SOLUTION PROPERTIES OF POLY(1-CHLORO-2,3-EPOXYPROPANE)

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From viscosimetric measurements of solutions of poly(1-chloro-2,3-epoxypropane) fractions in benzene the non-perturbed dimensions and the steric hindrance parameter of the polymer were determined. From experimental data on the polymer solubility (in 39 solvents) and from measurements of the intrinsic viscosity (in 19 solvents) the parameters δ_d and δ_a of the Hansen model were determined and compared with the parameters calculated with the use of the Blanks–Prausnitz theory.

Very little is known about the solution properties of poly(1-chloro-2,3-epoxypropane). Only the paper of Jasenkova and coworkers[1] concerns this subject; it deals with solutions of the polymer in tetrahydrofuran. This communication stems from the study of column elution fractionation of poly(1-chloro-2,3-epoxypropane)[2] and its aim is to widen the present knowledge by specifying more precisely the parameters which characterize the flexibility of the polymer chain in solutions and by studying the interaction of the polymer with various solvents.

EXPERIMENTAL

Poly(1-chloro-2,3,-epoxypropane) was prepared by the bulk polymerization at the laboratory temperature using the catalytic system diethylaluminium fluoride–water (molar ratio 1 : 0·25). Its molecular weight was 87 000.

Its fractionation was carried out by the column elution method described in ref.[2]. The separated fractions were characterized by the light-scattering method (in tetrahydrofuran) and by the viscosimetric method (in benzene at 25°C).

In the studies of the solubility of the polymer in various solvents about 0·1 g of the polymer was subjected to dissolving for 24 hours in 10 ml of the solvent at 25°C (in the case of cyclohexanole at 35°C). The viscosimetric measurements of the polymer solutions in various solvents were carried out with a non-fractionated sample at 25°C in the concentration region 0·5—0·1 g/dl. The measurement in each solvent was repeated and the differences of the intrinsic viscosities were found to be smaller than 1%.

The experimental method, the conditions of the measurements — including the kind and the concentration of the antioxidant-, and the method of evaluating the results were the same as described in ref.[2].

RESULTS AND DISCUSSION

Non-Perturbed Dimensions of Poly(1-chloro-2,3-epoxypropane)

From the characteristics of the poly(1-chloro-2,3-epoxypropane) fractions

$M \cdot 10^{-3}$:	18	43	59	80	110	200
$[\eta]$, dl/g	0·111	0·178	0·237	0·292	0·358	0·512

the constants of the Mark–Houwink relation were determined, $[\eta] = KM^a$ (benzene, 25°C): $a = 0{\cdot}65 \pm 0{\cdot}02$, $K = (1{\cdot}88 \pm 0{\cdot}34) \cdot 10^{-4}$ dl/g. The non-perturbed dimensions of the polymer were obtained by the extrapolation to the zero excluded volume using the equation suggested by Stockmayer and Fixman[3] and modified by Yamakawa[4] which holds for the expansion coefficient values $\alpha_\eta^3 < 2{\cdot}6$,

$$[\eta]/M^{1/2} = 1{\cdot}05\Phi(\bar{r}_0^2/M)^{3/2} + CM^{1/2} . \qquad (1)$$

Here, $[\eta]$ is the intrinsic viscosity, M the molecular weight, $\bar{r}_0^2$ the mean quadratic distance of the chain ends in the nonperturbed state, C is a parameter independent of the molecular weight, and Φ the Flory constant (its value for the fractions was $2{\cdot}5 \cdot 10^{21}$ dl/cm^{3}mol (ref.[5])). From the dependence $[\eta]/M^{1/2}$–$M^{1/2}$ (Fig. 1) the parameter $(\bar{r}_0^2/M)^{1/2}$ was determined; its value was $(6{\cdot}4 \pm 0{\cdot}1) \cdot 10^{-9}$ cm.

