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Original Scientific Paper

Fractionation of Polystyrene by Column Elution Method

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Polystyrene of commercial type from the firm Organsko Kemijska Industrija (OKI), Zagreb, has been fractionated by the column elution method with cyclohexane as a single solvent and with successive increase of temperature. Glass wool was applied as support in the column. In the experiments the following factors were varied: the height of support in the column, the rate of elution and the polymer concentration. The effects on the efficiency of fractionation were observed. On the basis of fractionation results graphs were constructed by plotting the reciprocals of the critical elution temperatures $1/T_c$, observed for the polymer fractions vs. $x^{-1/2}$, where x is the number of segments per polymer chain. The thermodynamic parameters were calculated from these plots using the slopes and intercepts. The critical elution temperature depends on molecular weight linearly in the manner predicted by theory.

INTRODUCTION

The first theoretical and experimental work concerning the fractionation of polymers by the column elution method was done by Desreux and his coworkers.¹⁻³ These authors, in introducing this method, described a procedure in which the polymer precipitated, on an inert support in a column, is fractionated by elution in a relatively short time. In their experiments either the composition of the solvent-nonsolvent mixture used for elution was varied while the temperature was held constant, or the solvent composition was fixed while the temperature of the column was increased. This method has been used successfully with all types of polymers.⁴ Krigbaum and Kurz⁵ investigated the efficiency of the molecular weight separation of fraction mixtures of atactic polystyrene dissolved in cyclohexane by elution from a column at different temperatures. Ruskin and Paravano⁶ fractionated polystyrene in cyclohexane by the method of zone melting under various operating conditions.

We also fractionated polystyrene by the column elution method at increasing temperatures and with cyclohexane as a solvent. We made several column fractionation experiments and changed the following factors from one experiment to another: the height of support in the column, the flow rate and the concentration of polymer solution. The molecular weight distribution curves were constructed and compared. The thermodynamic parameters were calculated for each fractionation experiment. It was shown that the values obtained were in good agreement. Since the early results of Krigbaum and

Kurz⁵ appear to be afflicted with a rather appreciable experimental error (the scattering of data around the linear regression line, which represents the dependence of the critical miscibility temperature on molecular weight is considerable), it seemed to be of interest to undertake new experiments with the same technique of fractionation.

EXPERIMENTAL

The sample of polystyrene fractionated in this work was OKIROL of commercial production obtained from the firm OKI, Zagreb.

The average molecular weight of each fraction was characterized by determining the limiting viscosity numbers of fractions by the extrapolation of reduced viscosities to zero concentration from data measured at $(34.50 \pm 0.05)^\circ$ for four or more concentrations of polymer in cyclohexane, starting with 0.8% solution. The viscosity was measured by a Ubbelohde dilution capillary viscometer, which had a flow rate for pure solvent of more than 170 seconds. The second virial coefficient was small but had a definite value, so extrapolations had to be made in any case. The slope of straight lines was generally increased with increased molecular weights.

The fractionation device consisted of a thermostated column with temperature controlled to $(\pm 0.1)^\circ$ C. The column, which was 125 cm. long and had an internal diameter of 2.6 cm., was filled with glass wool. In most experiments the height of the glass wool packing was 110 cm. A 3% solution of polystyrene in cyclohexane was prepared for fractionation. The column was filled with 400 ml. of polystyrene solution (12 g. of polystyrene in total) heated to a column temperature of 37° C. Simultaneously the cyclohexane flew out. In one experiment the height of glass wool support was shortened to 37 cm. and consequently the concentration of polystyrene solution had to be increased to 10%.

One single solvent, cyclohexane, was used for the elution. The polymer was completely precipitated by cooling the column, and addition of solvent started from a reservoir fitted to the top of the column. A calcium chloride drying tube attached to this reservoir prevented moisture to be taken up from the air. The elution of the fractions at a definite temperature was continued until no turbidity with a nonsolvent (*i. e.* methanol) was obtained. After raising the temperature, the procedure was repeated. The fractions were eluted at temperature interval from $+ 5$ to 35° C and the number of fractions was from 10 to 13. The yield of fractionation was 97–99%. The polymer eluted from the column was precipitated by pouring the solution under stirring into a beaker filled with methanol. The fractions were filtered and dried at 60° C in a vacuum oven.

