

ELUTION COLUMN FRACTIONATION OF POLYEPICHLOROHYDRIN

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Received December 22nd, 1974

Elution column chromatography of polyepichlorohydrin was carried out in the system benzene-methanol. The dependence $[\eta]-M_w$ for solutions of the obtained fractions in tetrahydrofuran was determined.

Despite the fact that polyepichlorohydrin belongs at the present time to polymers of which much is expected, little is known about its properties in solutions. Also, there has been no description published so far concerning its fractionation. Rather scarce and not very clear data on the solution properties of polyepichlorohydrin come from patent literature¹. Besides that this problem has been treated only in the paper of Jasenkova and coworkers².

The aim of this study is to verify and complement these data by describing the fractionation of polyepichlorohydrin with the use of the column elution method, by studying the solution properties of non-fractionated samples in α -chloronaphthalene and tetrahydrofuran, and by investigating the solution properties of fractions of a polydispersed sample in tetrahydrofuran.

EXPERIMENTAL

Compounds Used

Samples of the polymer were prepared by solution polymerization of epichlorohydrin in toluene using the catalytic system triisobutylaluminium-water-diethylether at 20°C (ref.³). The solvents used were purified by conventional laboratory methods.

Polymer Fractionation

The fractionation of polyepichlorohydrin was carried out using the column elution method⁴ at 25°C in the system benzene-methanol; the same system was used by the authors of ref.², too. The apparatus which enables the fractionation of polymers both by the column elution method and by the precipitation chromatography was described earlier⁵. 1.5 g of the polymer was deposited on the column packing (glass beads of grain diameter 0.15 mm) so that to a benzene solution of the polymer first propanol was added up to the high-molecular fraction precipitation threshold; then glass beads were stirred into the solution, and thereafter the mixture ben-

zene-propanol was slowly evaporated at the room temperature. In this way the tackiness of the polymer film was lowered⁶ and a partly selective deposition was achieved⁷. The glass beads with the deposited polymer were transferred into a column filled with methanol having the temperature 35°C. When the fractionation was started, the column temperature was lowered to 25°C. In this way the evolution of air bubbles in the column during the early stages of the elution process was substantially suppressed. The temperature was kept at 25°C during the entire fractionation procedure.

The polymer concentration in the eluate was determined by the evaporation residue method (evaporation of aliquot parts and drying *in vacuo* at 120°C for 3 hours). On the basis of the weight balance thus obtained the volumes of the subsequent siphons were joined together to form nine fractions. The polymer contained in them was isolated by evaporating the elution mixture in vacuum rotatory evaporator. Then it was transferred into a tetrahydrofuran solution. The polymer yield during the first (orientation) fractionation was 104%, during the second one it was 101%. In the subsequent processing of the results, however, the experimentally found value was taken as 100%.

The experience learned during the orientation fractionation helped in choosing a more suitable elution gradient for the second fractionation. Also, the necessity of a continuous addition of a stabilizer during the elution procedure was revealed. In the first experiment, the stabilizer (2,2'-methylene bis(2-methyl-4-*t*-butyl)phenol) was added only to the polymer solution during the polymer deposition on the support (1% with respect to the polymer amount). However, the fractions obtained changed with time (see further on). Therefore, in the second fractionation the stabilizer was introduced also into the elution mixture in the amount 15 mg/l of the mixture. The elution program of the second fractionation is shown in Fig. 1. The flow rate in both fractionations was 1 ml/min.

The integral molecular weight distribution curve was constructed using the procedure suggested by Schulz⁸. As shown by Kamide and coworkers⁹, this procedure is sufficiently accurate for the polymers with a wide distribution of molecular weights.

Molecular Weight Determination

Light scattering measurements were carried out on a Photo-gonio-difuse-mètre Sofica in non-polarized light of the wave-length 546.1 nm at $(25 \pm 0.5)^\circ\text{C}$. The increment of the refractive index (dn/dc) was determined by interferometry at 25°C (ref.³); the value for α -chloronaphthalene

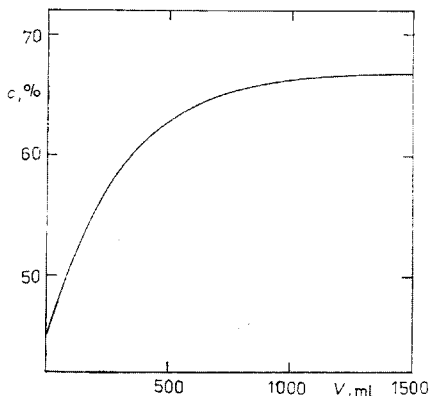


FIG. 1
Elution Program of Polyepichlorohydrin
Fractionation
 V elution volume, c benzene concentration in elution mixture (vol.%).

was -0.090 , that one for tetrahydrofuran was $+0.084$. Zimm's method was used for evaluating the light scattering measurement.