Furthermore, the value of the steric hindrance parameter $[\sigma = (\bar{r}_0^2/\bar{r}_{of}^2)^{1/2}]$ was determined as 1·68. The mean quadratic distance of the model chain with the free rotation $\bar{r}_{of}^2$ was calculated for the straight chain with all the valence angles of the same value (109·5°) and all the bonds of equal length. The bond length in the chain

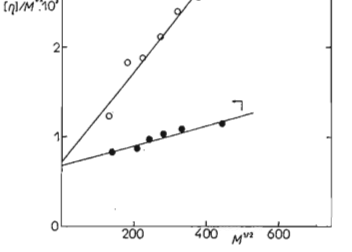

FIG. 1

Dependence $[\eta]/M^{1/2}$–$M^{1/2}$ for Poly(1-chloro-2,3-epoxypropane)

Solvents used (25°C): ● benzene, ○ tetrahydrofuran — data from ref.[2].

was taken as 0·15 nm (*i.e.*, the weighed average of the bond lengths $l_{C-O} = 0{\cdot}143$ nm and $l_{C-C} = 0{\cdot}153$ nm; see ref.[6]). In the calculation of $(\bar{r}^2_{of}/M)^{1/2}$ the relation[7] $(\bar{r}^2_{of}/M)^{1/2} = l(2n_0/M_0)^{1/2}$ was used; here, n_0 is the number of bonds through which the monomer unit contributes to the polymer chain (in our case $n_0 = 3$), and M_0 is the molecular weight of the monomer unit. These values characterizing the properties of the non-perturbed polymer molecule are in a good agreement with the values in ref.[1] obtained from the data measured in tetrahydrofuran.

Behaviour of the Polymer in Various Solvents

Entirely qualitative, though very important information from the practical point of view on the interaction of a polymer with various solvents can be obtained from solubility studies. It follows from these studies that the interaction of poly(1-chloro-2,3-epoxypropane) with solvents cannot be described by the Hildebrand solubility parameters δ_i ($i = 1$ for solvent, $i = 2$ for polymer)[8]. Thus, *e.g.*, acetophenone ($\delta_1 = 9{\cdot}68$) is a good solvent of the polymer, while octanol ($\delta_1 = 9{\cdot}66$) does not dissolve the polymer at all. Similarly, 1,1,1-trichloroethane ($\delta_1 = 8{\cdot}57$) does dissolve the polymer, while tetrachloromethane ($\delta_1 = 8{\cdot}65$) does not. In the first case, dissolving of the polymer can be hindered by the formation of hydrogen bridges between octanol molecules, in the second case, by the absence of polar interactions in tetrachloromethane. Far better results in characterizing the polymer solubility can be obtained by means of the parameters δ_d, δ_p, δ_h. These parameters, introduced by Hansen[9], concern non-polar interactions ($\delta_{d,i}$), polar interactions ($\delta_{p,i}$), and the energy of hydrogen bridge formation ($\delta_{h,i}$) of each of the system components. Fig. 2*a,b,c* shows the application of the Hansen model[10] in the solubility studies of poly(1-chloro-2,3-epoxypropane); each solvent is represented by a point in the 3D-space created by vectors $\delta_{d,1}$; $\delta_{p,1}$; $\delta_{h,1}$ (Table I). It follows from Table I that in this model the good solvents of the polymer fit within a certain enclosed, approximately spherically symmetric space.

It was found[13] by plotting the intrinsic viscosities against the Hildebrand solubility parameters δ_1 (of the solvents used) that the points cannot be fitted by a continuous curve, because their scatter surpassed possible experimental errors. This is in agreement with the theoretical conclusions of Blanks and Prausnitz[12] that the interactions in solutions of polar polymers can be described by the Hildebrand parameter δ_i only in exceptional cases. These authors suggest, *e.g.*, for the enthalpy part of the interaction parameter χ the following expression[12]

$$\chi_H = (V_S/RT)\left[(\delta_{d,2} - \delta_{d,1})^2 + (\delta_{a,2} - \delta_{a,1})^2\right], \qquad (2)$$

where V_S is the molar volume of the solvent; the parameter $\delta_{a,i} = (\delta^2_{p,i} + \delta^2_{h,i})^{1/2}$ and the index 2 refer to the polymer and the index 1 to the solvent. In spite