During the fractionation experiments the following factors were varied: the flow rate of eluent, the height of carrier in the column and the polymer concentration. In Table I the results from these five fractionation experiments are shown.

TABLE I
Fractionation of Polystyrene

Fractionation No.	Concn. of polym. sol. (% by volume)	Flow rate (ml/hr)	No. of fractions	Height of carrier (cm.)	Range of elution temp. ($^\circ$ C)
1	3	100	13	110	5–35
2	3	200	13	110	5–35
3	3	400	13	110	5–35
4	3	50	10	110	5–35
5	10	100	10	37	5–35

RESULTS

Molecular weights of fractions were obtained from limiting viscosity numbers by use of the equation for polystyrene fractions in cyclohexane at 34.5° C (Θ -temp.) given by Altares *et al.*⁷

$$[\eta] = 8.4 \cdot 10^{-4} M^{0.5}$$

The molecular weight distribution curves were then developed. The integral distribution curve was obtained by the method of Schulz and Dinglinger.⁸ Subsequent differentiation of the integral distribution curve gives the differential molecular weight distribution. The distributions thus obtained are given in Figs. 1 and 2.

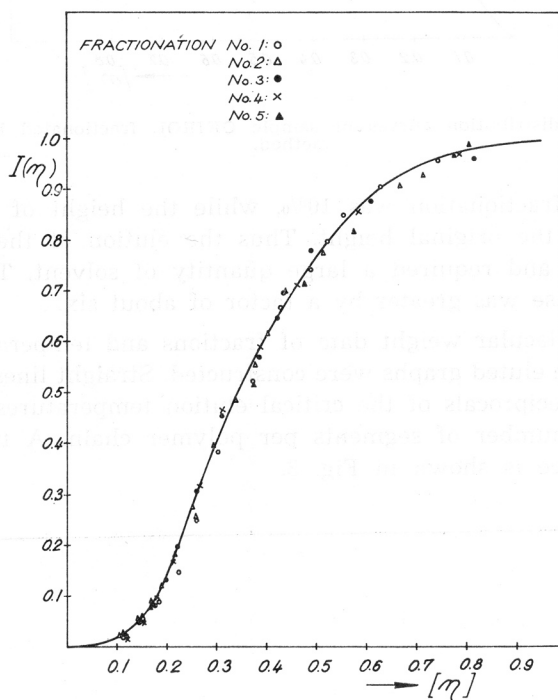


Fig. 1. Integral distribution curves of sample OKIROL fractionated by column elution method.

From these graphs it is evident that fractionations, made in all these five experiments, produced curves identical in shape. That is a proof that the efficiency in all fractionation experiments was similar, though some factors in these experiments were varied. The change of flow rate of eluent from 100 ml./hr to 200 ml./hr did not show discrepancies (fractionation No. 1 and 2 in Fig. 1). The results of fractionation No. 3 with a flow rate from 400 ml./hr deviate a little but not so much that it interferes with the general shape of distribution curves. The fractionation No. 4 with a flow rate of solvent of about 50 ml./hr gave the sharpest fractions, *i.e.* the best separation. In the fractionation No. 5 the flow rate was 100 ml./hr, the concentration of polymer

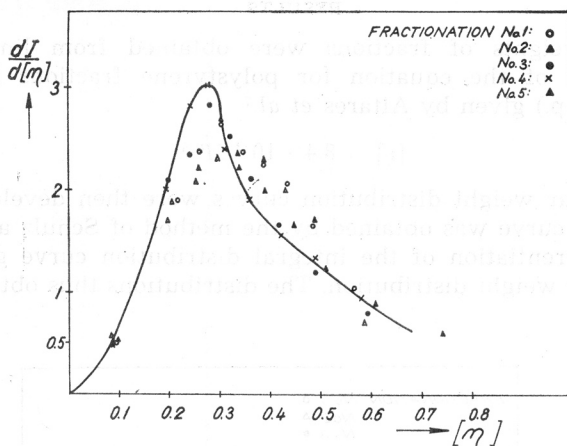


Fig. 2. Differential distribution curves of sample OKIROL fractionated by column elution method.

