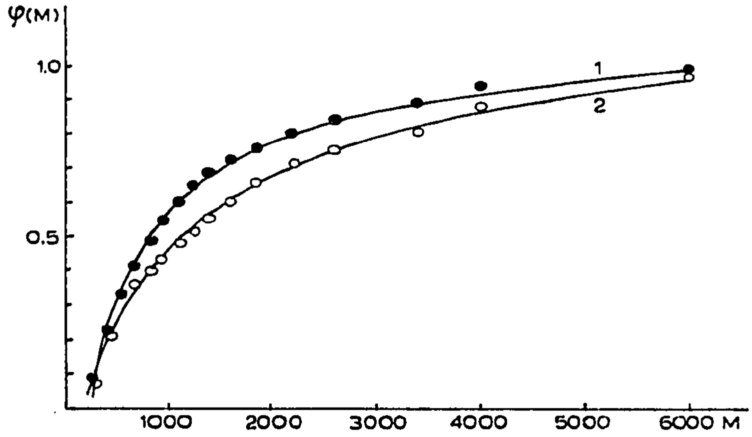

Fig. 1. Integral MWD curves obtained by paper chromatography: 1, PFNP No. 4; 2, PFNP No. 2.

TABLE I

CALIBRATION DATA FOR CONVERSION OF THE DISTRIBUTION ACCORDING TO STRIP NUMBER INTO MWD

Strip No.	*Mol. wt.*	*Strip No.*	*Mol. wt.*
1	6000	9	1250
2	4000	10	1100
3	3200	11	940
4	2600	12	830
5	2100	13	670
6	1850	14	550
7	1600	15	430
8	1400	16	280

TABLE II

MOLECULAR WEIGHTS DETERMINED BY PAPER CHROMATOGRAPHY AND EBULLIOSCOPY

Sample	*Paper chromatography*			*Ebullioscopy*	
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\Delta \bar{M}_n$ (%)
PFNP No. 1	770	1850	2.40	730	5.5
PFNP No. 2	720	1700	2.36	680	5.9
PFNP No. 3	790	1610	2.03	740	6.8
PFNP No. 4	660	1320	2.00	660	1.5
Fraction No. 1	1340	2710	2.02	1450	7.6
Fraction No. 2	1070	1900	1.77	1150	7.0
Fraction No. 3	920	1460	1.59	950	3.2
Fraction No. 4	820	1320	1.61	830	1.2
Fraction No. 5	790	1050	1.33	720	9.7
Fraction No. 6	630	820	1.30	580	8.6

tion (in the case of PFNP, water, formaldehyde and phenol) owing to evaporation during the development of the chromatograms.

(4) The method can be applied to the analysis of low-molecular-weight products (reaction mixtures in the initial stages of polycondensation; oligomers) as well as for the investigation of the change in MWD during polycondensation.

CONCLUSIONS

A simple and rapid paper chromatographic method has been developed for the determination of the MWD of polymers. The application of this method has been demonstrated for phenol–formaldehyde novolak resins.

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