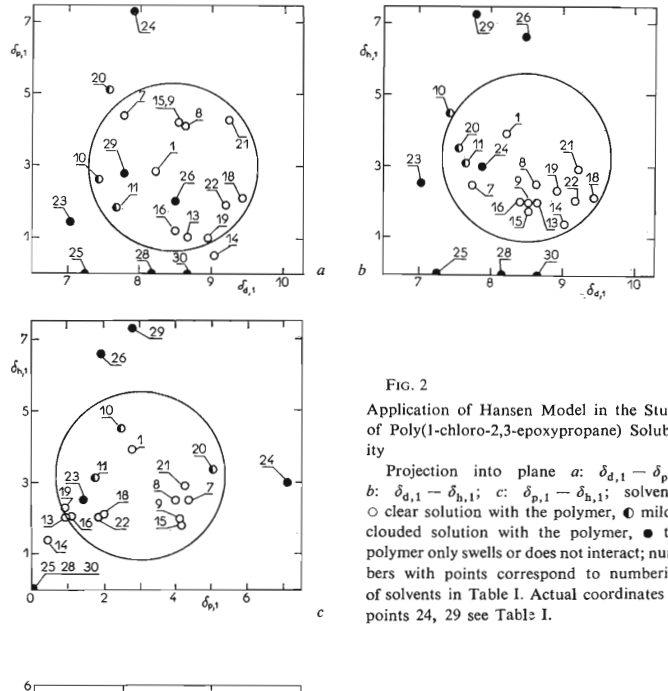

FIG. 2

Application of Hansen Model in the Study of Poly(1-chloro-2,3-epoxypropane) Solubility

Projection into plane *a*: $\delta_{d,1} - \delta_{p,1}$; *b*: $\delta_{d,1} - \delta_{h,1}$; *c*: $\delta_{p,1} - \delta_{h,1}$; solvents: ○ clear solution with the polymer, ◐ mildly clouded solution with the polymer, ● the polymer only swells or does not interact; numbers with points correspond to numbering of solvents in Table I. Actual coordinates of points 24, 29 see Table I.

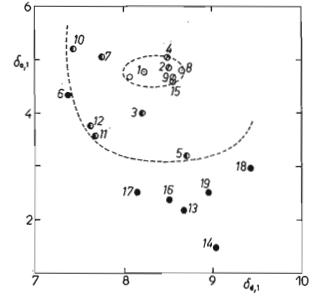

FIG. 3

Correlation of Parameters $\delta_{d,1}$ and $\delta_{a,1}$ of the Solvent Used according to the Intrinsic Viscosity of Poly(1-chloro-2,3-epoxypropane)

[η], dl/g: ● up to 0·299, ◐ 0·300—0·349, ◑ 0·350—0·399, ⊙ 0·400 and higher; ○ calculated correlation; numbers by which points correspond to numbering of solvents in Table I.

of several simplifications (the entropy part of χ is regarded as solvent-independent; possible specific interactions between the solvent and the polymer are disregarded) the theory gave good results for several polar polymers[12,14]. Therefore, the intrinsic viscosity of the polymer is regarded here as a function of the expression $[(\delta_{d,2} - \delta_{d,1})^2 + (\delta_{a,2} - \delta_{a,1})^2]$. The correlation between the intrinsic viscosity of poly-

TABLE I

Characteristics of the System Poly(1-chloro-2,3-epoxypropane)–Solvent at 25°C

Values of parameter δ from ref.[9,11,12]; interaction: 1 clear solution, 2 mildly clouded solution, 3 swelled polymer or no interaction.