solution in this fractionation was 10%, while the height of the glass wool was only 1/3 of the original height. Thus the elution of the fractions was excessively long, and required a large quantity of solvent. The quantity of solvent in this case was greater by a factor of about six.

From the molecular weight data of fractions and temperatures at which the fractions were eluted graphs were constructed. Straight lines were obtained by plotting the reciprocals of the critical elution temperatures, $1/T_c$ vs. $x^{-1/2}$, where x is the number of segments per polymer chain. A typical example of this dependence is shown in Fig. 3.

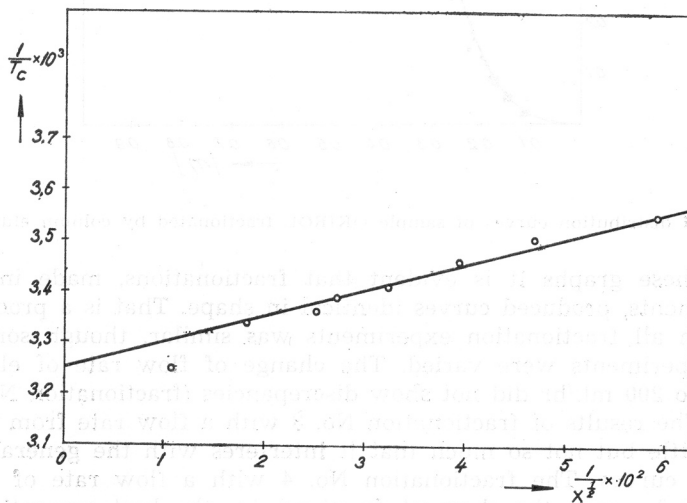


Fig. 3. Molecular weight dependence of the critical elution temperatures for various polystyrene fractions in cyclohexane (Fractionation No. 4).

On the basis of these graphs for the polystyrene-cyclohexane system, which was already described earlier by Shultz and Flory⁹, we calculated thermodynamic parameters (entropy parameter ψ_1 , enthalpy parameter χ_1 , critical miscibility temperature for infinite molecular weight polymer Θ ; interaction parameter χ_1). We calculated entropy parameter ψ_1 and Θ -temperature from the slopes and intercepts on the ordinate according to Shultz and Flory⁹, and the other parameters from expressions given below. The value of the critical miscibility temperature obtained by our measurements agrees with the one obtained by Shultz and Flory⁹ by measuring precipitation temperatures, while their values of the entropy parameter ψ_1 obtained from measurements of precipitation temperatures⁹, osmotic pressure¹⁰ and intrinsic viscosity¹⁰ are not in agreement with the results in this work. Substitution of ψ_1 and Θ values into eq. (1), which has the form

$$\chi_1 = \frac{1}{2} - \psi_1 + \psi_1 \frac{\Theta}{T} \quad (1)$$

gives the relation between the theoretical parameter χ_1 and the absolute temperature for each system.

The heat of dilution parameter (enthalpy parameter χ_1) was calculated by using the equation:

$$\chi_1 = \frac{\Theta \psi_1}{T} \quad (2)$$

The values of these thermodynamic parameters for all five fractionation experiments are given in Table II.