The viscosity of the polyepichlorohydrin solutions was measured in both solvents mentioned above (concentration region from $2 \cdot 10^{-3}$ g/ml to $3 \cdot 10^{-4}$ g/ml) at $(25 \pm 0.05)^\circ\text{C}$ using an automatic viscometer with an electronic registration of times of flow¹⁰. The kinetic energy correction was carried out in the usual manner. The intrinsic viscosity was determined by extrapolation from four points using the Huggins equation. Both the light scattering and the viscosity measurements were carried out in the presence of the antioxidant. Because the antioxidant was a colourless substance in an negligible concentration, no corrections were introduced.

RESULTS AND DISCUSSION

The results obtained with the fractions of polyepichlorohydrin from the fractionation without the antioxidant in the elution mixture³ show that in this case a certain change in the polymer structure occurred during the fractionation process. This follows, *e.g.*, from the comparison of the molecular weight of the non-fractionated sample ($\bar{M}_w = 7.94 \cdot 10^5$), with the average molecular weight both from the fractions of the first, orientation fractionation ($\bar{M}_{w1} = 1.2 \cdot 10^6$), and from the fractions of the second fractionation ($\bar{M}_{w2} = 8.03 \cdot 10^5$). While the agreement between \bar{M}_{w2} and \bar{M}_w may be regarded as satisfactory, the considerably higher value of \bar{M}_{w1} indicates that a partial crosslinking of chains took place, when the fractionation was carried out without a continuous addition of the antioxidant. An increase of the values of light scattering with time and lower viscosity values of the solutions of fractions from the orientation fractionation support this conclusion. The integral distribution curve from the second fractionation is shown in Fig. 2.

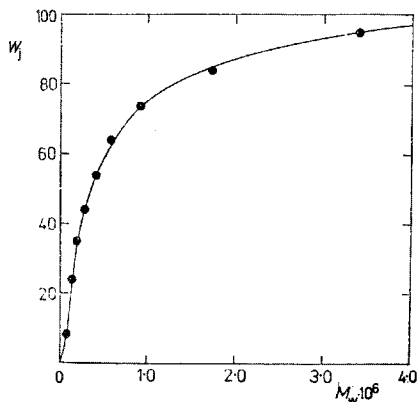


FIG. 2

Integral Distribution Curve of the Second Fractionation of Polyepichlorohydrin
 W_j cummulative weight⁸.

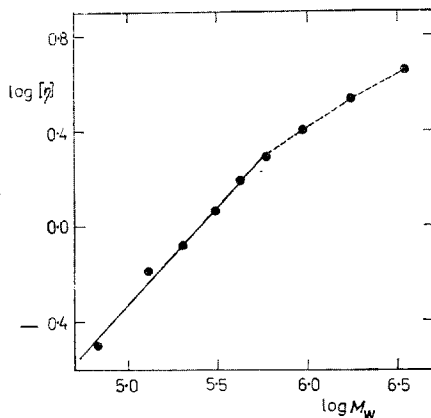


FIG. 3

Dependence $[\eta]-M_w$ for Polyepichlorohydrin Fractions (tetrahydrofuran, 25°C).
 Intrinsic viscosity $[\eta]$ in dl/g.

Fig. 3 shows the dependence $\log [\eta] - \log M_w$ for the polyepichlorohydrin fractions in tetrahydrofuran at 25°C. The first six points were used to determine (by the least square method) the constants of the dependence mentioned above: $a = 0.82 \pm 0.04$; $K = (3.78 \pm 0.18) \cdot 10^{-5}$ dl/g. It can be seen from this dependence and even better from the dependence $[\eta]/M^{1/2} - M^{1/2}$ (ref.¹¹) that in both cases from the seventh fraction up curving takes place. This is due to increased contributions of branched structures. The value of the constant a from our study is lower than that one from ref.². However, it has to be kept in mind that the authors of ref.² worked roughly in the lower half of the molecular weight region measured by us.

Because of the possibility of estimating the molecular weight from viscosity measurements, the values of the constants in the relation $[\eta] - M_w$ were measured for a series of solutions of non-fractionated samples of various mean molecular weights (molecular weight region $1 \cdot 10^6 - 4 \cdot 10^6$). The measurements were carried out in α -chloronaphthalene and tetrahydrofuran at 25°C. The following values were found: in α -chloronaphthalene $a = 0.71$, $K = 8.23 \cdot 10^{-5}$ dl/g; in tetrahydrofuran $a = 0.80$, $K = 3.35 \cdot 10^{-5}$ dl/g.

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Translated by Z. Herman.