Number	Solvent	$\delta_{d,1}$	$\delta_{p,1}$	$\delta_{h,1}$	$\delta_{a,1}$	$[\eta]$	Interaction
		$cal^{1/2}\,cm^{-3/2}$				dlg^{-1}	
1	tetrahydrofuran	8·22	2·8	3·9	4·78	0·434	1
2	1,2-dichloroethane	8·50	—	—	4·87	0·356	1
3	1,1-dichloroethane	8·19	—	—	3·99	0·305	1
4	dichloromethane	8·50	—	—	5·08	0·370	1
5	chloroform	8·7	—	—	3·2	0·316	1
6	1,1,1-trichloroethane	7·37	—	—	4·35	0·225	1
7	methyl ethyl ketone	7·77	4·4	2·5	5·06	0·322	1
8	cyclohexanone	8·65	4·1	2·5	4·79	0·404	1
9	1,4-dioxane	8·55	4·2	2·0	4·65	0·362	1
10	ethyl acetate	7·44	2·6	4·5	5·19	0·327	2
11	butyl acetate	7·67	1·8	3·1	3·58	0·335	2
12	amyl acetate	7·62	—	—	3·75	0·334	2
13	toluene	8·67	1·0	2·0	2·18	0·249	1
14	benzene	9·03	0·5	1·4	1·48	0·263	1
15	acetophenone	8·55	4·2	1·8	4·59	0·365	1
16	*m*-xylene	8·51	1·2	2·0	2·35	0·228	1
17	cumene	8·15	—	—	2·50	0·150	2
18	*o*-dichlorobenzene	9·43	2·1	2·1	2·95	0·270	1
19	styrene	8·95	1·0	2·3	2·51	0·283	1
20	acetone	7·58	5·1	3·4	6·13	—	2
21	pyridine	9·25	4·3	2·9	5·18	—	1
22	chlorobenzene	9·20	1·9	2·0	2·74	—	1
23	diethyl ether	7·05	1·4	2·5	2·88	—	3
24	acetonitrile	7·90	8·3	3·0	8·79	—	3
25	hexane	7·24	0·0	0·0	0·00	—	3
26	cyclohexanol	8·50	2·0	6·6	6·93	—	3
27	octanol	7·88	—	—	6·07	—	3
28	cyclohexane	8·18	0·0	0·0	0·00	—	3
29	butanol	7·81	2·8	7·7	8·20	—	3
30	tetrachloromethane	8·65	0·0	0·0	0·00	—	3

(1-chloro-2,3-epoxypropane) and the parameters $\delta_{d,1}$ and $\delta_{a,1}$ is shown in Fig. 3. For clarity, the values of intrinsic viscosities are not given directly at the particular points, but the points are distinguished graphically in order to show that they belong to various regions of intrinsic viscosity. It can be seen that the solvents in which the polymer exhibits highest intrinsic viscosity fall within a fairly small region of the figure. According to equation (2) the region of maximum viscosity can be used in estimating the parameters $\delta_{d,2}$ and $\delta_{a,2}$ of poly(1-chloro-2,3-epoxypropane). The interval within which these parameters fall with the highest probability can be defined as $8{\cdot}0 < \delta_{d,2} < 8{\cdot}7$ and $4{\cdot}6 < \delta_{a,2} < 5{\cdot}1$. (As the lower limit of the interval of $\delta_{d,2}$ values the arithmetic mean of $\delta_{d,1}$ for tetrahydrofuran and methylethylketone was used.)

The experimental data were compared with the values of $\delta_{d,2}$ and $\delta_{a,2}$ calculated from the known structure of poly(1-chloro-2,3-epoxypropane). As the low-molecular-weight substance similar in shape and size to the monomer unit, β-chloroethylmethylether was chosen; its Hildebrand parameter δ was calculated using the Small procedure[15], its critical temperature was determined according to Lindersen[16]. In addition, the dependence of the vaporization energy on the molecular volume for normal hydrocarbons was used at various reduced temperatures, as reported in ref.[12]. The following values were obtained by calculating δ_2 according to Small[15] and $\delta_{d,2}$ and $\delta_{a,2}$ according to Blanks and Prausnitz[12]: $\delta_2 = 9{\cdot}32\,(\mathrm{cal/cm^3})^{1/2}$; $\delta_{d,2} = 8{\cdot}07\,(\mathrm{cal/cm^3})^{1/2}$; $\delta_{a,2} = 4{\cdot}65\,(\mathrm{cal/cm^3})^{1/2}$. The calculated values of $\delta_{d,2}$ and $\delta_{a,2}$ thus lie within the intervals determined experimentally.

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