TABLE II

The Values of the Thermodynamic Parameters for Polystyrene in Cyclohexane

Fractionation No.	Θ (°K)	ψ_1	χ_1	χ_1	Range of measured mol. wts.
1	307.2	0.612	0.576	0.688	15,620—792,900
2	307.2	0.650	0.580	0.730	18,240—734,700
3	307.2	0.623	0.584	0.708	19,400—952,900
4	307.2	0.661	0.581	0.766	19,070—884,500
5	306.8	0.528	0.565	0.593	18,740—929,800

DISCUSSION

Based on the fractionation experiments accomplished under variable conditions (Table I) the molecular weight distribution curves were given in Figs. 1 and 2. It is evident that there are no considerable discrepancies between them. It can be seen that fractionation No. 4 was most successful with polymer concentration of 3%, height of carrier 110 cm., and flow rate of eluent 50 ml./hr. In fractionation experiment No. 5 the polymer concentration used was 10%, and the height of support in the column was reduced to 37 cm. That resulted in so long elution times, that such fractionation is of no practical

value. As the results obtained do not differ from others, we can conclude that it is possible to fractionate successfully even very concentrated polymer solutions (10%) with a much smaller surface and a shorter column, if one uses very large quantities of solvents and very long times of elution. The molecular weights of all fractions were determined according to the relation mentioned earlier. The critical temperature T_c for complete miscibility in a solvent depends on molecular weight of the polymer according to relation (3)¹¹:

$$\Theta/T_c = (1 + x^{1/2})^2/x \quad (3)$$

The parameter Θ was obtained in the way mentioned earlier⁹, and its values for polystyrene-cyclohexane system attained in this work, are represented in Table II. The temperature at which the elution of each single fraction was carried out was maintained constant within the range of (± 0.05)°C. The expected linear dependence between the reciprocal of the critical temperature $1/T_c$ (in °K) for incipient miscibility and the reciprocal of the square root of the molecular weight $x^{-1/2}$ was confirmed according to eq. (4):

$$\frac{1}{T_c} = \frac{1}{\Theta} \left[1 + \frac{1}{\psi_1} \left(\frac{1}{x^{1/2}} + \frac{1}{2x} \right) \right] \quad (4)$$

in which the second term in round brackets vanishes as x becomes large. This is represented by a typical example in Fig. 3. The values obtained from that graph show that the value for Θ -temperature for polystyrene-cyclohexane system is in agreement with that given by Shultz and Flory⁹ ($1/T_c = 3.25 \cdot 10^{-3}$), while the value for the entropy parameter ψ_1 deviates appreciably. The value of ψ_1 for the polystyrene-cyclohexane system in the papers of Shultz and Flory was 1.056. The values obtained in our work are about a half of this value (Table II). The value of $1/T_c$ according to our calculation by the method of least squares was $3.24 \cdot 10^{-3}$ and by the graphical method $1/T_c$ was $3.25 \cdot 10^{-3}$. All are in good agreement with the results cited earlier⁹.

On the basis of this work it is evident that the thermodynamic parameters can be calculated from the results obtained by fractionation experiments. Furthermore, it appears that the values for entropy parameters obtained in such a way are in agreement with the lattice theory of polymer solution, according to which ψ_1 should be approximately 1/2 and nearly independent of the system^{12,13}. However, this is not a final proof of the lattice theory, since it can be assumed that values of ψ_1 may depend on the nature of the system, on the concentration and on temperature.

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IZVOD

Frakcioniranje polistirena metodom ispiranja na stupcu

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Polistiren komercijalnog tipa proizveden u tvornici Organska kemijska industrija (OKI), Zagreb, frakcioniran je metodom ispiranja na stupcu cikloheksanom kao otapalom i uzastopnim povišenjem temperature. Staklena vuna bila je nosač u stupcu, a varirani su ovi faktori: visina nosača u stupcu, brzina ispiranja i koncentracija polimera. Promatran je utjecaj tih faktora na efikasnost frakcioniranja. Na osnovi rezultata frakcioniranja konstruirani su grafovi u kojima su nanese recipročne vrijednosti kritičnih temperatura ispiranja, $1/T_c$, za pojedine frakcije prema $x^{-1/2}$ gdje je x broj segmenata na polimernom lancu. Iz tih grafova izračunani su termodinamički parametri za polistiren otopljen u cikloheksanu. Kritična temperatura ispiranja linearna je funkcija molekularne težine kako to predviđa teorija.

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